

# CHALMERS



## **Binary-Feed Hydrogenation of Aldehydes and Product Purification at Perstorp Oxo AB**

*Master of Science Thesis in the Master Degree Programme: Innovative and Sustainable Chemical Engineering & Industrial Ecology for a Sustainable Society*

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## Abstract

Process Area 25 at Perstorp Stenugnsund can produce both butanol and propanol from their corresponding aldehydes. Today this is done one product at the time.

This report starts the first evaluations of the implementation of binary feed hydrogenation. Current equipment is investigated and capacities estimated. Produced byproducts are also discussed and the separation procedure in order to separate the two products from each other and from the contaminants.

The investigation has utilized simulation software in order to make predictions on the effects of binary feed operations. New equipment has been designed where it is necessary to meet the new emerging criteria.

Three different production levels for the binary feed mode has been investigated with the simulation platform and evaluated.

The major result from this project is that binary feed operation most likely is possible with only small changes to the process setup and equipment.

## Keywords

**Hydrogenation**

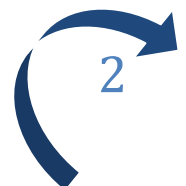
**1-propanal**

**1-butanal**

**Alcohol distillation**

**Simulation**

**UNIQUAC**



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## 1.0 List of Acronyms

BARA	Absolute pressure
BARG	Pressure above atmospheric pressure ((n+1) BARA = (n) BARG)
C1	Distillation column C-25201
C2	Distillation column C-25202
C3	Distillation column C-25203
C5	Distillation column C-25205
CFD	Computational Fluid Dynamic
HE	Heavy Ends
HP	High Pressure
IBAL	Iso-Butanal
IEA	International Energy Agency
i.d	Internal Diameter
LE	Lights Ends
Mol%	Mol based percentage
NBAL	1-Butanal
o.d	Outer Diameter
PFD	Process Flow Diagram
PRAL	1-Propanal
RX	Reactor
VLLE	Vapor Liquid Liquid Equilibrium
VPH	Vapor Phase Hydrogenation
Wt%	Weight based percentage
WEO	World Energy Outlook



## 2.0 Introduction

The oil industry is not what it used to be. In early November 2010 the International Energy Agency (IEA) released its annual report World Energy Outlook (WEO). The report states that crude oil production probably peaked out for good during 2006 at 70 million barrels per day. [9]

The report further predicts a highly volatile oil price market where oil demand will reach 99 million barrels of oil in the year of 2035. [9]

Crude oil is a raw material for many chemical processes. A significant part of the crude oil produced each year is processed further in the chemical process industry. It is therefore vital to study and evaluate other alternatives regarding the choice of raw material.

It is possible to produce synthesis gas,  $\text{CO} + \text{H}_2$ , from various resources such as biomass, natural gas and coal. See figure 2.0.1 for more details.

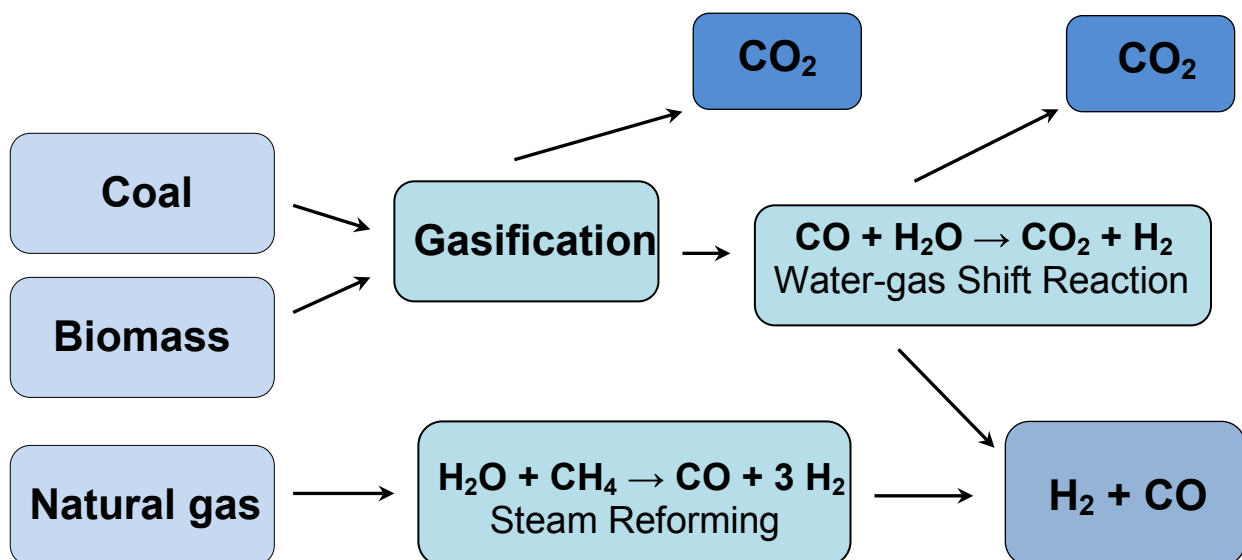


Figure 2.0.1 A Schematic process-view for the production of synthesis gas

The WEO report states that the natural gas production will steadily increase during the coming decades and could in that sense be regarded as a good raw material for the process. However natural gas is a fossil fuel and therefore it contributes to the net yield of  $\text{CO}_2$  emissions. Coal reserves and production is also believed to be rising during the coming decades but it produces significantly larger contribution to net yield of  $\text{CO}_2$  compared to natural gas. [9]

Biomass is a very broad term but usually it considers agricultural products, residue and material which consist of wood. Generally it is harder to process and more expensive to purchase, however it is a good alternative when any organizational unit wants to reduce its fossil fuel dependency.



When switching raw material for a chemical process it is vital to see what effects it will have on production yield and selectivity. Naturally also the economic effects are important to study since the biomass usually is more expensive and it will cause needs for new equipment design and retrofits.

## 2.1 Background

By fermenting hexoses into ethanol the raw material for the process is created. Hexoses are produced by photosynthetic organisms by turning  $\text{CO}_2$  and  $\text{H}_2\text{O}$  into molecules while utilizing the sunbeams energy. This process as such does not depend on fossil hydrocarbons in anyway however the refining process, production of necessary process equipment and transportations most likely is. Switching from fossil to bio based raw materials is nonetheless a great green step towards a more sustainable process industry.

One of the driving forces of the project is to use ethanol and green natural gas as raw material in the total production. This will significantly impact the carbon footprint of the products and reduce Perstorp's dependence on fossil fuels.

Today butanol is the main product from Perstorp but propanol is also being produced.

Perstorp is aiming to increase their alcohol production capacity and include the possibility of producing both butanol and propanol at the same time. This is done by introducing butanal and propanal to the alcohol unit in a binary feed concept.

### 2.1.1 Project objectives

The scope of this project is to achieve three main goals which can be divided into sub-goals. Only the main goals will be presented here.

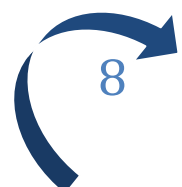
The first goal is to explore the possibility to process both 1-propanal and 1-butanal simultaneously into 1-propanol and 1-butanol.

To investigate the alcohol unit and its suitability to process binary feeds of aldehydes into alcohols is the second goal.

Finally, the last goal is to alter the current process setup or design a new process setup in order to handle the binary feed more efficiently.

### 2.1.2 Acknowledgements

We, the authors of this of this report, would like to take the opportunity to thank the supervisors at Perstorp Rickard Karlsson and Katarina Persson for great support throughout the project. We would also like to thank Krister Ström for being our examiner at Chalmers.





## 2.2 About Perstorp

Perstorp AB is one of the oldest chemical companies in Sweden. It was established in 1881 under the name *Stensmölle Kemiska Tekniska Industri* by Wilhelm Wendt (1854-1924) in Gustafsborg, close to the municipality of Perstorp. In the beginning only acetic acid, tare, charcoal and methanol was produced but in the early 20<sup>th</sup> century Perstorp also started the production of **formalin** and creosote. [21]

During the First World War the demand for acetic acid increased markedly. Acetic acid became so popular that for many years it would be Perstorp's best-known product by far. During the 1920's Perstorp introduced materials like *Isolit* (a kind of Bakelite) and a whole range of other new plastics. [21]

In The Second World War a need for quality coal to generate gas for automobiles arose and Perstorp, with their at the time newly built charcoal-burning plant, receives an economic boost. At the end of the war Perstorp had more than 10.000 different products, ranging from billiard balls to aerial masts and is thereby Scandinavia's first modern plastics industry. [21]

Throughout the 1950's and 1960's Perstorp's new decorative high-pressure laminates (Perstorpsplattan) was commonly utilized in Sweden's expanding house building industry. [21]

In 1966 the company got its present name, Perstorp AB and in the 1970's Perstorp shares were introduced on the open market. Perstorp soon became the world's largest exporter of decorative high-pressure laminates. [21]

During the 1980's Perstorp launches a laminate floor called Pergo, Pergo soon becomes one of the company's most important products. [21]

Under the 1990's Perstorp undergoes a period of focusing on the core business. Perstorp formulates its goal of becoming a world leader in the specialty chemicals area and all non-chemical and materials technology operations are sold off. In 2001, Perstorp is acquired by Sydsvenska Kemi AB, which is controlled by the private equity investment firm, Industri Kapital. In the same year Perstorp is delisted from the stock market and integration begins with Neste Oxo. [21]

In 2005 extensive capacity investments are made in order to meet growing demand. At the end of the year the private equity company PAI partners purchases the Perstorp Group from Industri Kapital. [21]

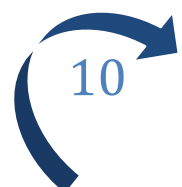


Figure 2.2.1



Figure 2.2.2 Pergo laminate floor [21]

Today the Perstorp Group has a world leading position in many sectors of the specialty chemicals market. Perstorp's products are used in the aerospace, marine, coatings, chemicals, plastics, engineering and construction industries etc. The company's production plants are strategically located in Asia, Europe, and North America and are supplemented by sales offices in all major markets. The Perstorp Group has a turnover of about 12.5 billion SEK and employs more than 2000 people.



## 3.0 Theory

### 3.1 Introduction to Process Area 25

The basic idea of Process Area 25 is to produce butanol from butyraldehyde and hydrogen gas. It does so by utilizing a reactor section and several separation steps. This report will divide Process Area 25 into two separate parts. The first part will be the reactor section and the second part will be the distillation section.

Today butanol is the main product produced in Area 25. However the facility can also produce propanol from propanal but the volumes are much lower. The hydrogenation is carried out in the mutual facility through what is commonly known as 'block operation', meaning that the products are produced in different campaigns or drives. {2}

The basis of this report is to investigate the possibility to produce butanol and propanol simultaneously and at what production rate this can be achieved.

#### 3.1.1 The Reactor Section: Hydrogenation

The aldehyde is hydrogenated with a high conversion and selectivity



### 3.1.2 The Distillation Section

In the first column (C-25201) the low boiling components, the light ends, together with water are taken out as distillate and lead to a decanter system where a phase separation takes place. {2}

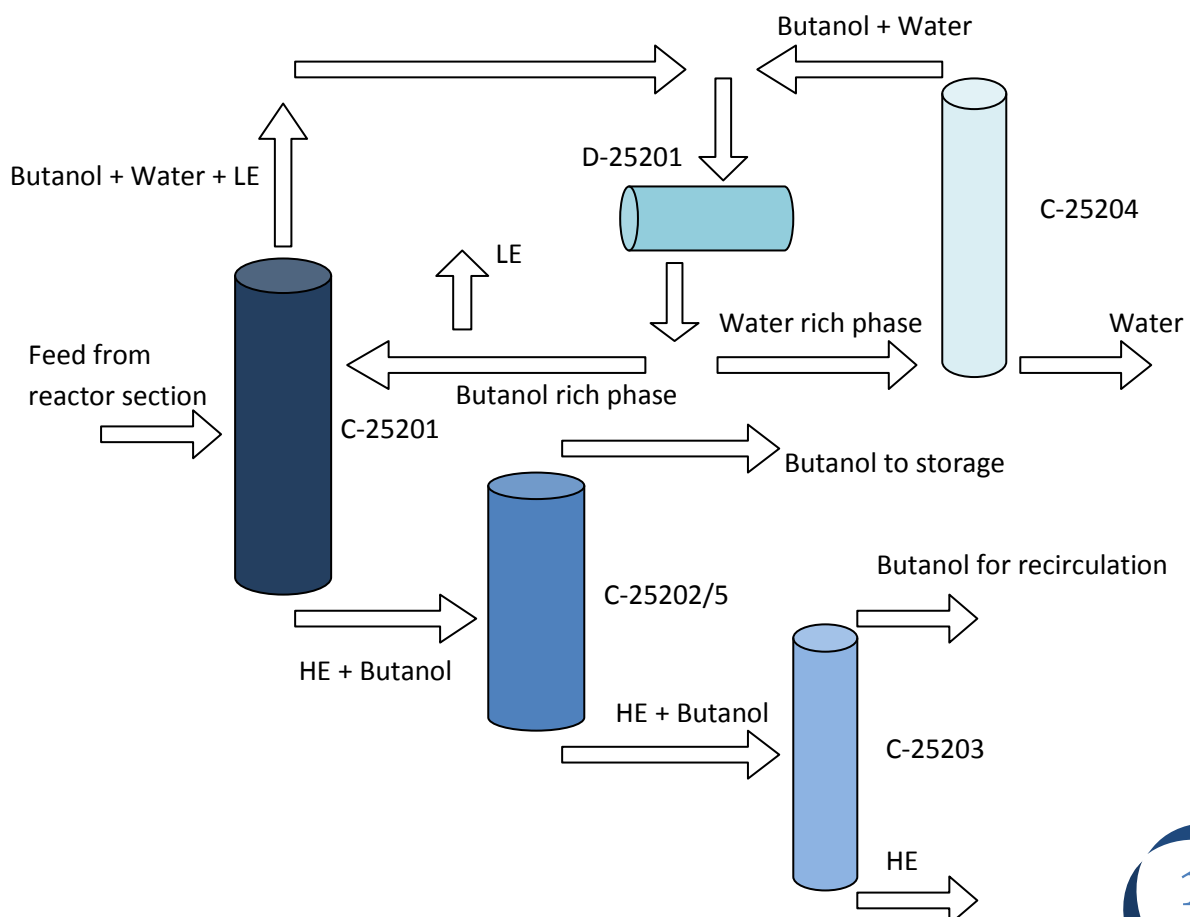
The organic phase is recirculated into the column, from this reflux stream a small side stream are taken out to a storage tank and used as fuel. From the bottom of the decanter the water phase are taken out, since butanol has the solubility in water of about 7.7g/100 ml water, the water contains a small amount of butanol.

The butanol contaminated water is then pumped to a stripper where the butanol is stripped of and recirculated into the decanter. The water is taken out in the bottom of the stripper column and is then pumped further to the sewage plant. {2}

From the bottom of the first column a stream consisting of butanol together with high boiling byproducts goes on to the second column (C-25202/5). In the second column butanol is taken out as distillate and pumped to storage. {2}

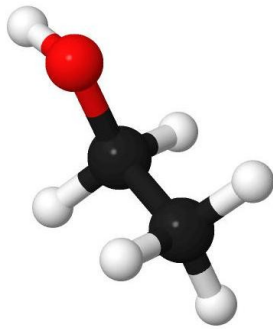
The bottom stream from the second column continues to the last and third column (C-25203), in this column most of the remaining alcohol is recycled to the first column while the bottom stream is taken out as fuel for the boilers. {3}

Schematic overview of the distillation section



## 3.2 Molecules

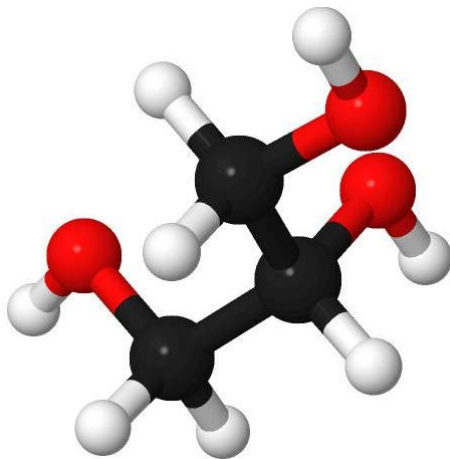
### 3.2.1 Alcohols



Alcohols are a group of hydrocarbons which are characterized by containing one or more of the functional group hydroxyl (-OH). The widely most known alcohol is ethanol which is present in alcoholic beverages, see figure 3.2.1. Ethanol contains one hydroxyl group and contains two carbons and the corresponding alkane would in this case be ethane.

