

LAPPEENRANTA UNIVERSITY OF TECHNOLOGY  
LUT School of Engineering Science  
Chemical Engineering

*Juho Ikävalko*

**INCREASING ENERGY EFFICIENCY IN BIOREFINERIES**

Examiners: Prof. Tuomas Koiranen  
MSc (Tech) Ilkka Rantanen

Instructor: MSc (Tech) Jaakko Siitonen

## **PREFACE**

This master's thesis was made for Pöyry Oyj in Vantaa between January and August of 2018.

I want to thank all the people in Vantaa who have helped me during this work, especially other thesis workers and trainees. Your support has made my workload much lighter. Also, thank you to all the people I've met during my time in Lappeenranta. These five years have probably been the best time of my life!

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In remembrance of Tuula.

Vantaa, 15<sup>th</sup> of July, 2018

## **ABSTRACT**

Lappeenranta University of Technology

LUT School of Engineering Science

Chemical Engineering

Juho Ikävalko

### **Increasing Energy Efficiency in Biorefineries**

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MSc. Ilkka Rantanen

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The aim of this thesis was to review the energy consumption of different biorefinery processes and to find ways to analyze and improve their energy efficiency. In the literature part of this thesis different methods to design energy efficient biorefinery and other chemical processes are reviewed and the overall energy balance of different biofuel process concepts is evaluated based on available case studies.

A large part of process design and process energy efficiency lies in accurate process simulation. An overview of different activity coefficient and equation of state methods used to model non-ideal systems in biorefineries is also presented in the literature part of this thesis.

In the experimental part of this thesis the accuracy of different thermodynamic methods was evaluated for a bioethanol process case study. From the process simulation results a pinch analysis was constructed and the energy saving potential of the process was determined.

The most accurate choice of thermodynamic method for the case simulation was observed to be UNIQUAC-HOC based on experimental and modelled binary and ternary VLE-data comparison. The pinch analysis of the process shows a possibility of saving 36 % heating and 47% of cooling energy consumption compared to the original heat exchanger network design. However, this is based on a theoretical heat exchanger network and its effect on the process operability should be studied first before further implementation.

## **TIIVISTELMÄ**

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### **Increasing Energy Efficiency in Biorefineries**

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Tämän diplomityön tavoitteena oli suorittaa katsaus erityyppisten biojalostamoiden energiankulutuksesta ja -tehokkuudesta. Kirjallisuusosassa tarkastellaan erilaisia energiatehokkaita suunnitteluratkaisuita biojalostamoissa ja prosessiteollisuudessa. Lisäksi käydään läpi erilaisen biopolttaineprosessien energiasuhdetta perustuen kirjallisuudesta saataviin tapaustutkimuksiin.

Tärkeä osa prosessisuunnittelua ja energiatehokkuutta on prosessisimulaation rakentaminen. Kirjallisuusosassa käydään läpi erilaisia aktiviteettikerroin- ja tilanyhtälömalleja, joiden avulla voidaan mallintaa monissa biojalostamoprosesseissa esiintyviä epäideaaleja systeemejä.

Tämän työn kokeellisessa osassa tarkasteltiin eri termodynaamisten menetelmien tarkkuutta bioetanoliprosessin mallintamisessa. Prosessisimulaation tuloksia käyttäen prosessille tehtiin pinch analyysi jonka perusteella prosessin energiansäästöpotentiaali määritettiin.

Kaikista tarkimmaksi termodynaamiseksi menetelmäksi tarkastellulle prosessille havaittiin olevan UNIQUAC-HOC perustuen kokeellisen ja mallinnetun kaasu-neste tasapainon vertailuun. Prosessin pinch analyysi osoitti, että prosessissa voitaisiin säästää 36 % lämmityskustannuksissa ja 47 % jäähdytyskustannuksissa. Tämä perustuu kuitenkin vain teoreettiseen lämmönsiirtoverkkoon, jonka vaikutus todellisen prosessin ajettavuuteen täytyy vielä tutkia.