**Figure 3.2.1** Ball and stick model of the ethanol molecule

In contrast to many hydrocarbons some alcohols are soluble in water. While methanol, ethanol and propanol are soluble in water in any mixture butanol and higher alcohols are not. When mixing butanol with water one will create a two phase system containing two liquids. In contrast to mixing oil and water where the two layers will contain only oil and water these two phases will partly contain water and partly butanol. This is known as a heterogeneous azeotrope which is more thoroughly discussed in section 3.8.



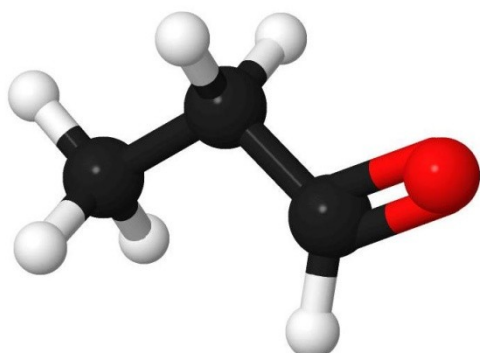
Alcohols can as mentioned above contain many hydroxyl groups, one common of those is glycerol which contains three hydroxyl groups, see figure 3.2.2.

The alcohols propanol and butanol are the two products which are proposed to be produced in the projected binary fed reactor.

**Figure 3.2.2** Ball and stick model of the glycerol molecule

### 3.2.2 Aldehydes

Aldehydes are hydrocarbons containing the functional group named carbonyl (C=O) where at least one of the remaining two bonds to the carbon atom is to a hydrogen atom. Propanal for instance



contains an ethyl group bound to the carbonyl group, see figure 3.2.3. Sometimes this setup of atoms in a carbonyl group can be more specifically referred to as the formyl functional group, -CHO. [4]

The aldehydes propanal and butanal are reactants for the proposed aldehyde hydrogenation process.

Figure 3.2.3 Ball and stick model of the propanal molecule

### 3.2.3 Hydrogen

Hydrogen is the simplest molecule of all molecules, consisting of two hydrogen atoms joint together by a single  $\sigma$ -bond.

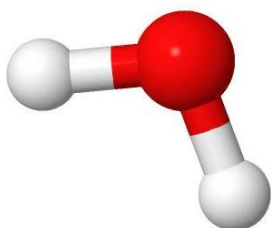
Hydrogen acts as a reactant in the hydrogenation of aldehydes process.

### 3.2.4 Inert Compounds

Two inert compounds are present in the process, carbon monoxide and nitrogen. These are only briefly named here since they do not interfere with the process.

### 3.2.5 Water

Water is a molecule which is made up of two hydrogen atoms bonded to an oxygen atom. Due to the higher electro negativity in the oxygen atom compared to the hydrogen atom the molecule has a high polarity.



Due to its ability create hydrogen bonds with other compounds it is a remarkably good solving agent.

Figure 3.2.4 Ball and stick model of the water molecule

Water is well known to create azeotrope with primary alcohols and is therefore by traditional separation difficult to separate from primary alcohols.

### 3.2.6 Byproducts

Several byproducts are present in small amounts. Some of them all have the functional carbonyl group present in their molecular structure.

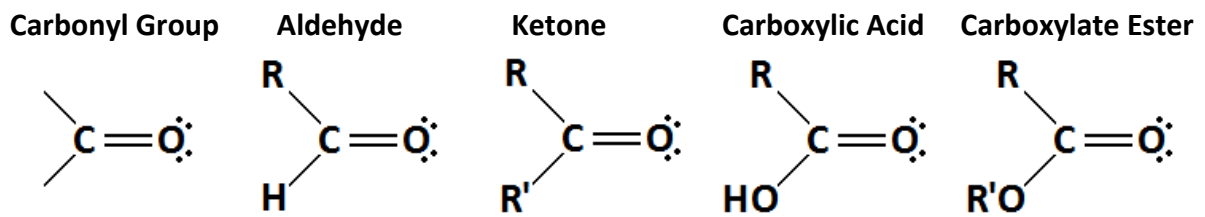


Figure 3.2.5 The carbonyl group in various oxidation states

Other byproducts are also present in the process such as alcohols containing more than four carbons, carbon monoxide, ethers, aldehydes containing more than four carbons and various similar organic compounds.

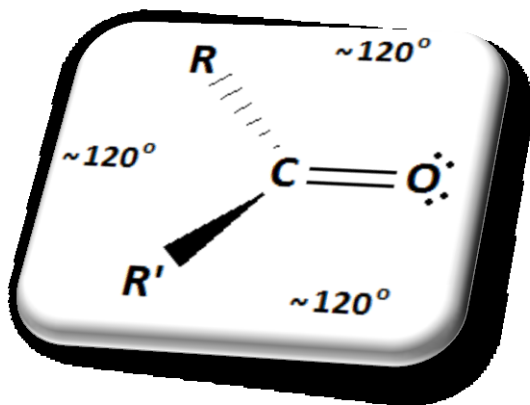
### 3.3 Reactions

There is only one desired reaction and that is the hydrogenation of the aldehydes into alcohols. There are also several unwanted reactions which contaminate the product flow and decreases the process efficiency. If it was not for the unwanted reaction and contaminants in the reactor area feeds there would be no need for a separation process of the reactor outlet stream in any pure aldehyde feed mode.

#### 3.3.1 Wanted Reactions

Hydrogenation Reaction:	Reaction enthalpy, $\Delta H$ kJ/mol
Propanal + $H_2 \rightarrow$ Propanol	-69.482 [1]
Butanal + $H_2 \rightarrow$ 1-Butanol	-70.137 [1]

The carbonyl group has essential physiochemical properties which facilitates the addition of two hydrogen atoms. [1]



**Figure 3.3.1** An illustration of the bond angles in the carbonyl group.

Due to the double bond between the carbon and the oxygen atoms the functional group has a  $sp^2$  hybridization. The double bond consists of one electron pair in a  $\sigma$ -bond and one electron pair in a  $\pi$ -bond. Because of the hybridization the functional group has a rigid planar structure. [1]

##### 3.3.1.1 The Dipole Moment in the Carbon-Oxygen Bond

The electro negativity of oxygen, carbon and hydrogen are 3.4, 2.6 and 2.2 respectively. [2] Due to the higher pulling power of the oxygen compared to the carbon an electron pair displacement towards the oxygen will occur. This displacement induces a dipole moment, thus making the oxygen atom slightly more negatively charged on an average basis.



These reactions are the product yielding reactions which after purification can be used downstream the process or put in a tank storage.

### 3.3.2 Unwanted Reactions

In the reactor section some unwanted reaction appears which leads to contaminating elements. It is important to choose reaction conditions which favor the wanted reaction pathways. By doing so the efficiency of the reactor is increased and less pressure is put on separation units downstream the reactor section.

The research and development team in the Perstorp organization has performed series of experiments for the present catalyst and continuous measurements of the composition of the flow downstream from the reactor throughout the process are the foundation of the assumed reaction mechanisms.

The most abundant chemical compound which was unwanted during these conditions was propyl propionate.

#### 3.3.2.1 Aldol Addition and Condensation

Aldehydes can undergo dimerization to create a molecule named aldol, a molecule containing both the alcohol and the aldehyde groups. These aldols can react further and create unsaturated aldehydes, enals. [1]

In the reactor section several different types of aldol additions and condensations can occur, creating various unwanted compounds. These unwanted compounds can vary in numbers and varieties. However they can be categorized into three distinct types. [1]

Type 1

2 Propanal  $\rightarrow$  Hydroxy-Methyl-Pentanal  $\rightarrow$  Methyl-Pentenal  $\rightarrow$  Methyl-Pentanal

Type 2

2 Butanal  $\rightarrow$  Hydroxy-Methyl-Heptanal  $\rightarrow$  Methyl-Heptenal  $\rightarrow$  Methyl-Heptanal

Type 3

Butanal + Propanal  $\rightarrow$  Hydroxy-Methyl-Hexanal  $\rightarrow$  Methyl-Hexenal  $\rightarrow$  Methyl-Hexanal

Investigations have been made on the composition on the outflow of the reactor section and no methyl-hydroxy compounds or enals can be detected. However methyl ketones and alcohols can be detected in small amounts.

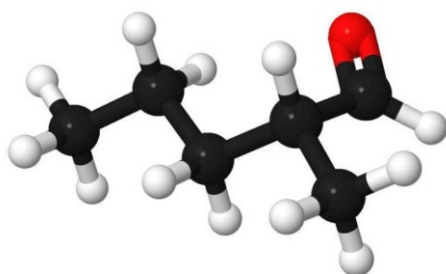
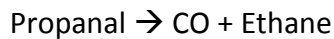


Figure 3.3.2 Ball and stick model of the methyl-2-pentanal molecule

### 3.3.2.2 Decarbonylation

This reaction represents the loss of the functional carbonyl group -CO from an organic compound. [3]



This is not a very likely reaction since it requires a highly specialized catalyst in order to occur in a significant proportion. [3] The very small amounts, if any at all, would eventually follow the gas stream to the flare system.

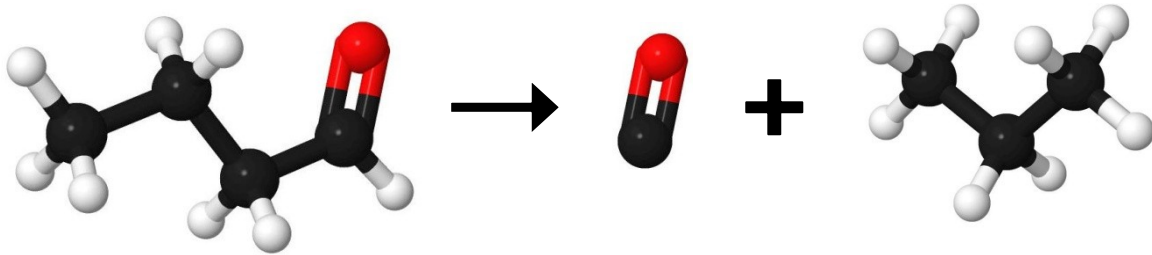


Figure 3.3.3 Ball and stick model of a 1-butanal molecule dissociating into a carbon monoxide and a propane molecule

### 3.3.2.3 Ether Formation

In the reactor section ethers can form when two alcohols react with each other. This phenomenon is also known as *Intermolecular Dehydration of Alcohols*. [1]

The reaction occurs when a protonated alcohol molecule interacts with an alcohol molecule creating a protonated ether molecule. Finally the protonated ether will transfer its proton to either another alcohol or water molecule becoming an ether molecule. [1]

Three different ethers can form in the reactor section

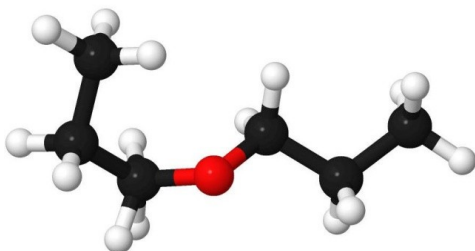
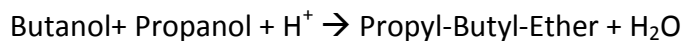
Type 1



Type 2



Type 3



Both dipropylether and dibutylether are present in the outlet of the reactor section. Propyl-Butyl-Ether will most likely occur when a binary feed of aldehyde is present.

Figure 3.3.4 A ball and stick image of the dipropylether molecule.

### 3.3.2.4 Ester Formation

In the presence of the catalytic material in the reactor esters are formed, see figure 3.3.5 for ball and stick model of an ester molecule. The most likely reaction pathway is the oxidation of two aldehydes into one ester. The resulting esters with six and eight carbons give some proof for that, six carbons for pure propanal feed and eight whilst in pure butanal mode.

The corresponding ester in pure butanal production is butyl butyrate and can during unwanted reaction conditions yield a high degree of contamination.

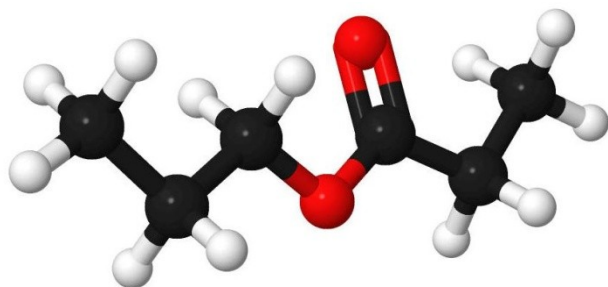
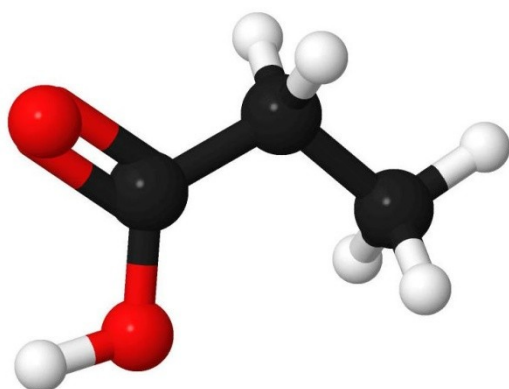


Figure 3.3.5 A ball and stick image of the propyl propanoate molecule.

The most likely reaction for this ester formation is the reaction between a carboxylic acid and an aldehyde on the catalyst surface. These two form a tetrahedral complex which can release an alkoxide ion leaving an ester molecule. One factor which promotes this reaction pathway or similar pathway is the catalyst surface and the formation of esters with only six or eight carbons. If it is true one can suspect that two esters with seven carbons will be formed during binary feed operations, propyl butyrate and butyl propanoate. [1]

### 3.3.2.5 Carboxylic Acid Formation

Carboxylic acids can form during regular operations and it should be avoided if possible.



Alcohols can be oxidized into aldehydes which can be oxidized into carboxylic acids. [1]

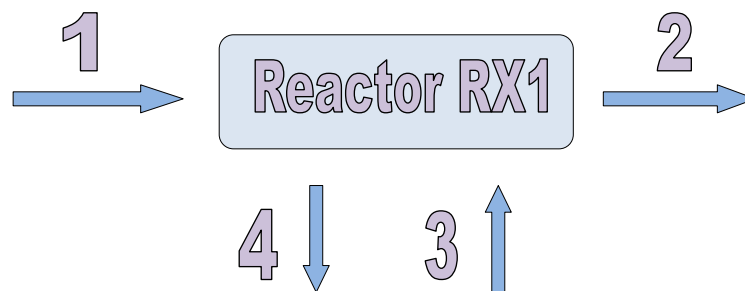
Figure 3.3.6 A ball and stick image of the propionic acid molecule.

### 3.4 Mass and energy balances

Mass and energy balances in a theoretical approach. While studying any process equipment it is important to perform mass and energy balances over the system. This is done to verify that no mass and energy is accumulated in the system but it is also done in order to understand the system creating a platform for more advanced calculations to be performed.

Below we have theoretical reactor RX1 which has one inlet flow of reactants and one outlet flow of products. RX1 is also connected to a cooling system which cools the fluid in the reactor with water.

The reactor is assumed isobaric and the temperature is kept constant by the cooling water.



#### Stream 1, Inflow of Reactants:

Temperature: 350 K

Pressure: 20 Bar

Composition: 97.3 w% NBAL + 2.7 w% H<sub>2</sub>

Mass Flow: 100 kg / h

Molar Flow: 1.349 kmol / h NBAL + 1.349 kmol / h H<sub>2</sub>

#### Stream 2, Outflow of Products:

350 K

20 Bar

100 w% Butanol

100 kg / h

1.349 kmol / h Butanol

#### Stream 3, Inflow of Cooling Water:

Temperature: 310K

Pressure: 1 bar

Composition: 100 wt% H<sub>2</sub>O

Mass Flow: 1000 kg / h

#### Stream 4, Outflow of Cooling Water:

332.6 K

1 bar

100 wt% H<sub>2</sub>O

1000 kg / h

It is crucial to consider the released or absorbed enthalpy change in the reactor

The hydrogenation reaction in the reactor

Enthalpy,  $\Delta H$  kJ/mol

Butanal + H<sub>2</sub> → 1-Butanol

-70.137[1]



94.6 MJ is released to the system each hour. The cooling water absorbs this entire release of heat. The isobaric specific heat capacity of water at 350k and 2 bar is 4194 J / (K and kg). While absorbing the heat the cooling water will increase its temperature.

General equation for energy balance which neglects kinetic and potential energy in a reactor system [10]:

During the energy balance of the reactor system RX1 H1 and H2 have been assumed to be equal.

General equation for mass balance which neglects generation of mass [10]:

A system can have many inlets and outlets and it is vital to mass and energy balance analysis to get all those marked out correctly. The example above does not include the moment where it is necessary to calculate the heat of vaporization.

When a liquid media is turned into a state of vapor an addition of energy is required. For instance one gram of liquid water at 373 K and one bar needs an addition 2.23 J in order to turn into vapor phase.  $\Delta H_{\text{vap}}$  is defined by the enthalpy difference between the liquid and the vapor phase. [2]

[2]



## 3.5 Distillation

Distillation is by definition an operation where the difference in vapor pressure of two or more compounds is used to separate the compounds from each other. Distillation got its name from the Latin word *destillo* which means to drip or trickle down. Distillation is a very old chemical technique which dates back to the first century AD in the city of Alexandria [15].

Usually the distillation processes is divided into two sub categories, distillation of binary mixtures and multistage distillation. Multi-step distillation may be necessary when more than two compounds are present. In some cases also reactive distillation also needs to be discussed however it is not a present phenomena in the process and therefore also beyond the scope of this report.

### 3.5.1 Distillation of binary mixtures

Consider a mixture of two unique compounds, A and B, where A is the desired compound. B can for instance be unreacted raw material. In order to achieve high efficiency it could be a good idea to separate A from B so that compound A can be treated as the desired product and B to be recirculated back to the reactor. In this case distillation might be a good alternative for separation of the two compounds.

If A and B have a very large difference in boiling points and vapor pressure it would be simple to separate them from each other by using a flash unit. A flash unit is a single-stage distillation unit. When the difference in volatility of A and B is not so large one stage might not suffice in order to achieve desired purity of each compound. More stages are necessary for desired separation when there is a lesser difference in vapor pressure of each compound.

#### 3.5.1.1 Distillation stage-cycle

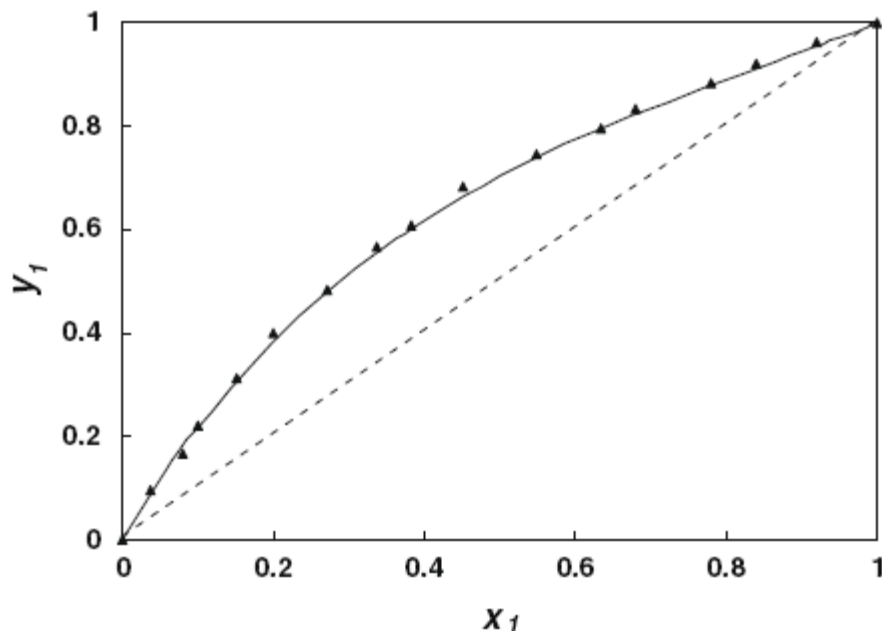
A distillation stage is defined as a cycle where parts of the liquid mixture is brought into a vapor phase and then condensed into a liquid again. Due to the difference in volatilities the vapor phase will contain more of the compound with the higher volatility. The higher pureness needed the more stages or cycles are required.

This is usually the first design parameter which is considered when designing a distillation unit, the number of stages required to achieve pure enough products. In order to obtain the theoretical minimum amount of stages needed for the separation process a McCabe-Thiele diagram is studied. [16]



### 3.5.1.2 McCabe-Thiele diagram

A McCabe-Thiele diagram displays the equilibrium line of a compound in the mixture. The x axis is the mole fraction of the lower-boiling component in the liquid phase and the vertical axis is the fraction of the lower-boiling component in the vapor phase. The equilibrium line denotes how much of each compound that is in its liquid state and how much that is in its vapor phase. [17]



**Figure 3.5.1** Plot of mole fraction in the vapor against mole fraction in the liquid at equilibrium for 1-propanol and 1-butanol at 53.3 kPa.

▲, Experimental liquid-phase mole fractions  
—, UNIQUAC [12]

Practically distillation stages are placed upon each other in a stack which is known as a distillation column. Vapor leaving a stage will enter the stage above and liquid leaving a stage will enter the stage below.

There are two different types of equipment functioning as a stage, packing and trays. One tray is one stage and one segment of packing is one stage.

### 3.5.1.3 Condenser

At the top of each distillation column there usually is a condenser. A condenser partially or fully condenses the outgoing vapor stream into a liquid state. A part of this stream is either returned to the column or leaving the column as the top product. The ratio between the leaving fraction and the returned fraction is known as the reflux ratio. The reflux ratio is a key parameter in distillation columns. A higher reflux ratio will increase the effectiveness of the tower and a purer product will leave the tower while it will also increase the heat consumption. Beside increase the heat demand it will also increase the mass flows in the columns and thus making it larger. It is essential to find a reflux ratio which will yield a pure enough stream leaving the top of tower. A lower reflux ratio will increase the number of stages needed in the separation. [10]

#### **3.5.1.4 Reboiler**

At the bottom of the distillation column there is a unit which is known as the reboiler. The reboiler vaporizes a part of the liquid at the last stage of the column. In order to get the distillation column to run satisfactory the reboiler needs to supply a certain amount of heat. No system is isothermal so there will be losses but they are small compared to the need of heat for evaporation. The condenser needs cooling utility in order to condensate the top vapor stream and this in turn requires heat utility in order to re-evaporate the liquid, hence the name reboiler. [10]

#### **3.5.1.5 Rectifying and Stripping Section and feed stage**

Each distillation column has a rectifying section and a stripping section; these two are suited above and below the feed point to the column respectively. The feed stage of a distillation column is the stage where the fluid of the binary mixture enters. In the rectifying section the light key component is enriched and in the stripping section the heavy key component is enriched. The light key component is the component which is more volatile whilst the heavy key component is the less volatile component. [16]

#### **3.5.1.6 Feed stage location**

An optimal feed stage is where the inlet stream composition is equal to that inside the distillation tower. [10]

### **3.6 Process Equipment**

As mentioned earlier area 25 is divided into two sections: the reactor area and the distillation area. Since the focus of this study lies on the distillation section, only the separation units are thoroughly discussed in this section.

#### **3.6.1 Separation units**

##### **3.6.1.1 C-25201**

The first distillation column is a tray column equipped with valve trays.

Under current working conditions two feed streams are coming in to the first column and before entrance they are mixed together. One of the streams consists of the raw butanol from the reactor section and the other stream comes from the top of C- 25203. In the column the lighter components are taken out on the top and the bottom stream, containing the heavier components together with the butanol continues to the second column. {3}

In the first columns condenser (E-25205), which is a partial condenser, the top stream is cooled by the cooling water on the plant, which keeps a temperature of about 20-30 °C. In addition to c- 25201's reboiler the column is also equipped with a built-in heater, but this is only utilized when starting up the process or when for some other reason the steady state in the process is lost. {3}





### 3.6.1.2 C-25202

The second column is also a tray column.

In this tower the heavier components are taken out in the bottom and on the top the purified butanol is obtained. {3}

The bottom of the second tower is heated with the reboiler E-25206; in this reboiler throttled 14 bar steam is utilized. The condensation of the top stream takes place in two serial condensers before some of it is returned to the top of the column as reflux and some of it is taken out as product.

### 3.6.1.3 C-25203

The third column is equipped with packing.

Under current working conditions this column is purifying the remaining butanol from the heavier components. The purified butanol leaves the tower on the top and is as mentioned earlier brought back to the first tower. The bottom fraction from the tower containing the heavy components is used as fuel in the boilers. {3}

The bottom of the third tower is heated with the reboiler E-25206; in this reboiler throttled 14 bar steam is utilized. {3} In the third columns condenser (E-25219) which is a partial condenser the top stream is cooled by the cooling water on the plant, which keeps a temperature of about 20-30 degrees. {2}

## 3.7 Software

Simulation, programming and data processing software are all very useful tools while working with chemical engineering. During this project various software utilities have been used in order to complete the task.

### 3.7.1 Chemcad

ChemStation Chemcad is a simulation software program which simulates real reactors, heat exchangers, pumps, control functions, distillation columns, flash units and much more.

The program considers many important physical and chemical features of a mass flow, where the ideal gas law is one of the most simple of thermodynamic equations. Chemcad uses a set of highly advance and much more accurate equations for thermodynamic calculations, some of the most common equations for this NRTL, UNIFAC and UNIQUAC.

What determines which thermodynamic model to use is the process features, different equations are superior to others under certain conditions and it can significantly improve the accuracy of a simulation if an appropriate model has been chosen from the beginning.



Each process unit in Chemcad has a number of input data and operations modes which after computerized calculations yields output data.

### 3.7.2 Aspen Process Explorer

Aspen Process Explorer is a software program which handles vast amount of process data. It continuously logs process conditions such as temperature, mass flow rate, flow composition, pressure and much more.

More importantly the program stores a process condition for a given moment. For instance a data point could be at the outlet of a reactor. In this point there might be many different indicators. In this theoretical case there are indicators for temperature and pressure. Aspen Process Explorer stores the specific temperature and pressure at time  $t$ . The time length between two measurements may differ from setup to setup but the program have graphical features which allows XY-axis charts to be generated where Y is the process value for an indicator and X the time axis.

### 3.7.3 Koch-Glitsch Tower, KG-TOWER

KG-TOWER is a free software given out by Koch-Glitsch, which is a company that specializes in design and supply of mass transfer equipment, including packed tower internals, structured and random packing, trays and demisters etc.

When deciding internals for towers with structured packing, it is first necessary to estimate the Height Equivalent to a Theoretical Plate (HETP). When this is done it is easy to approximate how many theoretical steps a certain tower may contain.

A similar procedure is performed for tray columns, where the required number of theoretical steps can be extracted from simulation software like Chemcad.

By inserting the hydraulic data, the diameter and the number of theoretical steps in a distillation tower, given by for example simulations in Chemcad, into KG-TOWER, the software will compute the tower load for a certain type of bed. Hence KG-TOWER is a very powerful tool when determining the tower size and the tower interior.

## 3.8 Heterogeneous Azeotrope

A heterogeneous azeotrope is a liquid system which is not limited to one single liquid phase but multiple liquid phases. [5]

There exists an equilibrium state for the compositions of the liquid phases which depends on the amount of each present species assuming pressure and temperature is constant. The mixture, if it is a heterogeneous azeotrope will have a constant boiling temperature. [5]

Two distinct different types of heterogeneous azeotropes exist. Type one produces vapor while boiling which has the same composition of the overall liquid system and type two does the opposite. [5]



An example of a heterogeneous azeotrope closely related to the hydrogenation process is the butanol-water system. When the facility is in butyraldehyde feed mode this chemo physical phenomenon is used to purify the product butanol. [6]

Butanol and water, 76.1 mol% water and 23.9 mol%, at 50 000 Pa creates an azeotrope with two liquid layers. The water rich liquid phase contains 97 mol% water and 3 mol% butanol while the butanol rich liquid phase contains 58 mol% butanol and 42 mol% water. [6]

The azeotropic boiling point for water and butanol at atmospheric pressure is 92.4 °C and the vapor phase will contain 44.5 wt% water and 55.5 wt% butanol. [7]

Due to the weight difference between the two liquid phases they will produce an upper and a lower layer. It is possible to separate the two layers by using what is known as a decanter which functions as a gravimetric separator.

By utilizing these properties of the mixture of butanol and water one can achieve separation of the two compounds into nearly 100 % pure products. A feed stream composed of a mixture of butanol and water will be processed by a distillation column to produce almost azeotropic vapor. Through condensing the azeotropic vapor it is possible to produce a binary liquid phase. The water rich phase will be returned to the initial column to be reprocessed while the butanol rich phase will be sent to a secondary column to be further distilled. The vapor leaving column two will be condensed and transported to the decanter. [8]

This design will produce two nearly pure streams of water and butanol in bottom of each column, the first producing water and the second producing butanol. [8]

### 3.8.1 Heterogeneous Azeotrope Distillation

While considering heterogeneous azeotrope distillation it is important to consider the various special features the fluid system has. One of those features is the Vapor Liquid Liquid equilibrium (VLLE). The mixture of compounds which forms a system of two liquid phases will behave differently while undergoing such separation process than systems of only one liquid phase. [13]

In the distillation section of process area 25 there is a possibility for a binary heterogeneous azeotrope to form. This is the distillation of n-butanol, n-propanol, water and byproducts. The byproduct content is very small and it is variable in amount and content. From a theoretical point of view it has to be neglected bearing in mind that it will affect the VLL equilibrium.

The distillation water-ethanol is a closely studied process and it does not form a heterogeneous azeotrope. However it does form an azeotrope where both water and ethanol has the same boiling point and cannot be separated by distillation. In order to address this issue an entrainer can be added to the azeotropic mixture. Benzene is such an entrainer for the azeotrope ethanol water.

Water will not mix well with benzene since it is a non polar molecule however ethanol will. The ternary system of ethanol water and benzene will form two liquid phases. Ethanol will be present in



both phases, benzene will only be present in the organic phase and water will only be present in the water phase. The organic phase can then be distilled into ethanol and benzene and the water phase can be recycled to the separation unit which produced the azeotropic mixture of water and ethanol for further purification. [14]

### **3.8.1.2 The binodal curve**

For the binary heterogeneous system of butanol and water there exists a binodal curve. Compositions above the binodal curve will create a stable homogenous liquid phase whereas under the binodal curve two stable liquid phases will form. The binodal curve changes level when the temperature and the pressure of the system changes. It is essential to make good predictions of the binodal curve in order to design an effective distillation column. [14]

## **4.0 Method**

### **4.1 Process Condition Data Gathering**

In order to get a clear overview of the process it is important to gather specific process data. Specific process data is information including where, when and what somewhere in the studied design.

Where in the process was the measurement done?

When was the measurement taken?

What was measured?

These three questions needs to be asked for many different data points in the process and several process variables have to be studied in order to obtain a satisfying overlook of the process.

All available indicators generate values which are continuously stored. These stored values can then be evaluated and compared. A change in a process parameter is easily identified and the subsequent effect it has on product quality and downstream conditions can be obtained.

In order to understand the mechanism of a process unit it is useful to gather specific process information inside and around that unit.

To explain, understand and make predictions on heat exchangers it is necessary to measure the temperature, composition and mass flow for each of the two inlets and outlets.