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## NOMENCLATURE

$E_{0,i}^{0l}$	Standard exergy for liquid fraction, kJ
$E_{0,i}^{0v}$	Standard exergy for vapor fraction, kJ
$S_m^{ig}$	Mixture ideal gas entropy, kJ/K
$A$	Helmholtz free energy, kJ/mol
$A^{ideal}$	Ideal-gas Helmholtz free energy, kJ/mol
$A_{ij}$	Wilson parameter, -
$A^{res}$	Residual Helmholtz free energy, kJ/mol
$b$	NRTL parameter, -
$B$	The overall virial coefficient, $\text{cm}^3/\text{g mol}$
$B_{bound}$	Bound pair interaction parameter, -
$B_{chem}$	Chemical pair interaction parameter, -
$B_{free}$	Free pair interaction parameter, -
$B_{i,j}$	The 2 <sup>nd</sup> virial coefficient, $\text{cm}^3/\text{g mol}$
$B_{metastable}$	Metastable pair interaction parameter, -
$b_v$	The excluded volume, $\text{m}^3$
$C$	Constant, 0,12
$c$	NRTL parameter, -
$d$	NRTL parameter, -
$D_{ij}$	Dispersion constant, -
$E$	Exergy, kJ
$e$	NRTL parameter, -
$e/k$	Constant, -
$E_{CH}$	Chemical exergy, kJ
$E_{in}$	Exergy going into the system, kJ
$E_{in}$	Required exergy change in the system, kJ
$E_K$	Kinetic exergy, kJ
$E_{Out}$	Exergy going out of the system, kJ
$E_P$	Potential exergy, kJ
$E_{PH}$	Physical exergy, kJ
$E_{tot}$	Total exergy of a stream, kJ
$E_{TR}$	Transiting exergy, kJ
$f_i^l$	Liquid phase fugacity, Pa
$f_i^v$	Vapor phase fugacity, Pa
$G$	NRTL parameter, -
$g$	The radial distribution function, -
$G^E$	Excess gibbs free energy, kJ/mol
$h$	Number of parameters, -
$H^{*,v}$	Pure component vapor enthalpy, kJ
$H_0$	Enthalpy of the stream at initial state, kJ
$H_1$	Enthalpy of the stream at environment state, kJ
$H^E$	Excess enthalpy, kJ
$i$	Data point number within a data group, -
$j$	Measured variable for data point, -
$k$	Total number of points in a data group, -
$l$	Constant, -
$L_0$	Liquid fraction in reference conditions, -

$\dot{m}$	mass flow, kg/s
$M$	Number of association site per molecule, -
$m$	The number of spherical segments per molecule, -
$M^l$	Thermodynamic property of a mixture in liquid phase, kJ/mol
$m_n$	Number of measured variables for a data point
$M^v$	Thermodynamic property of a mixture in vapor phase, kJ/mol
$n$	Amount of substance, mol
$o$	data group number in regression case, -
$p$	pressure, Pa
$q, q'$	Molecular structure constants, -
$R$	The ideal gas constant, J/molK
$S$	Weighted sum of squares, -
$S_0$	Entropy of the stream at initial state, kJ/K
$S_1$	Entropy of the stream at environment state, kJ/K
$S_E$	The root mean square error, -
$S_m$	Mixture entropy, kJ/K
$T$	Temperature, K
$t$	Total number of data groups used, -
$T_0$	Reference temperature, K
$u$	Dispersion energy of interaction, -
$u^0/k$	Dispersion energy parameter, -
$V$	Volume, m <sup>3</sup>
$v^0$	Close-packed hard-core volume of the fluid, cm <sup>3</sup> /mol
$V_0$	Vapor fraction in reference conditions, -
$v^{00}$	Temperature independent soft-core volume of the fluid, cm <sup>3</sup> /mol
$v_k$	The number of groups of type k, -
$V_m$	Molar volume, cm <sup>3</sup> /g mol
$w$	Weighting factor for data group, -
$x$	Liquid mole fraction, -
$x_0$	Molar fraction in liquid phase in standard conditions, -
$X^A$	Mole fraction of molecules not bonded at site A, -
$y$	vapor mole fraction, -
$y_0$	Molar fraction in vapor phase in standard conditions, -
$Z$	Compressibility factor, -
$z_i$	Mole fraction of a substance in a mixture, -
$Z_{ij}$	Calculated value
$ZM_{ij}$	Measured value, -

### Greek letters

$\alpha$	Non-randomness parameter, -
$\alpha^{\text{assoc}}$	Association contribution parameter, kJ/mol
$\alpha^{\text{chain}}$	Chain contribution parameter, kJ/mol
$\alpha^{\text{disp}}$	Dispersion contribution parameter, kJ/mol
$\alpha^{\text{hs}}$	Hard sphere contribution parameter, kJ/mol
$\beta$	The SRK energy term, bar/L mol <sup>2</sup>
$\beta^{A_i B_j}$	Association volume parameter, -
$\Gamma$	Group residual activity coefficient, -

$\gamma_i$	Activity coefficient, -
$\Delta^{AB}$	Association strength, -
$\Delta E_{Out}$	Desired exergy output from the system, kJ
$\Delta H$	Enthalpy change, kJ
$\Delta_{mix}M$	Property change of mixing, kJ/mol
$\Delta S$	Entropy, kJ/K
$\Delta T$	Temperature change, K
$\Delta_{vap}H^*$	Component vaporization enthalpy, kJ
$\epsilon^{AB}/k$	Energy of association,
$\epsilon^{A_i B_j}$	Associating energy, bar/L mol
$\eta$	Reduced density, kg/mol
$\eta_e$	Simple efficiency, -
$\theta, \theta'$	Area fractions, -
$\kappa^{AB}$	Volume of association,
$\mu_i$	Pure component ideal gas chemical potential, kJ/mol
$\mu_i^0$	Chemical potential of component i in ideal gas mixture, kJ/mol
$\rho$	Density of the fluid, kg/m <sup>3</sup>
$\sigma$	Standard deviation
$\tau$	Interaction parameter, -
$\phi, \phi'$	Segment fractions, -
$\phi_i^l$	Liquid phase fugacity coefficient, -
$\phi_i^v$	Vapor phase fugacity coefficient, -
$\chi$	Efficiency with transiting energy, -
$\psi$	Rational efficiency, -