It can happen that the optimal indicators for a process unit are not present or malfunctioning. For instant a mass flow indicator may not be present prior a reactor unit, however there might be one present several units upstream. If no mass has been added to the flow this mass flow indicator will be valid as an indicator for the reactor inlet.



If the flow out from the reactor is separated by a flash unit into two flows and there is one indicator available for each of the flows then these two combined will be valid to use as an indicator for the reactor outlet.

Data about the process studied in this project has been gathered through Aspen Process Explorer.

It should be stated that all data gathered from Aspen Process Explorer has been collected only when the process facility operated in steady state mode.



## 4.2 Chemcad Simulations

Many different types of simulations are needed to be described in order to evaluate the possibility to use a binary feed of aldehydes.

### 4.2.1 Simulation of the Reactor Area

In order to get an accurate simulation model for the reactor section the PFD chart for the reactor section in process area 25 was built up in Chemcad.

### 4.2.2 Simulation of Distillation Area for Binary Feed

In order to handle the binary feed, the existing distillation arrangement will not be sufficient. To view the existing arrangements please see section 3.1.2, schematic overview of the distillation. A new arrangement was therefore set up in Chemcad.

To view the new arrangement please see figure 4.2.1, Distillation Area with C-25201 as Splitter.

The simulation model chosen for the distillation towers are the regular VLE and the thermodynamic model are UNIQUAC, the towers are SCDS columns. For explanation of the thermodynamic model please see section 4.3.1

For the simulations to converge, it was necessary to limit the molecules included. To view the exact in and output of the distillation simulations, please see appendix 9.3

All distillation columns in the new arrangement are columns that already exist in area 25 today.

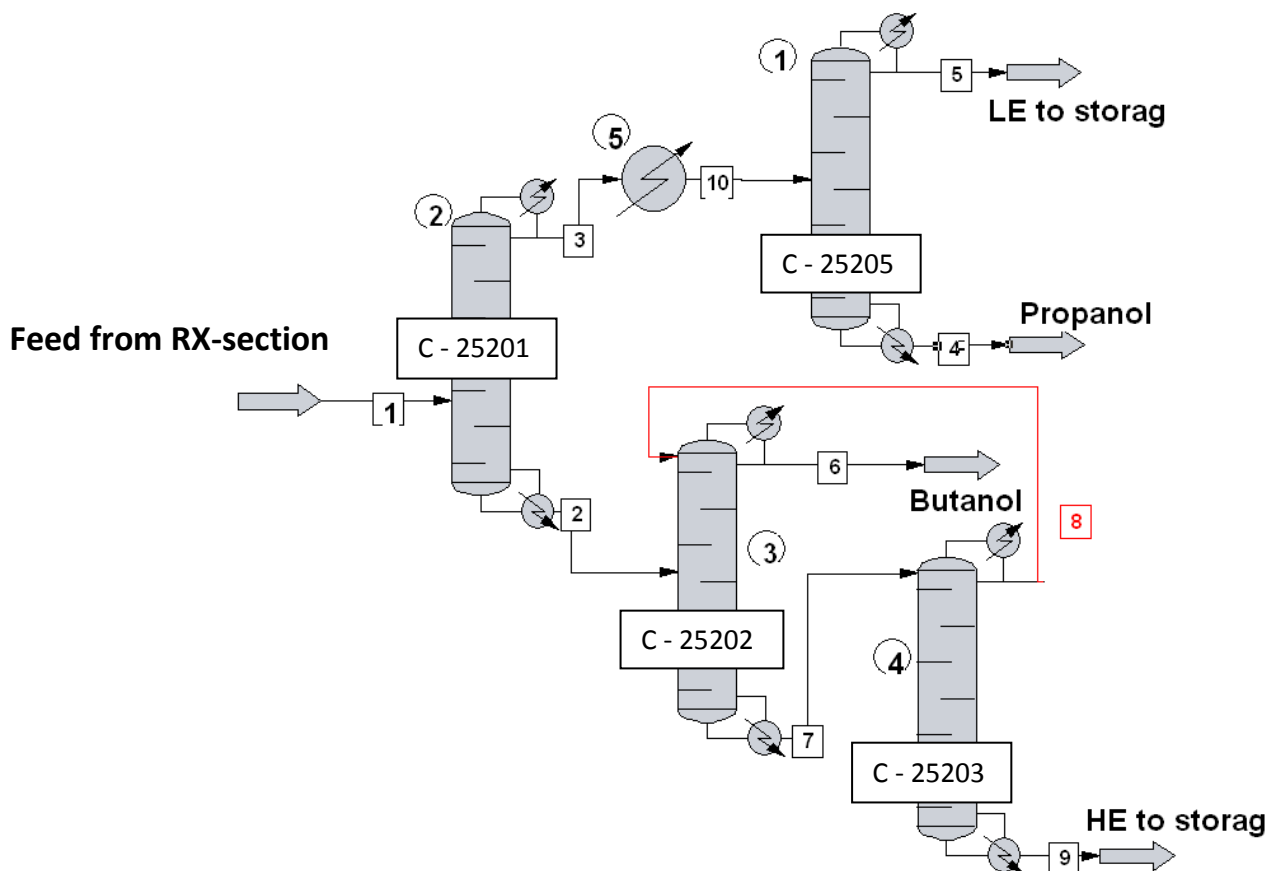


Figure 4.2.1 Distillation Area with C25201 as Splitter



#### 4.2.3 Simulation of C-25201 for production level 1

For handling production level 1, simulations in Chemcad together with data from KG-TOWER have shown that the new arrangement with present interiors of the towers is sufficient.

#### 4.2.4 Simulation of C-25201 for production level 2

For production level 2, results from the Chemcad simulation and KG-TOWER, revealed that a new interior for C-25201 will be necessary. Please see section 5.3.3 for the new internals for C-25201.

#### 4.2.5 Distillation product stream compositions

Tables over the distillation production levels and important product stream compositions such as the butanol stream, propanol stream, LE-stream and HE-stream.

Chemcad Distillation Simulation Results		
	Propanol	Butanol
Binary Feed Level 1 (kg/h)	1626	4645
Binary Feed Level 1 (kton/y)	14.04	40.13
Binary Feed Level 2 (kg/h)	3334	7869
Binary Feed Level 2 (kton/y)	28.81	67.99
Binary Feed Level 3 (kg/h)	4836	11166
Binary Feed Level 3 (kton/y)	40.91	96.47

Table 4.2.1

Simulation stream compositions			
	Level 1	Level 2	Level 3
Butanol End Product (Wt %)	99.9	99.8	99.9
Propanol End Product (Wt %)	98.4	97.9	97.7
Contaminants entering the distillation area			
Water (kg/h)	62.7	114.8	165
Di-n-Propyl Ether (kg/h)	5	5	5
Di-n-Butyl Ether (kg/h)	5	5	5
Isobutanol (kg/h)	2.53	4.3	6.2
N-Propyl Propionate (kg/h)	1.2	9.2	3.6
N-Butyl Propionate (kg/h)	5	5	5
N-Propyl N-Butyrate (kg/h)	5	5	5
N-Butyl N-Butyrate (kg/h)	9.3	15.6	22.1
Propionic Acid (kg/h)	1.4	4.1	4.1
N-Butyric Acid (kg/h)	5.7	9.5	13.5
2-Ethylhexanol (kg/h)	5	5	5
Total weight (kg/h)	107.8	182.5	239.2
Contaminants in LE			
Water (kg/h)	47.6	60.9	75.6
Di-n-Propyl Ether (kg/h)	0.4	0.5	0.5
Di-n-Butyl Ether (kg/h)	0	0	0
N-Propanol (kg/h)	175.9	358.6	513.2
Isobutanol (kg/h)	0	0	0

<b>Total weight (kg/h)</b>	224.0	420	589.3
<b>Contaminants in HE</b>			
<b>Water (kg/h)</b>	0	0	0
<b>Di-n-Propyl Ether (kg/h)</b>	0	0	0
<b>Di-n-Butyl Ether (kg/h)</b>	4.5	4.5	4.5
<b>N-Propanol (kg/h)</b>	0	0	0
<b>Isobutanol (kg/h)</b>	0	0	0
<b>N-Butanol (kg/h)</b>	80.1	68.6	63.1
<b>N-Propyl Propionate (kg/h)</b>	0.3	2.4	0.9
<b>N-Butyl Propionate (kg/h)</b>	4.7	4.7	4.7
<b>N-Propyl N-Butyrate (kg/h)</b>	4.6	4.6	4.6
<b>N-Butyl N-Butyrate (kg/h)</b>	9.3	15.5	22.0
<b>Propionic Acid (kg/h)</b>	1.4	4.1	4.1
<b>N-Butyric Acid (kg/h)</b>	5.7	9.5	13.5
<b>2-Ethylhexanol</b>	5.0	5.0	5.0
<b>Total weight (kg/h)</b>	115.6	119.0	122.4

Table 4.2.2

### 4.3 Scenario simulations and production levels

Three possible production levels have been predicted and this section aims to describe and characterize these production levels. The different levels serve as possible future scenarios for the binary aldehyde feed production.

Each level is the basis for the various computerized simulations of the process. Mainly every level has a distinct proposed maximum and minimum production level which then can be simulated through existing equipment under many different conditions. This is done partly to investigate current equipment capacity and if the capacity for any given piece of equipment is exceeded what requirements new equipment would have.

A very basic example would be if a simulation of production level 2 yields the result that pump A needs a pumping capacity of 10 liters per minute. If current capacity exceeds 10 liter then it could be concluded that the current pump A can be used for production level 2, however if pump A only can pump 7 liters per minute then it cannot be used and a new pump would at least need a capacity of 10 liters per minute.

It should be noted that each level is calculated to have an availability of 354 days of production per year or 8498 hours of production per year.





#### 4.3.1 Production level 1

The production capacity for level 1 should at least be 14.5 kton propanol and 39 kton butanol per year. This corresponds to production rate of 6.4 ton alcohol per hour

#### 4.3.2 Production level 2

Production level 2 is higher than production level 1. The aim is to produce 8 ton butanol per hour and 3.34 ton propanol per hour totaling 11.34 ton per hour.

#### 4.3.3 Production level 3

This production level is the largest of the three and its target is to produce 5.25 ton propanol per hour and 11.214 ton butanol per hour.

Where it is necessary new preliminary design will be created to meet the aims of the production level.

### 4.4 Evaluation of Simulation Models

While working with simulation software it is important to compare generated results with the values which represent the reality. No simulation model is perfect and they will always deviate less or more from the true values.

The computer programs in this project do not consider any physical or fluid dynamics in any of the unit operators. For instance the reactor simulations do not recognize the flow properties around catalyst pellets present in the reactor tubes.

A Computational Fluid Dynamic (CFD) study which compares laminar and turbulent flows around catalyst particles has shown that there is no major difference between the velocity profile around the particles however the Re number has an impact on the heat transfer from the fluid through the wall. [11]

CFD simulations provide much more accurate solutions than Chemcad but on the other hand they are much more time consuming both in computational time and while setting up the simulation model.

The simulation models must nonetheless be evaluated and the scope and accuracy of the model should preferably be estimated.

A Chemcad simulation generates process values which could be directly compared to real process values but it is also possible to compare the model setup in Chemcad with laboratory and high accurate studies for thermodynamic data.



#### 4.4.1 Thermodynamic model

Various models were evaluated for the Chemcad simulations and finally the UNIQUAC model came out as the model which would provide the best results.

Several different scientific reports which contained measured VLE and VLL data compared to UNIQUAC was studied

One such study was “*Isobaric (vapour + liquid) equilibria for the (1-propanol + 1-butanol) binary mixture at (53.3 and 91.3) kPa*” published in J. Chem. Thermodynamics 42 (2010) [12]. The study contains vital data for this project and its simulations. Especially since the distillation of propanol and butanol will occur in pressures below atmospheric pressure.

Unfortunately an improved version of the UNIQUAC model known as the extended UNIQUAC model is not available in the Chemcad. Experiments compared to predicted VLE data by the extended UNIQUAC model for a ternary system consisting of water, 1-propanol and 1-butanol shows high accuracy for the model. [22]

Results from the above mentioned report can be viewed in figure 4.4.1

**Table 5**  
VLE data for water (1)+ n-propanol (2)+ n-butanol (3) when  $P=98.6$  kPa.

Temperature (K)	Literature data <sup>a</sup>				Calculated data			Comparison		
	$x_1$	$x_2$	$y_1$	$y_2$	$T_{cal}$	$y_{1,cal}$	$y_{2,cal}$	$\Delta T$	$\Delta y_1$	$\Delta y_2$
363.39	0.8457	0.0605	0.7040	0.1483	363.27	0.7072	0.1403	0.12	-0.0032	0.0080
363.37	0.8925	0.0430	0.7068	0.1492	363.17	0.7012	0.1349	0.20	0.0056	0.0143
363.14	0.8724	0.0593	0.7008	0.1668	362.93	0.6935	0.1649	0.21	0.0073	0.0019
363.08	0.8928	0.0544	0.6960	0.1815	362.75	0.6867	0.1768	0.33	0.0093	0.0047
362.87	0.8983	0.0577	0.6928	0.1899	362.51	0.6787	0.1992	0.37	0.0141	-0.0093
362.80	0.8529	0.0771	0.6962	0.1952	362.66	0.6853	0.1930	0.14	0.0109	0.0022
361.93	0.7907	0.1466	0.6592	0.2675	361.68	0.6543	0.2769	0.25	0.0049	-0.0094
361.80	0.8007	0.1457	0.6595	0.2749	361.51	0.6484	0.2890	0.29	0.0111	-0.0141
361.72	0.8166	0.1397	0.6569	0.2841	361.35	0.6427	0.3005	0.37	0.0142	-0.0164
Average								0.25	0.0088	0.0081

Figure 4.4.1 the imported table from the experimental studies shows that the extended UNIQUAC has a high level of accuracy.

All though the extended version of UNIQUAC is not incorporated in Chemcad this study still gives confidence to the chosen thermodynamic model.

The UNIQUAC model is suitable for prediction of thermodynamic equilibriums such as liquid-liquid and vapor-liquid data. It is also suitable for systems which are both miscible and immiscible which is advantageous to the projects simulations since binary liquid phases does exists in some places. [10]

Scientific reports indicate that UNIQUAC gives satisfactory correlation on VLE data while simulating ternary systems of water and alcohols. [22][23][24]

The UNIFAC model and the NRTL model are also two good choices for simulations of VLE and VLEL equilibriums however UNIQUAC has in this case been chosen in favor of those due to its superior results in scientific studies.

## 4.5 Design of New Equipment

### 4.5.1 Splitter Column Design X1 for production level 3

A new distillation column will be needed to split the feed stream of butanol and propanol from reactor section. The column was set to achieve two conditions

Condition 1

Desired Split 0.9999 of inlet flow of butanol in bottom

Condition 2

Desired Split 0.9995 of inlet flow of propanol on top

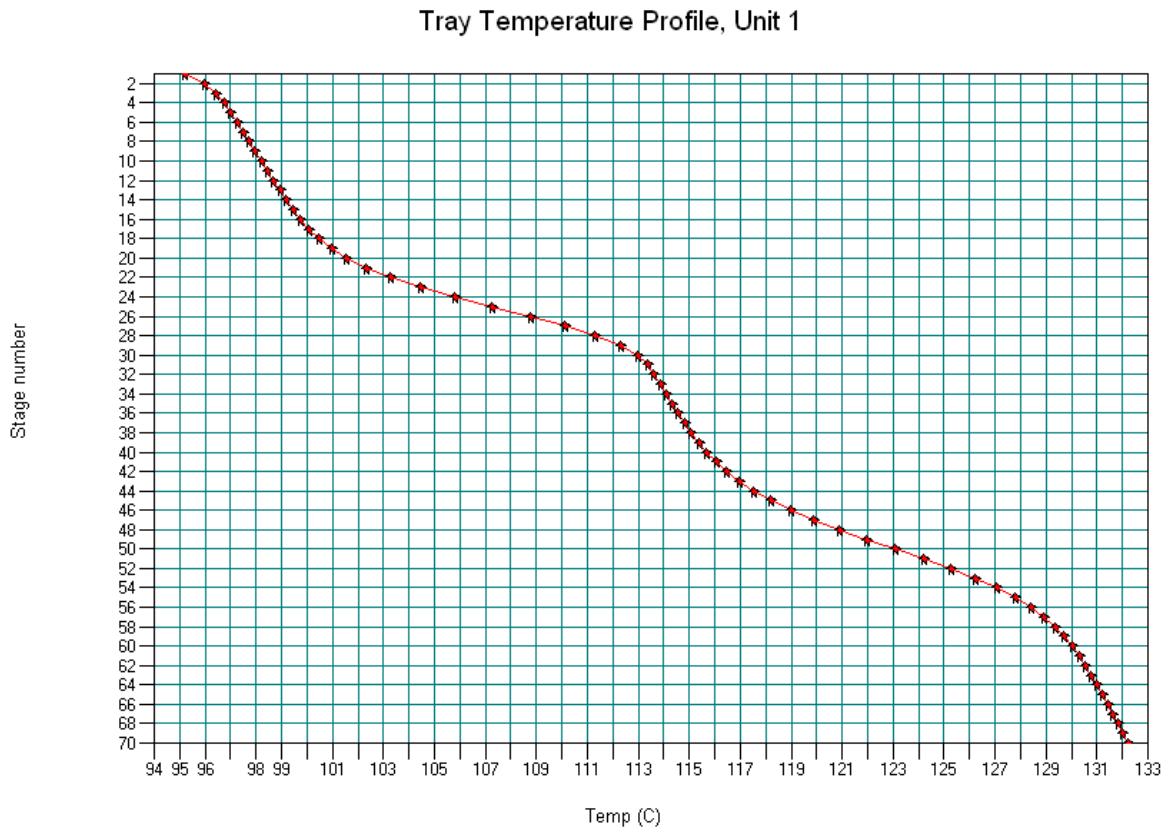
It should be noted that these are very harsh conditions for distillation column while separating propanol from butanol.

Inlet flow estimation	
Molar flow kmol/h	248
Mass flow kg/h	16712
Temp C	90
Pres bar	1
Average mol wt	67
Actual dens kg/m <sup>3</sup>	739
Actual vol m <sup>3</sup> /h	22
Composition of inlet flow (Flowrates in kg/h)	
Hydrogen	0.0084
N-Butyraldehyde	0.84
N-Butanol	<b>11230</b>
1-Propanal	0.061
N-Propanol	<b>5244</b>
Water	165
Isobutanol	4.2
N-But N-Butyrate	22
Propanoic Acid	4.1
Butanoic Acid	13.4
4-octanone	2.9
2-Methyl 3-Penta	2.2
3-methyl-3-penta	13.6
N-Propyl Propion	3.6
5-Methyl-1-Hexan	4.9

Table 4.5.1

#### 4.5.1.1 Preliminary design Data of Splitter X1

The tray temperature profile is an essential tool to achieve satisfactory distillation and is displayed in figure 4.5.1 below.



**Figure 4.5.1** Temperature profile for splitter X1

The feed tray of Splitter X1 is tray number 29 and the column consists of 70 trays in total. Reflux ratio has been set to 2.672 and the theoretical number of trays was 54. It is impossible to achieve 100% tray efficiency and therefore an additional number of trays were added corresponding to a tray efficiency of 77 % (slightly lower than tabulated values for the given conditions). [10]

Delta T for the tower is 37 °C and a good distribution of delta T on the trays is achieved.

Tray spacing has been set to 0.5 m and the pressure drop per tray is estimated to be 1013.25 Pa. Top pressure of the splitter is assumed to be atmospheric.

The splitter will be 35 meters high, excluding reboiler and condenser height, and have two sections. Section one, top section, is calculated to have a diameter of 1.65 meter and section 2, bottom section, is estimated to have a diameter of 2 meter.

The reboiler will consume 16504.1 MJ/h and the condenser will release 10803.2 MJ/h.

With a SCDS VLE column the proposed design will yield the two following output streams:

Stream Name	Top Stream	Bottom Stream	
Temp C	95.2	132.2	
Pres bar	1	1.64	
Enth MJ/h	-23938	-46287	
Vapor mole frac.	1	0	
Total kmol/h	96	152	
Total kg/h	5410.5	11301.4	
<b>Flowrates in kg/h</b>			
Hydrogen	0.0084	<b>N-Butanol</b>	<b>11229</b>
N-Butyraldehyde	0.84	<b>N-Propanol</b>	<b>1</b>
<b>N-Butanol</b>	<b>0.02</b>	Isobutanol	3.8
1-Propanal	0.061	N-But N-Butyrate	22
<b>N-Propanol</b>	<b>5243</b>	Propanoic Acid	4
Water	165	Butanoic Acid	13
Isobutanol	0.44	4-octanone	2.9
2-Methyl 3-Penta	0.0001	2-Methyl 3-Penta	2.2
		3-methyl-3-penta	13.5
		N-Propyl Propion	3.6
		5-Methyl-1-Hexan	4.9
Propanol Purity	96.913%	Butanol Purity	99.362%
Propanol Purity w/o H <sub>2</sub> O	99.997%		

Table 4.5.2

In order to achieve specified product quality additional steps will be needed for both output streams. For stream five (bottom butanol stream) only one separation unit is estimated to be needed and for stream 3 (top propanol stream) one or two separation steps are most likely needed.

#### 4.5.1.2 Assumptions regarding design data

Assumed design data based on recommendations in *Chemical Engineering Design* [10]:

85% Flooding

Cross flow single pass

Tray spacing 0.5m

Hole: active area 0.1

Downcomer area 0.12

Pressure drop per plate 1013 Pa (100mm water)



#### 4.5.1.3 Equations used for the design of X1

The following equations were used in order to predict the necessary preliminary design data

Eqn 4.1, Flooding velocity:

$\rho_L$  = density liquid,  $\rho_v$  = density vapor,  $K_1$  = constant obtained from "figure 11.34." in *Chemical Engineering Design* [10]

Eqn 4.2, Liquid-vapor flow factor:

$L_w$  = Liquid mass flow,  $V_w$  = vapor mass flow

Eqn 4.3, Percentage Flooding:

$u_n$  = flooding velocity based on actual net area

Eqn 4.4, Minimum vapor design velocity:

$u_h$  = minimum vapor velocity,  $d_h$  = diameter of plate holes,  $K_2$  = constant obtained from "figure 11.37." in *Chemical Engineering Design* [10]

Eqn 4.5, Pressure drop:

$h_t$  = total plate pressure drop (liquid),  $\Delta P_t$  = total plate pressure drop (Pa)

Eqn 4.6, 85% of flooding:

Eqn 4.7, Maximum volumetric flow:

$V$  = vapor rate,  $m_w$  = molecular weight

Eqn 4.8, Column cross-sectioned area required:

Eqn 4.9, Column cross-sectioned area 12 %dc:

Eqn 4.10, Column diameter:

#### 4.5.1.4 Further studies of splitter X1

The column needs to be checked for various traits such as minimum capacity and additional tray design such as pressure drop, weir height, valve design, downcomer liquid back-up and weeping.

#### 4.5.2 New condenser Design X2 for production level 3

A new condenser will be needed for c-25201 to handle the production levels 2 and 3. Condenser X2 will be a horizontal shell and tube condenser. The condensation will take place on the shell-side of the condenser while the cooling media, in this case water, will flow on the inside of the tubes. The condenser will have two tube pass and one shell pass. The baffle spacing will be equal to the shell diameter and the baffle cut will be 45 % of the shell diameter.

The condenser must be able to handle the mixed-product vapor flow from the top of c-25201 of 15995 kg/h. The condenser will operate at 0.24 bara. The vapors will enter the condenser saturated at 62.9°C and the condensation will be complete at 62.7°C. Cooling water on the plant is available at 27 °C and the temperature rise is limited to 10°C. The condenser duty will according to simulations in Chemcad be: – 12613.4 MJ/h = 3.5037 MW.

To manage this duty the cooling water flow will have to be 83.8 kg/s. Since the temperature change during the condensation is small the temperature correction factor ( $F_t$ ) is 1 and therefore the mean temperature difference will be equal to the logarithmic mean temperature difference. Equation 4.11 will yield a mean temperature difference of 30.54°C

Hence

Eqn 4.11: \_\_\_\_\_

Where

Inserting the mean temperature difference of 30.5°C together with an assumed overall coefficient of 750 W/m<sup>2</sup>°C into equation 4.12 will give an exchanger area of 153 m<sup>2</sup>.

Eqn 4.12:

Where

#### 4.5.2.1 Tube arrangements

The tubes in a heat exchanger are usually arranged in an equilateral triangular, square or rotated square pattern, see figure 4.5.2:

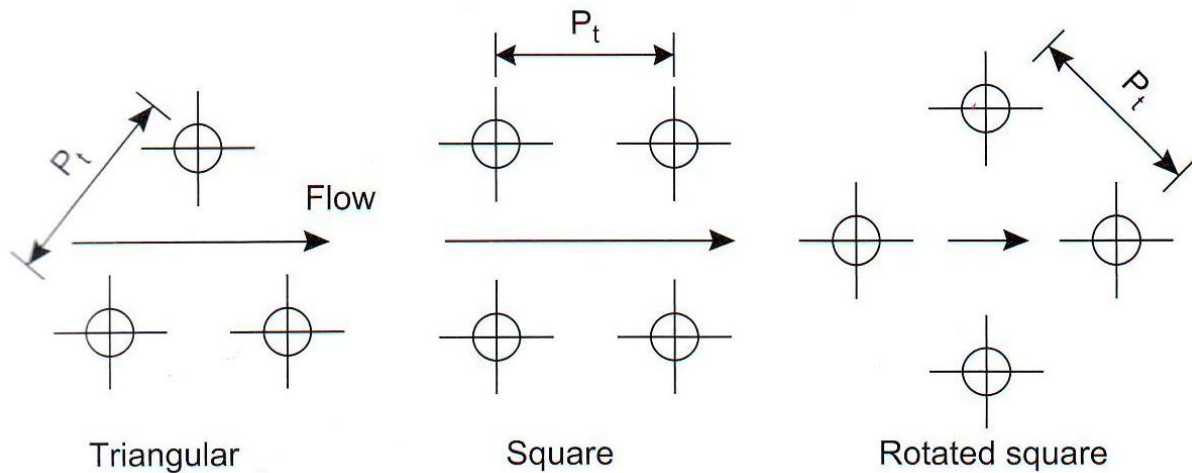


Figure 4.5.2 Tube arrangement in heat exchangers, [13]

The triangular and rotated square patterns help to yield higher heat-transfer rates but at the expense of higher pressure drop than the square pattern. Another advantage with the square arrangement is that it is easier to mechanically clean the outside of the tubes. [10] X2 will hence have a square tube arrangement. The tube pitch, the distance between the tube centers, will be 1.25 times the outside diameter.

#### 4.5.2.2 Tube- Side Passes

The fluid in the tube is usually directed to flow back and forth in a number of “passes” through a group of tubes arranged in parallel, to increase the length of the flow path. The number of passes is selected to give the required tube-side design velocity. Exchangers are built with one to up to 16 tube passes. [10]

X2 will be equipped with two tube-side passes.

#### 4.5.2.3 Shell Types (Passes)

There are many different shell arrangements available on the market but the most common type is single pass. [10] X2 will have one shell pass



#### 4.5.2.4 Baffles

Baffles are used in the shell to direct the fluid steam across the tubes, to increase the fluid velocity and to improve the heat transfer. [10] X2 will be equipped with the most common type of baffle, the single segmental baffle shown in figure 4.5.3:

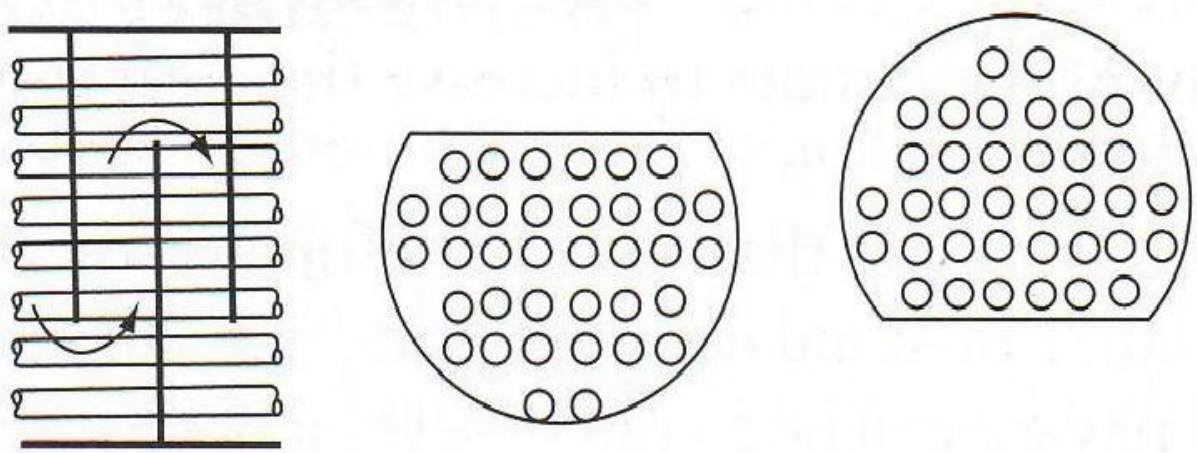


Figure 4.5.3 Baffle design of a single segment [10]

The term ‘baffle cut’ is used to specify the dimensions of a segmental baffle. The baffle cut is the height of the segment removed from the baffle-disc and is expressed as a percentage of the baffle-disc diameter. X2 will have a baffle cut of 45%

#### 4.5.2.5 Number of tubes and tube dimensions

X2 will be outfitted with stainless steel-tubes with an inside diameter of 16 mm and an outside diameter of 19 mm, these are standard dimensions and are selected since they can handle the requested duty, they are compact and relatively cheap. The thickness of the tubes, the gauge, will be 3 mm. This thickness will not only give the condenser the adequate corrosion allowance, it will also give it the ability to withstand the pressure difference. [10] The length of the tubes will be 3.66 meters. Accordingly one tube will have a total surface area of  $0.2185 \text{ m}^2$  (tube-sheet thickness ignored). By dividing the area of one tube with the total required exchanger area, the number tubes required in the exchanger are derived, in the X2 there will be 700 tubes. When calculating the tube bundle diameter, equation 4.13 is used, giving the exchanger a bundle diameter of 746 mm

Eqn 4.13: — —

Where

#### 4.5.2.6 Shell-Side Coefficient

The mean temperature of the condensate in the X2 is according to Chemcad equal to 62.8 see figure 4.5.4, where the vertical axis represents the temperature in °C and the horizontal axis represents the duty in kW.