## Abbreviations

CEM	Circular economy mode
CGM	Cogeneration mode
CHP	Combined heat and power
CPA	Cubic plus association
CPM	Conventional production mode
EOS	Equation of state
GC	Group contribution
HEN	Heat exchanger network
HIDiC	Internally heat-integrated distillation columns
HOC	Hayden-O'Connell
LLE	Liquid-liquid equilibrium
MER	Minimum energy requirement/maximum energy recovery
MVR	Mechanical vapor recompression
NRTL	Non-random two liquid
PC	Perturbed chain
SAFT	Statistical associating fluid theory
TVR	Thermal vapor recompression
UNIFAC	UNIQUAC Functional-group activity coefficient
UNIQUAC	Universal quasi-chemical
VLE	Vapor-liquid equilibrium
VR	Variable range

## **1. INTRODUCTION**

Process industry strives towards energy efficiency. The benefits of energy efficient processing include higher energy security, conservation of resources and increase in global competitiveness and decrease in emissions. Energy efficient technologies are being designed all the time, but their implementation can be challenging due to often perceived possible economic or other risks. However, often simple, well known technologies can be adapted for process design to achieve substantial energy recovery on an industrial and national level. (ACS Presidential Roundtable on Sustainable Manufacturing, 2009)

Biorefineries, especially biofuel production plants, have gained a lot of interest in recent years. Many companies have caught on the bioethanol and other biofuel production due to the increase in demand for renewable fuels. Energy efficiency of these plants is important not only from an economic but especially from an environmental perspective. The advantage of using renewable resources is clear but since working with these resources can be challenging the energy efficiency of these processes can suffer. The total environmental impact of a fuel is not only based on its raw materials or emissions but also the energy economy of the production process.

### **1.1. The objective**

The objective of this master's thesis is to get a clear outlook on the methodologies used for increasing energy efficiency in biorefineries. In the theoretical part of this thesis first the basic idea of energy efficiency and what it includes in process industry is reviewed. This information is extended to different biorefinery concepts by looking at the most common energy intensive unit operations. Different methods for analyzing and designing energy efficient processes are also reviewed and their effectiveness is evaluated. Also, using available literature, some case studies considering the current outlook of biofuel production energy efficiency and balance are collected and reviewed.

Biorefinery processes include complex and often non-ideal chemical systems that can be challenging to model accurately using process simulation software. To get reliable simulation results for both the stream compositions and energy usage, the right choice of thermodynamic method for each unit operation is of great importance. Different equation of state

and activity coefficient methods are presented in this thesis and especially methods used to estimate systems with associating species such as carboxylic acids are focused on.

In the practical part one of the reviewed methodologies, namely pinch-analysis, is used to optimize a bioethanol production plant in design phase. The aim is to find the minimum amount of external utilities needed and to compare how much energy could be saved by building a heat exchange network for the whole process according to the pinch principle. To acquire reliable results, the thermodynamic method for the process simulation made using Aspen Plus is also chosen using the information obtained from the theoretical part.

## **2. ENERGY EFFICIENCY**

Energy efficiency is a widely discussed subject in many different industries. Despite this the definition of energy efficiency is not always straightforward. The industry specific ideas of energy efficiency can vary greatly, and it can be viewed from both process and product lifecycle point of view. (Heikkilä et al., 2008)

Like other efficiency criteria such as economic or thermodynamic efficiency, energy efficiency is often measured in terms of units of products produced. Efficient energy usage can mean two things: The minimization of energy losses in the process or the optimization of the energy usage based on the amount of energy needed by the process i.e. removing unneeded energy consumption. Finding and optimizing these losses and inefficiencies is a critical part of process design. (Heikkilä et al., 2008)

The investment required for increasing the energy efficiency of a process always includes uncertainties. Both energy and product prices are subjected to economic changes and the investment for energy efficient technologies should be studied thoroughly (Svensson & Berntsson, 2014).

Some of the big contributors where energy efficiency possibilities can be found in process industry are (Heikkilä et al., 2008):

- Steam generation
- Heat recovery and exchange
- Burning processes
- Cogeneration

- Supply and transmission of electricity
- Motor powered systems
- Air pressure systems
- Pumping
- Heating & air conditioning
- Lighting
- Drying, thickening & separation processes

Steam generation and cogeneration are shortly reviewed in this chapter. Heat recovery and exchange is discussed in more detail in chapter 4. Certain energy intensive separation processes are also discussed in chapter 3. The other systems presented here are important when considering overall process energy efficiency. For example, approximately two thirds of electricity used in process industry is consumed by different motor systems when electricity used for creating chemicals i.e. electrolysis is excluded (Cefic aisbl, 2013). However, they are out of the scope of this thesis which focuses more on efficient use of heating and cooling utilities. An outlook of the basic characteristics of energy efficient design of these systems has been made for example by Heikkilä et al. (2008).

## **2.1. Steam generation**

Steam is one of the most used heating utility in process industry. Steam is a popular heat transfer medium due to its high heat capacity, non-toxicity, stability and low price. It can be used for heating or pressure control of the process. Other uses for steam are for example stripping, fractionation and drying processes (U.S. Department of Energy, 2012). Process steam can be distributed in different pressures. Both low and high-pressure steam have their advantages: (Heikkilä, et al., 2008)

High pressure steam:

- Higher achievable temperature for saturated steam
- Smaller volume
- Pressure can easily be lowered for each application

Low pressure steam:

- Less energy losses in the boiler and pipes
- Less heat in the condensate
- Less risk of leaks in the pipes
- Less scaling in the boiler

It is often recommended to use steam at suitable pressure to reach the needed temperature for the process. However, overpressurized steam creates unneeded energy losses.

Steam is generated in boilers where water is heated using a fuel such as oil or biomass. The pressure inside the boiler is adjusted so that steam can be generated at needed temperature. This steam is then distributed to the process over steam distribution network. Steam traps are scattered throughout the network to collect and recycle condensate steam. (Einstein et al., 2001) A simple diagram of steam system is show in Figure 1.

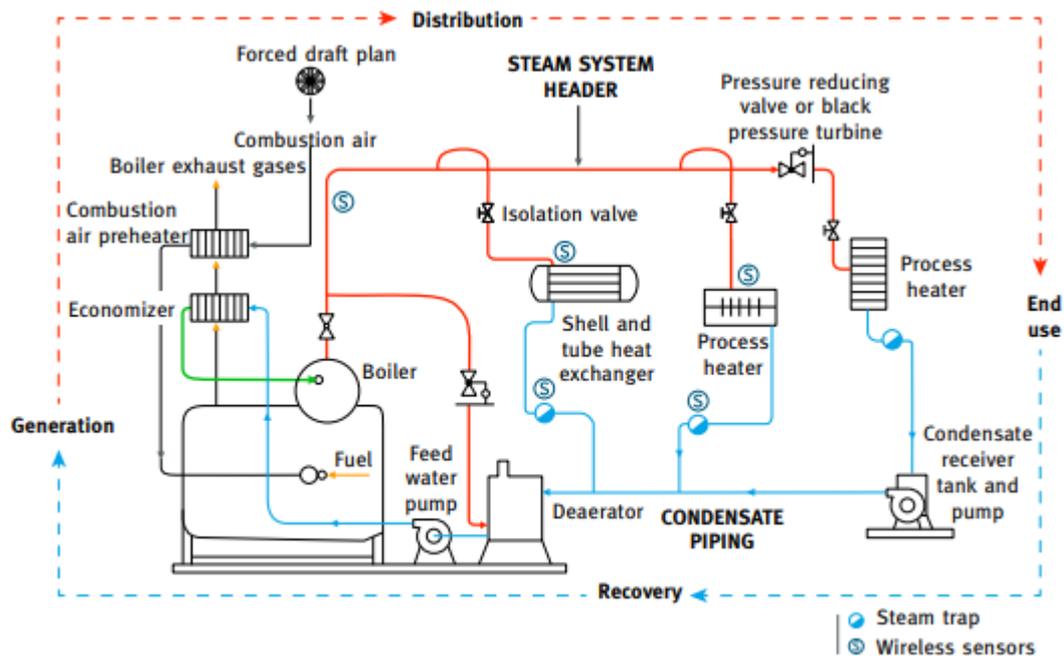


Figure 1 Steam generation system. (U.S. Department of Energy, 2012)

The different parts of a steam system (steam generation, distribution, recovery and use) are presented in Figure 1. In terms of energy usage most inefficiencies in steam generation system are tied to the boiler and fuel burning. For example, inefficient monitoring of oxygen during burning can cause incomplete burning of the fuel and induce inefficient heat

recovery. (UNIDO, 2014) There are many ways to design an efficient steam generation system. Some of the main characteristics of energy efficient steam generation system are shown in Table I.

Table I Characteristics of a high efficiency steam generation system. (UNIDO, 2014)

System part	Characteristics
Steam generation	Combustion gas oxygen monitoring Sootblowing in heavy fuel using boilers Flue gas thermal energy recovery Boiler water quality maintenance
Steam distribution	Steam leak prevention and repair Proper insulation in piping, valves & fittings Steam trap maintenance
Steam recovery	High condensate recovery High recovery of flash steam

In many industries working with biomass there are obvious opportunities for using biomass in the boiler for creating steam. The efficiency of the boiler is dependent on the fuel used so the suitability of biomass as a steam generation fuel needs to be determined first.