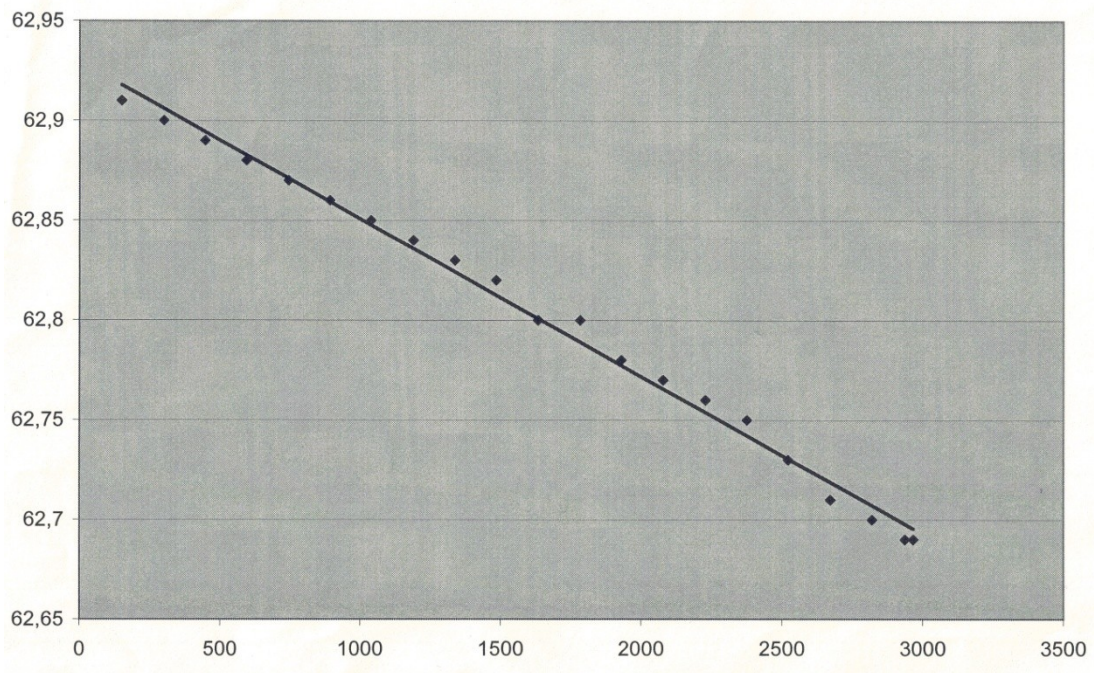


Figure 4.5.4 Condensation temperature profile in X2, from Chemcad

To be able to calculate the shell-side coefficient it is first necessary to determine the tube loading, this is done by equation 4.14. [10]

Eqn 4.14: —

Where

By inserting the tube loading together with ChemCad data on the physical properties of the

condensate at the mean temperature into equation 4.15, the shell-side coefficient is obtained. The X2 will have a shell-side coefficient of 1354 W/m<sup>2</sup>°C

Eqn 4.15: \_\_\_\_\_ -

Where

[19]

#### **4.5.2.7 Tube-Side Coefficient**

The tube cross-sectional area is 0.0352 m<sup>2</sup>. The mass-flow of cooling water is as mentioned earlier 83.8 kg/s and the density of the water at 30 degrees is 995.7 kg/m<sup>3</sup> [18], giving the exchanger a cooling water velocity of 2.39 m/s. The inside coefficient for the water is obtained by equation 4.16 and in X2 it will be 9638 W/m<sup>2</sup>°C.

Eqn 4.16: \_\_\_\_\_

Where

#### **4.5.2.8 Fouling factor**

Fouling is a general term that includes any type of deposit of material that appears on the heat-transfer surface of the heat exchanger. The deposited material will reduce the overall coefficient due to its low thermal conductivity. The designer must consider the effect of fouling upon heat exchanger performance and make provisions in his design for sufficient extra capacity. In equation 4.17 the effect of fouling is allowed for in design by including the inside and the outside fouling coefficient. Typical values of fouling coefficients for common process fluids in tube and shell exchangers are shown in figure 4.5.5. As neither of the fluid in X2 is heavily fouling 6000 W/m<sup>2</sup>°C is used for each side, please see figure 4.5.5 for typical fouling factor values.

<b>Fluid</b>	<b>Coefficient (W/m<sup>2</sup> °C)</b>	<b>Factor (resistance) (m<sup>2</sup>°C/W)</b>
River water	3000–12,000	0.0003–0.0001
Sea water	1000–3000	0.001–0.0003
Cooling water (towers)	3000–6000	0.0003–0.00017
Towns water (soft)	3000–5000	0.0003–0.0002
Towns water (hard)	1000–2000	0.001–0.0005
Steam condensate	1500–5000	0.00067–0.0002
Steam (oil free)	4000–10,000	0.0025–0.0001
Steam (oil traces)	2000–5000	0.0005–0.0002
Refrigerated brine	3000–5000	0.0003–0.0002
Air and industrial gases	5000–10,000	0.0002–0.0001
Flue gases	2000–5000	0.0005–0.0002
Organic vapours	5000	0.0002
Organic liquids	5000	0.0002
Light hydrocarbons	5000	0.0002
Heavy hydrocarbons	2000	0.0005
Boiling organics	2500	0.0004
Condensing organics	5000	0.0002
Heat transfer fluids	5000	0.0002
Aqueous salt solutions	3000–5000	0.0003–0.0002

Figure 4.5.5 Typical fouling factor values [10]

#### 4.5.2.9 Overall Coefficient

The thermal conductivity of the tube wall material is set to 16 W/m°C, please see figure 4.5.6

Metal	Temperature (°C)	$k_w$ (W/m°C)
Aluminium	0	202
	100	206
Brass (70 Cu, 30 Zn)	0	97
	100	104
	400	116
Copper	0	388
	100	378
Nickel	0	62
	212	59
Cupro-nickel (10% Ni)	0–100	45
Monel	0–100	30
Stainless steel (18/8)	0–100	16
Carbon steel	40	60
	100	58
	260	51
Titanium	0–100	16

Figure 4.5.6 Thermal conductivity of the tube wall [10]

When deriving the overall coefficient for X2 from equation 4.17 it is 743 W/m<sup>2</sup>°C.

Eqn 4.17: — — — — —

Where



#### *4.5.2.10 Shell and tube velocities*

High velocities will give high heat-transfer coefficients but also a high pressure drop. The velocities must be high enough to prevent any suspended solid settling, but not so high as to cause erosion [10].

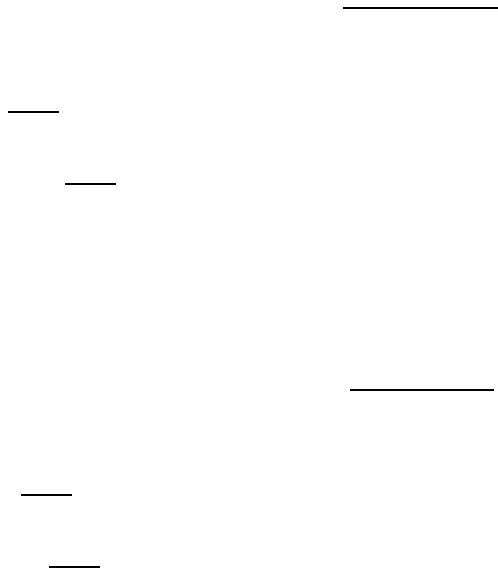
The X2 will have a liquid flow inside the tubes of 2.34 m/s and a vapor flow on the shell side of 65 m/s.



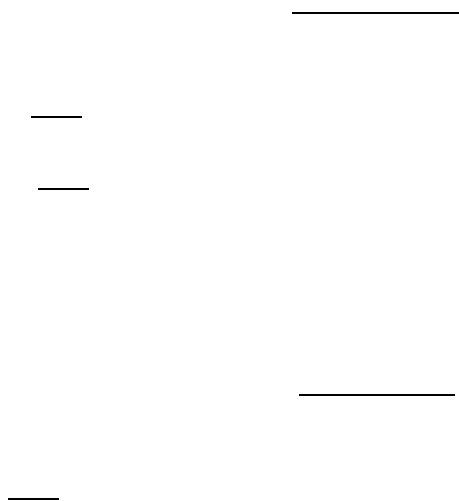
## 4.6 Calculation of Production Yield and Efficiency

From the simulation results 3 different yields was calculated; yield over the reactor section, yield over the distillation section and the total yield

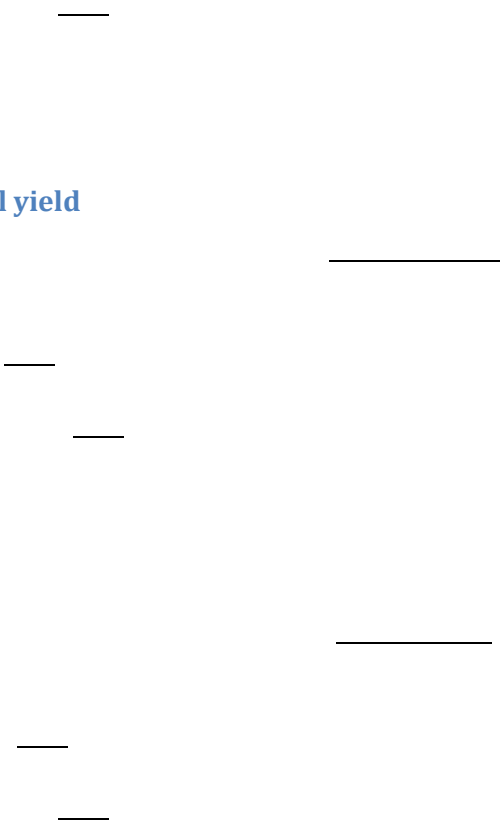
### 4.6.1 Yield over the reactor area



### 4.6.2 Yield of the distillation area



### 4.6.3 Total yield





## 5.0 Results

The result of this project will focus on proposed changes on process design and estimations on the effect of introducing a binary feed of aldehydes. Production modes and the corresponding capacity to each of them will also be presented here.

Were new equipment is needed in order to achieve a production level, preliminary designing has been made.

### 5.1 Process Simulations

Appendix 9.1.2 shows the final distillation section. This simulation setup has been used for each and every simulation in this report.

## 5.1.2 Table of the Distillation Simulations

Chemcad Distillation Simulation Results		
Total feeds to storage (kg/h)	Propanol	Butanol
Binary Feed Level 1	1626	4645
Binary Feed Level 2	3334	7869
Binary Feed Level 3	4836	11167

Table 5.1.1

## 5.2 New Process Design

### 5.2.1 Splitter X1 Preliminary Design

Splitter X1 is a column designed to handle the flows present while in operation mode level 3.

Splitter X1 Preliminary Design Data	
Split 0.9995 propanol on top	
Split 0.9999 butanol in bottom	
Pressure Drop	70 000 Pa
Minimum Reflux:	2.147
Theoretical No. Stages (inf. Reflux)	24 stages
With reflux 2.672	52.47 stages
Tray Efficiency: 77%<	70 stages
Feed stage	29
Condenser Duty	-10803.2 MJ/h
Reboiler Duty	16504.1 MJ/h
Diameter Stripping Section	1.7m
Diameter Rectifying Section	2m
Flooding Design	85%
Downcomer Area	12%
Tray Spacing	0.5m

Table 5.2.1



## 5.2.2 Condenser X2 Preliminary Design

Condenser X1	
<b>Total condensate flow</b>	15995.33 kg/h
<b>Duty</b>	3.5037 MW
<b>Overall coefficient</b>	743 W/m <sup>2</sup> °C
<b>Flow of cooling water</b>	83.32 kg/s
<b>Number of tubes</b>	700
<b>Shell i.d</b>	839 mm
<b>Shell clearance</b>	93 mm
<b>Tube i.d</b>	16 mm
<b>Tube o.d</b>	19 mm
<b>Tube length</b>	3.66 m
<b>Heat transfer area</b>	153 m <sup>2</sup>
<b>Tube material</b>	s.s
<b>Tube side velocity</b>	2.39 m/s
<b>Shell side velocity</b>	65 m/s
<b>Baffel spacing</b>	839 mm
<b>Baffel cut</b>	377 mm

Table 5.2.2

## 5.3 Process Limits

### 5.3.1 Distillation Equipment Internals

The stripping section of C-25201 will be equipped with 8 meters of high performance structured packing of the type FLEXIPAC 2Y from Koch-Glitsch.

The rectifying section of C-25201 will be equipped with 8 meters of high performance structured packing of the type FLEXIPAC 1Y from Koch-Glitsch.

## 5.4 Process Yield

The calculated process yield over the distillation section can be seen in table 5.4.1

Process Yield	Dist. Yield
<b>Butanol</b>	0.990
<b>Propanol</b>	0.900

Table 5.4.1

## 6.0 Discussion

### 6.1 Simulations

Any computerized simulation is a subject for speculations and discussion. It is very important to consider the limits of the models included and what parameters the program in question does not consider.

Perhaps the most important parameter which is not included in the Chemcad software is fluid dynamic. The fluid dynamic is a critical parameter for almost any process involving moving fluids. Distillation is a very good example of a piece of process equipment with many moving fluids of various compositions.

One other important thing to remember is that the thermodynamic model is always wrong, the question is how close to reality it can get and how consistent it is in its predictions. The model chosen for this project is UNIQUAC. The model has continuously shown that it produces good correlation for systems including the most present chemicals. However there is always a small difference between the model and the experimental results. With that given together with the fact that a great number of chemicals in small amounts are present, the model cannot be relied on too far.

Tray efficiency is also an unknown parameter for the binary feed case that would alter the simulations if it was included.

Chemcad does not consider any losses of energy. No real system is entirely isolated or one hundred percent efficient. This needs to be considered when analyzing simulation software.

A major unknown parameter for this project is the outcome of the binary feed operation mode in the reactor area. With a high degree of certainty it will not affect the process however it is far from an absolute truth.

Simulations might seem realistic and valid however it is important due to the reasons stated above and others to see them as initial approximations.

### 6.2 New Equipment

Preliminary designing of new equipment is part of this project and as such it needs to be discussed. The design of new equipment is not to provide schematics but rather to provide information on what kind of equipment needed and what capacities it should have.

The data which the new design is based on is approximate data and the design equations are of the more simple kind. Design of entirely completed equipment is time consuming and it does not lie within the frame of the project to produce any.

Nonetheless this report tries to identify where new equipment is needed and how it could be designed.



### 6.3 Capacity Levels

The capacity levels for this project were determined early on in order to have distinct production levels for the setup of the simulations. As distinct levels they try to mirror the limits of the equipment installed.

New equipment needs capital investments in order to be realized and it is therefore important to early sort out the limiting equipment to see how much potential each individual investment has to increase the production capacity. This lays the basis of the capacity levels.

Level 1 needs no investments in order to be functional.

Level 2, Minor investments in the reactor section and new internals in the first distillation tower are required.

Level 3 needs, in addition to minor investments in the reactor section, a new separation unit for the raw propanol/butanol flow coming from the reaction area.

As production capacity is increasing existing equipment will reach their respective limits and it is vital to consider this when evaluating a production level increase.

## 7.0 Conclusions

- Existing Equipment can only suffice production of level 1 when operating in binary feed mode.
- Minor investments in the reactor section, a new condenser on top of C-25201 along with new internals in C-25201 are needed if production level 2 is to be utilized.
- A new distillation tower instead of distillation tower C-25201 will be needed if production level 3 is to be reached.
- Simulations have indicated that it will be harder to reach product specifications for both butanol and propanol under co-feed operation in comparison to single feed operation.
- Water content in the ingoing aldehyde needs to be kept at a minimum to avoid losses in the propanol purification.
- The UNIQUAC model generates accurate values for the water-butanol-propanol system with only small deviations.
- No VLE system is predicted by the model in the binary feed mode while it is present in the pure butanol mode.

### 7.1 Future Recommendations

- It is vital to run laboratory scale experiments on the binary feed in order to identify the optimum process conditions
- To increase the accuracy of the distillation model the reactor section needs to be modeled rigorously.
- It is recommended to further study the consistency of the UNIQUAC model for the more complex molecules in order to see how their VLE data is predicted.



## 8.0 List of References

Two distinct categories for references exist in this project and those are resources gathered Perstorp produced data and resources gathered externally from databases and literature.

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Author: Neste oxo AB

Year of production: 1992

{7} *Destillations kolumn 3 (c-25203), sammanställning (Distillation column 3 (c-25203), compilation)*

Drawing number: 2-c-25203-020

Author: Neste oxo AB

Year of production: 2001

{8} *Destillations kolumn 5 (c-25205), sammanställning (Distillation column 5 (c-25205), compilation)*

Drawing number: 25205, 21328-D

Author: Koch-Glitsch

Year of production: 2007

{9} *HP-REACTOR, R-25201, compilation*

Drawing number: 2-R-25201-001-1-E

Author: Ekström & Son

Year of production: 92

It should be noted that [www.wolframalpha.com](http://www.wolframalpha.com) has, among others, been used to confirm calculations.