## 2.2. CHP-systems

Combined heat and power (CHP), also known as cogeneration is a technology where both electricity and thermal energy are created simultaneously. In biorefineries this can be achieved using fuels that can be obtained from the process waste and side streams that cannot be otherwise used in the production. This is especially important for many biofuel production processes where all biomass is not completely processed, and a lot of waste solids are left after processing. Also, in some of processes the produced fuel is used in the cogeneration system to produce the needed process heat. This lowers the need of outside energy at the cost of some of the product. (Morales et al., 2015)

Using biomass or biofuels in cogeneration systems in biorefineries can lead to significant economic savings and reduce the environmental impact. Since the raw material for the cogeneration plant can be obtained from the main process the overall energy efficiency of the plant increases and some processes have said to achieve even self-sufficiency in energy production. (Ali Mandegari et al., 2017) Sometimes the excess energy and heat can also be distributed to nearby residential areas close to the production site which increases the economic viability of the process.

The purpose of CHP-system in a basic biorefinery concept is to burn various organic by-products. In many biorefineries these byproducts can include lignin, unconverted cellulose and hemicellulose. In many cases there are other sidestreams such as biogas and biomass sludge available from an integrated wastewater treatment plant along with other organic and inorganic byproducts depending on the process. These byproducts can always be combined with untreated biomass or biofuel if self-sufficiency is to be achieved. (Ali Mandegari et al., 2017)

Compared to conventional condensing power plants and separate heat generation, CHP-plants are significantly more energy efficient. This is because CHP-processes can use the energy released from condensation of the process fluid for heat generation whereas this energy goes to waste in the conventional power plant (Alakangas & Flyktman, 2001). Sankey diagram explaining the basic difference of traditional and CHP-energy generation is shown in Figure 2.

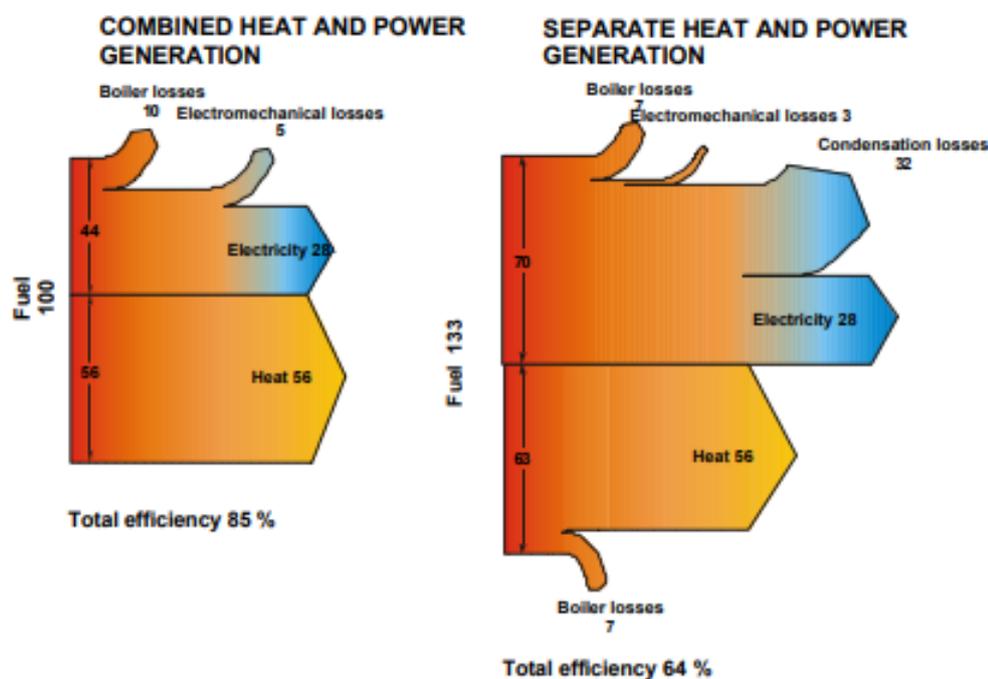


Figure 2 Energy consumption of conventional and CHP-energy generation systems. (Alakangas & Flyktman, 2001)

Sankey diagram presented in Figure 2 shows the overall energy losses in the process. These diagrams are often presented in unit operation basis demonstrating which parts of the process are the most energy demanding. They are useful tools for obtaining an overview of the energy efficiency of a process. Based on Figure 2 it can be seen that the CHP plant has higher efficiency and fewer losses compared to separate heat and power generation plants.

There are many types of designs for CHP-plants used in biorefineries. Some of the conventional designs include normal and high-pressure biomass rankine cycles and biomass gasification based combined cycle. In the conventional boiler type plants biomass is burned in a large boiler and used to generate superheated steam. Part of this superheated steam can be used for process heating and the rest of the steam is turned into medium and low-pressure steam and electricity using a steam turbine. The boiler can also be operated in high pressure and the resulting high-pressure flue gas can be fed through a generator to generate electricity. (Wan et al., 2016) The basic principle of this type of conventional rankine cycle CHP-plant is shown in Figure 3.

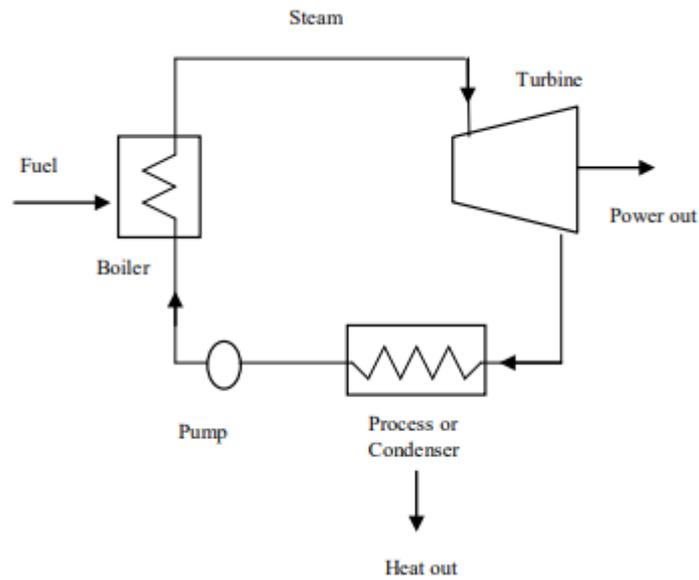


Figure 3 Basic rankine cycle used in many CHP-plants  
(U.S Environmental Protection Agency, 2017)

Other type of cogeneration system is a biomass gasification-based CHP. This type of process doesn't only generate heat and electricity but also generates very clean syngas that has a potential for use in many different applications besides heat and electricity generation. In these processes biomass is gasified using a gasification reactor. These reactors are available in many different configurations such as fixed, moving, fluidized and entrained bed configurations. The created syngas is then cleaned and filtered and fed through a gas turbine or gas engine to generate electricity. The resulting exhaust gas from the gas turbine can then be used to heat up and to generate superheated steam which can be converted into electricity and low-pressure steam like in the boiler type process. (Wan et al., 2016)

### 3. BIOREFINERY PROCESSES

This part of the thesis focuses on different biofuel production processes. The use of biomass for production of renewable fuels has increased in recent years due to increasing energy demand and the need to reduce global warming and greenhouse gasses. Bioethanol is the most used biofuel in transportation and it has been marketed as the clean and sustainable fuel compared to fossil fuels (Modarresi et al., 2012). However, these processes also require considerable amount of energy. An energy efficient outlook on the process design

is needed to make biofuel production sustainable from both economic and environmental point of view.

### **3.1. Generations of biofuels**

Biofuels are often divided into generations based on the raw materials used for their production. Currently there are three generations of biofuels. The first-generation biofuels are produced from feed crops such as wheat, corn or sugar through fermentation process. These biofuels are often a cause of debate because of their questionable benefits. Their energy balance is often much worse than farther biofuels generations and since they are made from food sources, it is often questioned whether it is socially acceptable to use food as a raw material for fuel production. (Biofuel.org.uk, 2010)

Second generation biofuels are produced from waste products such as waste vegetable oil or lignocellulosic materials such as wood. They are more socially acceptable than first generation biofuels, but their processing is much more challenging. (Biofuels.org.uk, 2010)

Second generation biofuels, also known as advanced biofuels, have been researched thoroughly in the recent years. They are currently being promoted by many policies around the world. Their high efficiency and non-food nature bring a lot of incentive to research. Also, many countries have several types of second generation biomass which can be used for production of fuels. (Valdivia et al., 2016). However, there aren't many commercial plants in operation currently since the research for most efficient technologies is still ongoing.

Third generation biofuels were separated from second generation biofuels due to their much higher efficiency. Third generation biofuel are derived from different species of algae which produce oils that can be refined into diesel or other fuels. These algae can be genetically manipulated in order to produce a huge range of different kinds of fuels. This makes the process very adaptable. Algae that are used for biofuel generation are also said to have great yields compared to other generation biofuel processes. The problem with third generation of biofuels is tied to the cultivation process of the algae. Algae need large amounts of light, water and nutrients in order to sustain growth. The nutrient and water requirement is often so high that currently the production of third generation biofuels is not viable in most situations. (Biofuels.org.uk, 2010)

### **3.2. Biorefinery process**

There are many different types of biorefinery processes. The choice of the process depends on the desired product as well as the raw materials used in the process. Processes producing bioalcohols, such as bioethanol commonly operate using a fermentation process. For the first-generation biofuels this process is fairly straightforward where the fermentable sugars are easily extracted from the raw material (Dias et al., 2009). Second generation raw materials however require more complex processes.

One of the common processes used for producing bioethanol along with other alcohols is the enzymatic hydrolysis process. To obtain sugars to be fermented from the biomass the biomass needs to be pretreated first, making the cellulose molecules more accessible for the next process step where enzymes convert cellulose into sugars. The sugars are then processed into alcohols using the well-known fermentation process. These alcohols then need to be purified and concentrated using different separation processes such as distillation. This is the basics of most commercial bioethanol processes although individual differences of course exist.

A block diagram showing an example of a bioethanol process with different unit operations is shown in Figure 4.