### 8.3 Other resources

Molecular images were created with the open-source program Jmol. Jmol recommends the following citation:

**Jmol: an open-source Java viewer for chemical structures in 3D.** <http://www.jmol.org/>



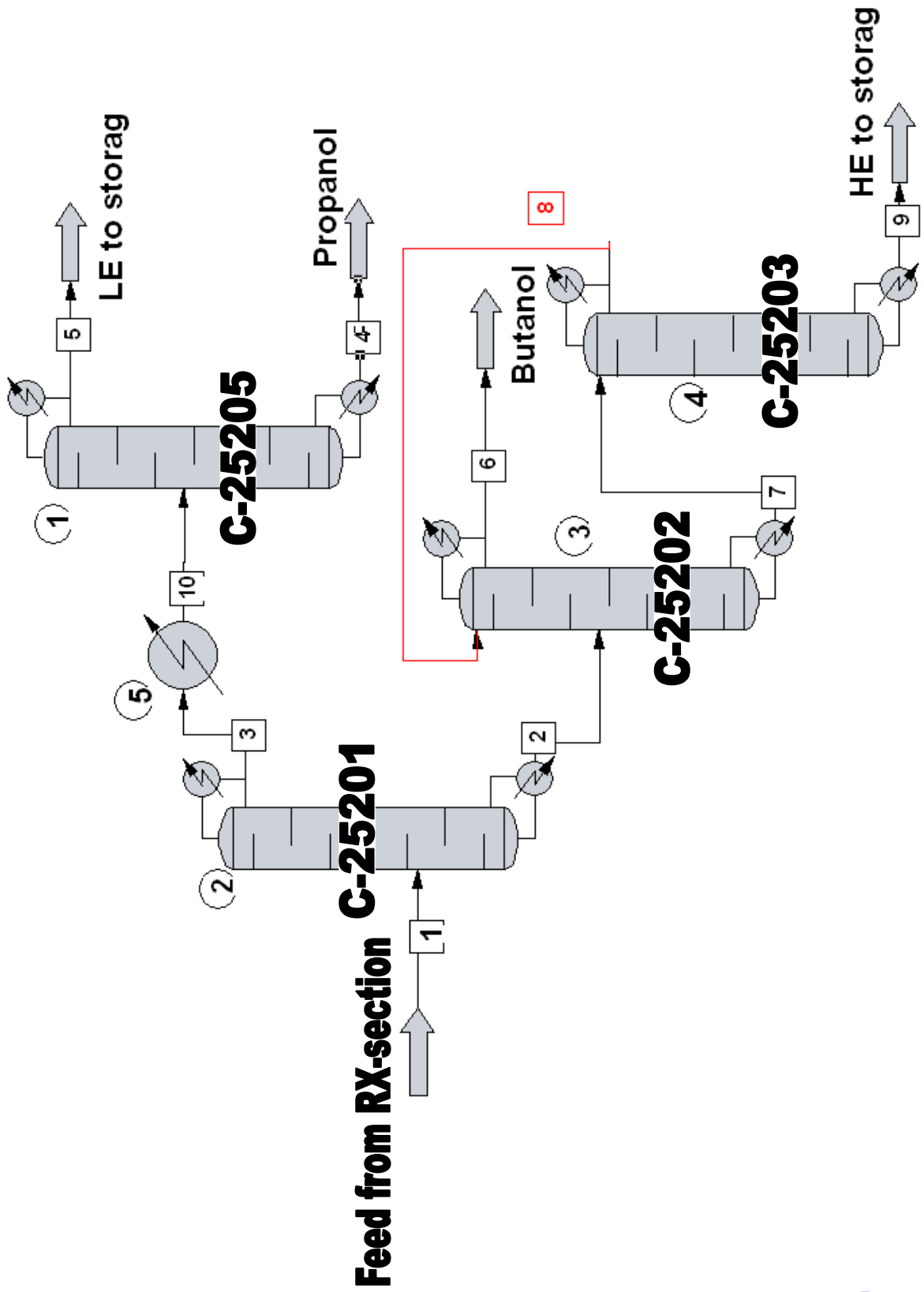
## 9.0 Appendix

### 9.1 Chemcad Simulation Overviews



# Distillation Area with C-25201 as Splitter

## 9.1.2 Distillation Area with C-25201 as Splitter



## 9.2 Simulations of the distillation area

### 9.2.1 Simulations of the distillation area level 1,

#### 9.2.1.1 Column C-25201, level 1

FLOW SUMMARIES:			
Stream No.	1	2	3
Stream Name	Feed from RX	Bottom product from C1	Top product from C1
Temp C	55	101,1797	62,6115
Pres bar	2	0,539	0,239
Enth MJ/h	-30483	-20000	-9795,6
Vapor mass frac.	0	0	0
Total kmol/h	97,1938	64,0302	33,1635
Total kg/h	6609,9504	4760,1693	1849,7811
Total std L m3/h	8,1021	5,8341	2,2681
Total std V m3/h	2178,47	1435,15	743,32
Flowrates in kg/h			
Water	62,74	0	62,74
Di-n-Propyl Ethe	5	0	5
Di-n-Butyl Ether	5	5	0
N-Propanol	1777,0501	1,7767	1775,2734
Isobutanol	2,53	0,4825	2,0475
N-Butanol	4725,05	4720,3311	4,7188
N-Propyl Propion	1,22	1,2185	0,0015
N-Butyl Propiona	5	5	0
N-Propyl N-Butyr	5	5	0
N-Butyl N-Butyra	9,29	9,29	0
Propionic Acid	1,4	1,4	0
N-Butyric Acid	5,67	5,67	0
2-Ethylhexanol	5	5	0

#### 9.2.1.2 Column C-25202, level 1

FLOW SUMMARIES:				
Stream No.	2	8	7	6
Stream Name	Bottom product C1	Top product C3	Bottom product C2	Butanol
Temp C	101,2	117,6	130,1	117,5
Pres bar	0,5	1,0	1,5	1,0
Enth MJ/h	-20000,0	-2834,1	-3274,1	-19267,0
Vapor mass frac.	0,0	0,0	0,0	0,0
Total kmol/h	64,0	9,2	10,6	62,7
Total kg/h	4760,2	683,7	799,3	4645,1
Total std L m3/h	5,8	0,8	1,0	5,7
Total std V m3/h	1435,2	206,3	237,2	1404,5
Flowrates in kg/h				
Water	0,0	0,0	0,0	0,0
Di-n-Propyl Ethe	0,0	0,0	0,0	0,0
Di-n-Butyl Ether	5,0	1,0	5,6	0,5



N-Propanol	1,8	0,0	0,0	1,8
Isobutanol	0,5	0,0	0,0	0,5
N-Butanol	4720,3	680,4	760,5	4640,7
N-Propyl Propion	1,2	0,6	1,0	0,9
N-Butyl Propiona	5,0	0,7	5,4	0,3
N-Propyl N-Butyr	5,0	0,9	5,5	0,4
N-Butyl N-Butyra	9,3	0,0	9,3	0,0
Propionic Acid	1,4	0,0	1,4	0,0
N-Butyric Acid	5,7	0,0	5,7	0,0
2-Ethylhexanol	5,0	0,0	5,0	0,0

### 9.2.1.3 Column C-25203, level 1

FLOW SUMMARIES:			
Stream No.	7	8	9
Stream Name	Bottom product C2	Top product C3	HE to storage
Temp C	130,1	117,6	134,8
Pres bar	1,5	1,0	1,5
Enth MJ/h	-3274,1	-2834,1	-468,7
Vapor mass frac.	0,0	0,0	0,0
Total kmol/h	10,6	9,2	1,4
Total kg/h	799,3	683,7	115,6
Total std L m3/h	1,0	0,8	0,1
Total std V m3/h	237,2	206,3	30,8
Flowrates in kg/h			
Water	0,0	0,0	0,0
Di-n-Propyl Ethe	0,0	0,0	0,0
Di-n-Butyl Ether	5,6	1,0	4,5
N-Propanol	0,0	0,0	0,0
Isobutanol	0,0	0,0	0,0
N-Butanol	760,5	680,4	80,1
N-Propyl Propion	1,0	0,6	0,3
N-Butyl Propiona	5,4	0,7	4,7
N-Propyl N-Butyr	5,5	0,9	4,6
N-Butyl N-Butyra	9,3	0,0	9,3
Propionic Acid	1,4	0,0	1,4
N-Butyric Acid	5,7	0,0	5,7
2-Ethylhexanol	5,0	0,0	5,0

### 9.2.1.5 Column C-25205, level 1

FLOW SUMMARIES:			
Stream No.	3	4	5
Stream Name	Top product C1	Propanol	LE to storage
Temp C	62,6	107,8	94,4
Pres bar	0,2	1,5	1,0
Enth MJ/h	-9795,6	-7951,9	-1594,6



Vapor mass frac.	0,0	0,0	0,0
Total kmol/h	33,2	27,6	5,6
Total kg/h	1849,8	1625,8	224,0
Total std L m3/h	2,3	2,0	0,3
Total std V m3/h	743,3	618,4	125,0
<b>Flowrates in kg/h</b>			
Water	62,7	15,1	47,6
Di-n-Propyl Ethe	5,0	4,6	0,4
Di-n-Butyl Ether	0,0	0,0	0,0
N-Propanol	1775,3	1599,3	175,9
Isobutanol	2,0	2,0	0,0
N-Butanol	4,7	4,7	0,0
N-Propyl Propion	0,0	0,0	0,0
N-Butyl Propiona	0,0	0,0	0,0
N-Propyl N-Butyr	0,0	0,0	0,0
N-Butyl N-Butyra	0,0	0,0	0,0
Propionic Acid	0,0	0,0	0,0
N-Butyric Acid	0,0	0,0	0,0
2-Ethylhexanol	0,0	0,0	0,0

## 9.2.2 Simulations of the distillation area level 2

### 9.2.2.1 Column C-25201, level 2

<b>FLOW SUMMARIES:</b>			
Stream No.	1	2	3
Stream Name	Feed from RX	Bottom product from C1	Top product from C1
Temp C	55	101,1656	62,6877
Pres bar	2	0,539	0,239
Enth MJ/h	-54499	-33578	-19754
Vapor mass frac.	0	0	0
Total kmol/h	174,3536	107,4969	66,8566
Total kg/h	11741,9233	7988,1621	3753,7595
Total std L m3/h	14,3947	9,7897	4,605
Total std V m3/h	3907,9	2409,4	1498,5
<b>Flowrates in kg/h</b>			
Water	114,8278	0	114,8278
Di-n-Propyl Ethe	5	0	5
Di-n-Butyl Ether	5	5	0
N-Propanol	3626,4311	3,6263	3622,8048
Isobutanol	4,25	1,0794	3,1706
N-Butanol	7933,0072	7925,0613	7,9442
N-Propyl Propion	9,2138	9,2018	0,012
N-Butyl Propiona	5	5	0
N-Propyl N-Butyr	5	5	0
N-Butyl N-Butyra	15,565	15,565	0
Propionic Acid	4,1177	4,1177	0



N-Butyric Acid	9,5102	9,5102	0
2-Ethylhexanol	5	5	0

### 9.2.2.2 Column C-25202, level 2

FLOW SUMMARIES:				
Stream No.	7	6	8	2
Stream Name	Bottom product from C2	Butanol	Top product from C3	Bottom product from C1
Temp C	130,4655	117,5426	117,6185	101,1656
Pres bar	1,5	1	1	0,539
Enth MJ/h	-3276,1	-32642	-2812	-33578
Vapor mass frac.	0	0	0	0
Total kmol/h	10,4756	106,1351	9,1138	107,4969
Total kg/h	797,3598	7869,211	678,4057	7988,1621
Total std L m3/h	0,9723	9,6488	0,8313	9,7897
Total std V m3/h	234,8	2378,88	204,27	2409,4
Flowrates in kg/h				
Water	0	0	0	0
Di-n-Propyl Ethe	0	0	0	0
Di-n-Butyl Ether	5,5563	0,5044	1,0608	5
N-Propanol	0	3,6263	0	3,6263
Isobutanol	0	1,0794	0	1,0794
N-Butanol	739,6444	7856,452	671,0271	7925,0613
N-Propyl Propion	7,022	6,7695	4,5949	9,2018
N-Butyl Propiona	5,3987	0,3117	0,7104	5
N-Propyl N-Butyr	5,5135	0,4478	0,9612	5
N-Butyl N-Butyra	15,5968	0,0191	0,0509	15,565
Propionic Acid	4,1179	0,0001	0,0003	4,1177
N-Butyric Acid	9,5102	0	0	9,5102
2-Ethylhexanol	5	0	0	5

### 9.2.2.3 Column C-25203, level 2

FLOW SUMMARIES:			
Stream No.	7	8	9
Stream Name	Bottom product from c2	Top product from c3	HE to storage
Temp C	130,4655	117,6185	137,8052
Pres bar	1,5	1	1,5
Enth MJ/h	-3276,1	-2812	-491,53
Vapor mass frac.	0	0	0
Total kmol/h	10,4756	9,1138	1,3618
Total kg/h	797,3598	678,4057	118,9541
Total std L m3/h	0,9723	0,8313	0,141



<b>Total std V m3/h</b>	234,8	204,27	30,52
<b>Flowrates in kg/h</b>			
<b>Water</b>	0	0	0
<b>Di-n-Propyl Ethe</b>	0	0	0
<b>Di-n-Butyl Ether</b>	5,5563	1,0608	4,4956
<b>N-Propanol</b>	0	0	0
<b>Isobutanol</b>	0	0	0
<b>N-Butanol</b>	739,6444	671,0271	68,6173
<b>N-Propyl Propion</b>	7,022	4,5949	2,427
<b>N-Butyl Propiona</b>	5,3987	0,7104	4,6883
<b>N-Propyl N-Butyr</b>	5,5135	0,9612	4,5522
<b>N-Butyl N-Butyra</b>	15,5968	0,0509	15,546
<b>Propionic Acid</b>	4,1179	0,0003	4,1176
<b>N-Butyric Acid</b>	9,5102	0	9,5102
<b>2-Ethylhexanol</b>	5	0	5

#### 9.2.2.4 Column C-25205, level 2

<b>FLOW SUMMARIES:</b>			
<b>Stream No.</b>	10	4	5
<b>Stream Name</b>	Top product from C1	Propanol	LE to storage
<b>Temp C</b>	110	107,6184	94,7125
<b>Pres bar</b>	1	1,5	1
<b>Enth MJ/h</b>	-16498	-16564	-2685,6
<b>Vapor mass frac.</b>	1	0	0
<b>Total kmol/h</b>	66,8566	57,505	9,3516
<b>Total kg/h</b>	3753,7595	3333,7595	420,0001
<b>Total std L m3/h</b>	4,605	4,101	0,504
<b>Total std V m3/h</b>	1498,5	1288,9	209,6
<b>Flowrates in kg/h</b>			
<b>Water</b>	114,8278	53,9496	60,8783
<b>Di-n-Propyl Ethe</b>	5	4,4909	0,509
<b>Di-n-Butyl Ether</b>	0	0	0
<b>N-Propanol</b>	3622,8048	3264,1927	358,6121
<b>Isobutanol</b>	3,1706	3,17	0,0006
<b>N-Butanol</b>	7,9442	7,9442	0
<b>N-Propyl Propion</b>	0,012	0,012	0
<b>N-Butyl Propiona</b>	0	0	0
<b>N-Propyl N-Butyr</b>	0	0	0
<b>N-Butyl N-Butyra</b>	0	0	0
<b>Propionic Acid</b>	0	0	0
<b>N-Butyric Acid</b>	0	0	0
<b>2-Ethylhexanol</b>	0	0	0