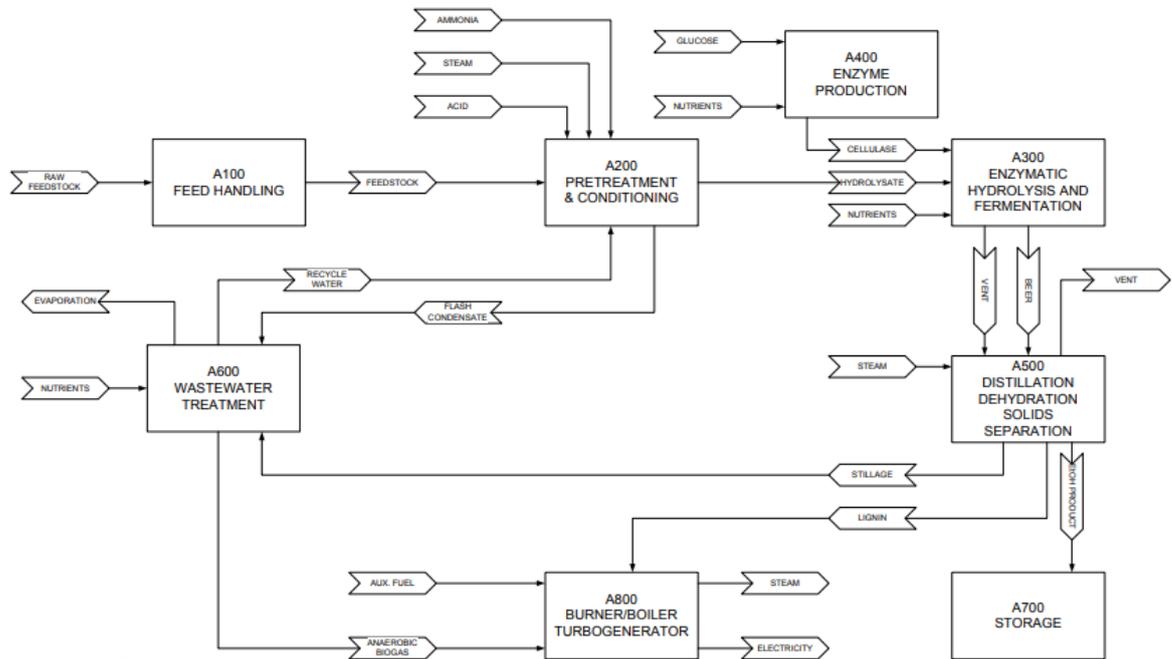


Figure 4 Simple block diagram for enzymatic hydrolysis process for production of bioethanol from lignocellulosic biomass. (Humbird et al., 2011)

Figure 4 shows the basic enzymatic hydrolysis process of a second-generation bioethanol plant. Besides the basic process steps explained earlier it can also be seen that these processes include side processes such as wastewater treatment and energy generation from side and waste streams.

### 3.3. Unit operations in biorefineries

Production of biofuels from lignocellulosic biomass has been investigated a lot in recent years. Many types of processes have been implemented for biofuel production. The choice of process depends on the type of biofuel being produced as well as the type of biomass used as the raw material. Certain unit operations are commonly seen in most of these processes. Some of these unit operations are reviewed in this chapter along with their overall effect on the process energy economy and efficiency.

#### 3.3.1. Pretreatment technologies

Pretreatment is an essential step when producing bioethanol from lignocellulosic biomass through the hydrolysis route as well as in certain biodiesel processes. The purpose of pretreatment is to break down lignin and to disrupt the crystalline structure of cellulose. This

is especially important in enzymatic hydrolysis processes where the enzymes need a good access to the cellulose structure to achieve good conversion. Pretreatment technologies can be roughly divided into four groups (Sun & Cheng, 2002):

- Physical pretreatment
- Physicochemical pretreatment
- Chemical pretreatment
- Biological pretreatment

The choice of pretreatment technology greatly affects the subsequent hydrolysis and fermentation effectiveness. In terms of energy consumptions both physical and physicochemical routes often require high temperatures, pressures or large amounts of electricity. However, steam explosion has been recognized as one of the most energy efficient pretreatment methods especially compared to physical pretreatment methods. Chemical and biological methods may also require medium temperatures and long residence times depending on the process. For this reason, these processes could have potential for heat integration. (Sun & Cheng, 2002)

Mechanical treatment of biomass includes breaking down biomass using physical methods such as chipping, grinding and milling. The physical breaking down of fibers has been proven to reduce cellulose crystallinity and to improve the digestibility of the biomass. Another type of physical process is slow pyrolysis process where the biomass is treated in very high temperatures and it is reduced to gaseous products and solid residues. These residues can then be processed in the same way as with other pretreatment products. By cooling the pyrolysis gas rapidly in fast pyrolysis liquid hydrocarbons are also generated which can be processed into biofuels. (Sun & Cheng, 2002)

Physicochemical processes are based on simultaneous chemical and physical treatment of the biomass. These processes include methods such as steam explosion (autohydrolysis) and ammonia fiber explosion. In these processes the biomass goes through a sudden reduction in pressure in presence of water or other chemicals which causes physical and chemical changes in the fiber structure. Other physicochemical processes include microwave treatment, wet oxidation and ultrasound treatment. (Alvira et al., 2010)