## 9.2.3 Simulations of the distillation area level 3

### 9.2.3.1 Column C-25201, level 3

FLOW SUMMARIES:			
Stream No.	1	2	3
Stream Name	Feed from RX	Bottom product from C1	Top product from C1
Temp C	55,0	101,2	62,7
Pres bar	2,0	0,5	0,2
Enth MJ/h	-77661,0	-47455,0	-28555,0
Vapor mass frac.	0,0	0,0	0,0
Total kmol/h	248,7	152,0	96,6
Total kg/h	16714,7	11289,1	5425,6
Total std L m3/h	20,5	13,8	6,7
Total std V m3/h	5573,3	3407,1	2166,2
Flowrates in kg/h			
Water	165,9	0,0	165,9
Di-n-Propyl Ethe	5,0	0,0	5,0
Di-n-Butyl Ether	5,0	5,0	0,0
N-Propanol	5244,3	5,2	5239,1
Isobutanol	6,0	1,6	4,4
N-Butanol	11230,2	11219,0	11,2
N-Propyl Propion	3,6	3,6	0,0
N-Butyl Propiona	5,0	5,0	0,0
N-Propyl N-Butyr	5,0	5,0	0,0
N-Butyl N-Butyra	22,1	22,1	0,0
Propionic Acid	4,1	4,1	0,0
N-Butyric Acid	13,5	13,5	0,0
2-Ethylhexanol	5,0	5,0	0,0

### 9.2.3.2 Column C-25202, level 3

FLOW SUMMARIES:				
Stream No.	7	6	8	2
Stream Name	Bottom product from C1	Top product from C 3	Butanol 3	Bottom product from C2
Temp C	101,2	117,6	117,5	130,7
Pres bar	0,5	1,0	1,0	1,5
Enth MJ/h	-47455,0	-2812,9	-46319,0	-3293,2
Vapor mass frac.	0,0	0,0	0,0	0,0
Total kmol/h	152,0	9,1	150,6	10,5
Total kg/h	11289,1	678,6	11166,7	800,9
Total std L m3/h	13,8	0,8	13,7	1,0
Total std V m3/h	3407,1	204,6	3376,6	235,2
Flowrates in kg/h				



Water	0,0	0,0	0,0	0,0
Di-n-Propyl Ethe	0,0	0,0	0,0	0,0
Di-n-Butyl Ether	5,0	1,1	0,5	5,6
N-Propanol	5,2	0,0	5,2	0,0
Isobutanol	1,6	0,0	1,6	0,0
N-Butanol	11219,0	674,0	11155,9	737,1
N-Propyl Propion	3,6	1,7	2,7	2,6
N-Butyl Propiona	5,0	0,7	0,3	5,4
N-Propyl N-Butyr	5,0	1,0	0,4	5,5
N-Butyl N-Butyra	22,1	0,1	0,0	22,1
Propionic Acid	4,1	0,0	0,0	4,1
N-Butyric Acid	13,5	0,0	0,0	13,5
2-Ethylhexanol	5,0	0,0	0,0	5,0

### 9.2.3.3 Column C-25203, level 3

FLOW SUMMARIES:			
Stream No.	7	8	9
Stream Name	Bottom product from c2	Top product from c3	HE to storage
Temp C	130,7	117,6	140,0
Pres bar	1,5	1,0	1,5
Enth MJ/h	-3293,2	-2812,9	-508,3
Vapor mass frac.	0,0	0,0	0,0
Total kmol/h	10,5	9,1	1,4
Total kg/h	800,9	678,6	122,4
Total std L m3/h	1,0	0,8	0,1
Total std V m3/h	235,2	204,6	30,6
Flowrates in kg/h			
Water	0,0	0,0	0,0
Di-n-Propyl Ethe	0,0	0,0	0,0
Di-n-Butyl Ether	5,6	1,1	4,5
N-Propanol	0,0	0,0	0,0
Isobutanol	0,0	0,0	0,0
N-Butanol	737,1	674,0	63,1
N-Propyl Propion	2,6	1,7	0,9
N-Butyl Propiona	5,4	0,7	4,7
N-Propyl N-Butyr	5,5	1,0	4,6
N-Butyl N-Butyra	22,1	0,1	22,0
Propionic Acid	4,1	0,0	4,1
N-Butyric Acid	13,5	0,0	13,5
2-Ethylhexanol	5,0	0,0	5,0

### 9.2.3.4 Column C-25205, level 3

FLOW SUMMARIES:			
Stream No.	10	4	5
Stream Name	Top product from C1	Propanol	LE to storage



<b>Temp C</b>	110,0	107,6	94,8
<b>Pres bar</b>	1,0	1,5	1,0
<b>Enth MJ/h</b>	-23848,0	-24162,0	-3663,1
<b>Vapor mass frac.</b>	1,0	0,0	0,0
<b>Total kmol/h</b>	96,6	83,9	12,7
<b>Total kg/h</b>	5425,6	4836,3	589,3
<b>Total std L m3/h</b>	6,7	5,9	0,7
<b>Total std V m3/h</b>	2166,2	1880,6	285,6
<b>Flowrates in kg/h</b>			
<b>Water</b>	165,9	90,2	75,6
<b>Di-n-Propyl Ethe</b>	5,0	4,5	0,5
<b>Di-n-Butyl Ether</b>	0,0	0,0	0,0
<b>N-Propanol</b>	5239,1	4725,9	513,2
<b>Isobutanol</b>	4,4	4,4	0,0
<b>N-Butanol</b>	11,2	11,2	0,0
<b>N-Propyl Propion</b>	0,0	0,0	0,0
<b>N-Butyl Propiona</b>	0,0	0,0	0,0
<b>N-Propyl N-Butyr</b>	0,0	0,0	0,0
<b>N-Butyl N-Butyra</b>	0,0	0,0	0,0
<b>Propionic Acid</b>	0,0	0,0	0,0
<b>N-Butyric Acid</b>	0,0	0,0	0,0
<b>2-Ethylhexanol</b>	0,0	0,0	0,0

## 9.4 List of Chemicals

Hydrogen  
Butyraldehyde  
Propionadehyde  
1-Butanol  
N-Propanol  
Propyl propionate  
2-Methyl-1-pentanol  
Di-butyl-ether  
Butyl-butanoate  
Butyric acid  
4-octanone (3-methyl-4-heptanone)

### 9.4.1.1 Hydrogen

symbol | H<sub>2</sub>  
atomic number | 1  
atomic weight | 2.00794  
phase at STP | gas  
melting point | -259.14 °C (rank: 101st)  
boiling point | -252.87 °C (rank: 93rd)  
(properties at standard conditions)  
density |  $8.99 \times 10^{-5}$  g/cm<sup>3</sup> (rank: 96th)  
sound speed | 1270 m/s (rank: 61st)  
thermal conductivity | 0.1805 W/(m K) (rank: 83rd)  
(properties at standard conditions)  
magnetic type | diamagnetic  
color | (colorless)  
refractive index | 1.000132  
valence | 1  
electronegativity | 2.2  
electron affinity | 72.8 kJ/mol (kilojoules per mole)  
ionization energies | 1312 kJ/mol  
molar heat of combustion | 285.8 kJ/mol (kilojoules per mole)





### 9.4.1.2 Butyraldehyde

formula | CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CHO  
compound formula | C<sub>4</sub>H<sub>8</sub>O  
name | butyraldehyde  
IUPAC name | butanal,  
molecular weight | 72.1057 g/mol  
phase | liquid (at STP)  
melting point | -96 °C  
boiling point | 75 °C  
density | 0.8 g/cm<sup>3</sup>  
density | 0.8 g/cm<sup>3</sup>  
vapor pressure | 89.98 mmHg  
viscosity | 4.3×10<sup>-4</sup> Pa s (at 25 °C)  
surface tension | 0.0299 N/m  
refractive index | 1.38  
specific heat capacity c<sub>p</sub> | gas | 1.434 J/(g K)  
specific heat of formation Δ<sub>f</sub>H° | gas | -2.84 kJ/g  
specific heat of vaporization | 0.4674 kJ/g |  
specific heat of combustion | 34.38 kJ/g |  
specific heat of fusion | 0.1494 kJ/g |  
critical temperature | 537 K |  
critical pressure | 4.32 MPa |(at STP)



### 9.4.1.3 Propionaldehyde

formula | CH<sub>3</sub>CH<sub>2</sub>CHO  
compound formula | C<sub>3</sub>H<sub>6</sub>O  
name | propionaldehyde  
IUPAC name | propanal  
molecular weight | 58.0791 g/mol  
phase | liquid (at STP)  
melting point | -81 °C  
boiling point | 48 °C  
density | 0.805 g/cm<sup>3</sup>  
solubility | very soluble in water  
density | 0.805 g/cm<sup>3</sup>  
vapor pressure | 970.4 mmHg  
viscosity | 3.21×10<sup>-4</sup> Pa s (at 25 °C)  
surface tension | 0.0234 N/m  
refractive index | 1.362  
specific heat capacity c<sub>p</sub> | gas | 1.389 J/(g K)  
specific heat of formation Δ<sub>f</sub>H° | gas | -3.196 kJ/g  
specific heat of vaporization | 0.511 kJ/g |  
specific heat of combustion | 31.32 kJ/g |  
critical temperature | 505 K |  
critical pressure | 5.26 MPa |  
(at STP)



#### 9.4.1.4 1-Butanol

molecular weight | 74.1216 g/mol  
phase | liquid (at STP)  
melting point | -90 °C  
boiling point | 117 °C  
density | 0.81 g/cm<sup>3</sup>  
density | 0.81 g/cm<sup>3</sup>  
vapor pressure | 7.24 mmHg (at 25 °C)  
viscosity | 0.002544 Pa s (at 25 °C)  
surface tension | 0.02628 N/m  
refractive index | 1.399  
specific heat of formation  $\Delta_f H^\circ$  | gas | -3.709 kJ/g  
specific heat of vaporization | 0.626 kJ/g |  
specific heat of combustion | 36.05 kJ/g |  
specific heat of fusion | 0.12641 kJ/g |  
critical temperature | 563 K |  
critical pressure | 4.42 MPa |  
(at STP)

#### 9.4.1.5 Properties of N-Propanol

molecular weight | 60.095 g/mol  
phase | liquid (at STP)  
melting point | -127 °C  
boiling point | 97 °C  
density | 0.804 g/cm<sup>3</sup>  
solubility | miscible in water  
density | 0.804 g/cm<sup>3</sup>  
vapor pressure | 9.998 mmHg  
viscosity | 0.001945 Pa s (at 25 °C)  
surface tension | 0.02375 N/m  
refractive index | 1.384  
specific heat capacity  $c_p$  | gas | 1.424 J/(g K)  
| liquid | 2.395 J/(g K)  
specific heat of formation  $\Delta_f H^\circ$  | gas | -4.245 kJ/g  
specific heat of vaporization | 0.79 kJ/g |  
specific heat of combustion | 33.635 kJ/g |  
specific heat of fusion | 0.0894 kJ/g |  
critical temperature | 536 K |  
critical pressure | 5.2 MPa | (at STP)



#### 9.4.1.6 Propyl propionate

formula |  $\text{CH}_3\text{CH}_2\text{COOCH}_2\text{CH}_2\text{CH}_3$   
compound formula |  $\text{C}_6\text{H}_{12}\text{O}_2$   
name | propyl propionate  
IUPAC name | propanoic acid propyl ester  
molecular weight | 116.158 g/mol  
phase | liquid (at STP)  
melting point |  $-76\text{ }^\circ\text{C}$   
boiling point |  $123\text{ }^\circ\text{C}$   
density |  $0.881\text{ g/cm}^3$   
refractive index | 1.393  
critical temperature | 570 K  
critical pressure | 3.06 MPa  
(at STP)

#### 9.4.1.7 2-methyl-1-pentanol

formula |  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}(\text{CH}_3)\text{CH}_2\text{OH}$   
compound formula |  $\text{C}_6\text{H}_{14}\text{O}$   
name | 2-methyl-1-pentanol  
IUPAC name | 2-methylpentan-1-ol  
molecular weight | 102.175 g/mol  
phase | liquid (at STP)  
boiling point |  $148\text{ }^\circ\text{C}$   
density |  $0.824\text{ g/cm}^3$   
solubility | slightly soluble in water  
density |  $0.824\text{ g/cm}^3$   
vapor pressure | 1.5 mmHg  
viscosity | 0.01327 Pa s (at  $25\text{ }^\circ\text{C}$ )  
surface tension | 0.02645 N/m  
refractive index | 1.418  
specific heat capacity  $c_p$  | liquid |  $2.427\text{ J/(g K)}$   
specific heat of vaporization |  $0.5814\text{ kJ/g}$  |  
specific heat of combustion |  $28.78\text{ kJ/g}$  |  
critical temperature | 604 K |  
critical pressure | 3.45 MPa |  
(at STP)

#### 9.4.1.8 Di-butyl-ether



formula | [CH3(CH2)\_3]\_2O  
compound formula | C8H18O  
name | dibutyl ether  
IUPAC name | 1-butoxybutane  
molecular weight | 130.228 g/mol  
phase | liquid (at STP)  
melting point | -98 °C  
boiling point | 142.5 °C  
density | 0.764 g/cm<sup>3</sup>  
solubility | insoluble in water  
density | 0.764 g/cm<sup>3</sup>  
vapor pressure | 4.799 mmHg  
viscosity | 6.37×10<sup>-4</sup> Pa s (at 25 °C)  
surface tension | 0.02347 N/m  
refractive index | 1.399  
specific heat capacity c<sub>p</sub> | liquid | 2.136 J/(g K)  
specific heat of vaporization | 0.3455 kJ/g |  
specific heat of combustion | 40.64 kJ/g |  
critical temperature | 588 K |  
critical pressure | 3.01 MPa | (at STP)

#### 9.4.1.9 Butyl butanoate

formula | CH3CH2CH2COO(CH2)\_3CH3  
compound formula | C8H16O2  
name | butyl butanoate  
IUPAC name | butanoic acid butyl ester  
molecular weight | 144.211 g/mol  
phase | liquid (at STP)  
melting point | -91.5 °C  
boiling point | 164.5 °C  
density | 0.869 g/cm<sup>3</sup>  
solubility | insoluble in water  
density | 0.869 g/cm<sup>3</sup>  
vapor pressure | 1.9 mmHg (at 25 °C)  
viscosity | 9.8×10<sup>-4</sup> Pa s (at 25 °C)  
surface tension | 0.02611 N/m  
refractive index | 1.406  
specific heat of vaporization | 0.279 kJ/g  
critical temperature | 612 K (at STP)



#### 9.4.1.10 Butyric acid

formula |  $\text{CH}_3\text{CH}_2\text{CH}_2\text{COOH}$   
compound formula |  $\text{C}_4\text{H}_8\text{O}_2$   
name | butyric acid  
molecular weight | 88.1051 g/mol  
phase | liquid (at STP)  
melting point |  $-4.5\text{ }^\circ\text{C}$   
boiling point |  $162\text{ }^\circ\text{C}$   
density |  $0.964\text{ g/cm}^3$   
solubility | soluble in water  
density |  $0.964\text{ g/cm}^3$   
vapor pressure | 0.4299 mmHg  
viscosity |  $0.001426\text{ Pa s}$  (at  $25\text{ }^\circ\text{C}$ )  
surface tension |  $0.0268\text{ N/m}$   
refractive index | 1.398  
specific heat of formation  $\Delta_f H^\circ$  | gas |  $-5.402\text{ kJ/g}$   
specific heat of vaporization |  $0.722\text{ kJ/g}$  |  
specific heat of combustion |  $24.74\text{ kJ/g}$  |  
specific heat of fusion |  $0.1315\text{ kJ/g}$  |  
critical temperature |  $618\text{ K}$  |  
critical pressure |  $3.95\text{ MPa}$  |  
(at STP)

#### 9.4.1.11 4-octanone (3-methyl-4-heptanone)

formula |  $\text{C}_8\text{H}_{16}\text{O}$   
name | 4-octanone  
IUPAC name | octan-4-one  
molecular weight | 128.212 g/mol  
phase | liquid (at STP)  
melting point |  $16.6\text{ }^\circ\text{C}$   
boiling point |  $166\text{ }^\circ\text{C}$   
density |  $0.819\text{ g/cm}^3$   
solubility | insoluble in water  
density |  $0.819\text{ g/cm}^3$   
vapor pressure | 2.1 mmHg (at  $25\text{ }^\circ\text{C}$ )  
surface tension |  $0.02577\text{ N/m}$   
refractive index | 1.4173  
specific heat of vaporization |  $0.312\text{ kJ/g}$   
critical temperature |  $623.8\text{ K}$   
(at STP)