Chemical pretreatment includes processes such as alkali and acid pretreatment, ozonolysis, organosolv process and ionic liquid pretreatment. These methods are based on the chemical removal of lignin and subsequent change of cellulose structure to more accessible to enzymes. The process conditions in these processes are usually less harsh than in the physical processes in terms of pressure and temperature. (Alvira et al., 2010)

Biological pretreatment of lignocellulosic biomass is based on using different microorganisms such as fungi to break down cellulose. The advantage of these processes is their low cost and lower environmental impact. However, the cultivation and treatment times are often much longer than in other methods and some sugars may be lost due to microbial activity. (Sindhu et al., 2016)

### **3.3.2. Distillation**

Distillation is a unit operation present in almost every biofuel production process. Distillation is used to separate and purify the final product from the other substances using the difference in volatility between different components. In a basic distillation column setup, the feed stream is a liquid mixture that is fed to the column at the feed stage. Vapor phase flows upwards the column whereas the liquid phase flows downwards. The column is filled with either plates or packing depending on the column type. The vapor and liquid phases are brought into contact with each other. The vapor that comes out from the top of the column is then condensated and part of this condensate is recycled back to the column to provide feed flow above the column. This is called the reflux stream. Part of the bottom product is also reboiled and recycled back to provide liquid stream. The basic construction of single and multifeed column is shown in Figure 5. (Towler & Sinnott, 2013)

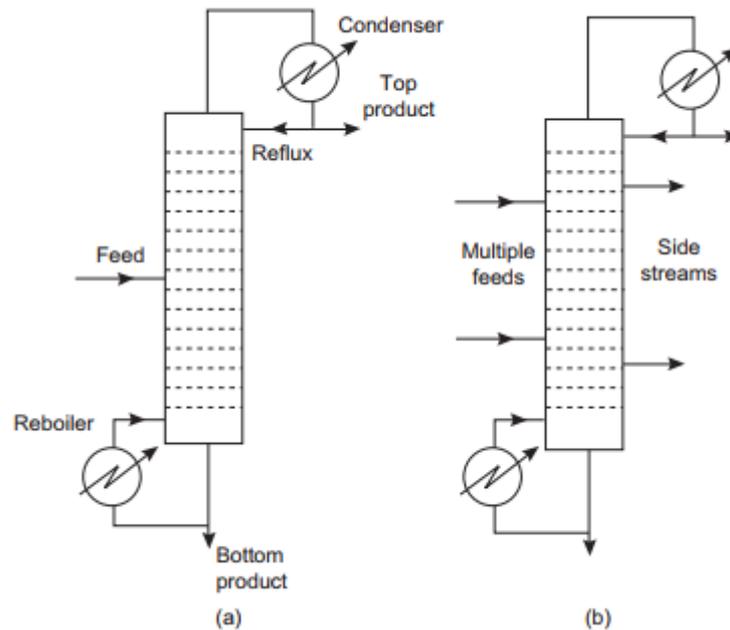


Figure 5 Basic distillation column construction for a) basic single feed column and b) multistream column. (Towler & Sinnott, 2013)

When designing a distillation column there are few basic design variables that need to be solved: the reflux ratio, number of ideal/real stages and the feed stage. Nowadays this is almost always done using commercial simulation software. Shortcut models, such as Winn-Underwood-Gilliam method, allow the designer to estimate the stage and reflux requirements to reach the required purity product with minimum information. The results from shortcut models can be used for an initial estimation that can be inserted into a rigorous model that can carry out a stage-by-stage mass and energy balances. Graphical methods for determining these variables also exist but they are no longer in use in any practical context. It is important to note that the results obtained from distillation simulations are very dependent on the phase equilibrium model used. (Towler & Sinnott, 2013) In terms of energy consumption, the proper design is imperative in order to minimize the inefficiencies inside the column.

Distillation is one of the most energy intensive processes in chemical industry (Tarighaleslami et al., 2012). It has been in use for a long time and is considered a mature technology. However, due to the demand for lower energy consumption and lower CO<sub>2</sub> emissions has led to the need for finding more energy efficient separation solutions. Certain distillation column arrangements have been proven to lower the overall energy con-

sumption of a distillation process. Some of the proposed arrangements are (Halvorsen & Skogestad, 2011):

- Petlyuk arrangement
- Extended Petlyuk arrangement
- Kaibel arrangement
- Multi-effect columns
- Internally heat-integrated distillation column (HIDiC)
- Dividing wall column (Aspirion & Kaibel, 2010)

These arrangements might not be feasible for every process, but they should still be considered. Quite significant energy savings could be obtained when using a suitable arrangement. (Halvorsen & Skogestad, 2011). Methods such as pinch-analysis and exergy analysis can also be used to design energy efficient distillation columns. These methods are presented in chapter 4.

### **3.3.3. Evaporation**

Evaporation, along with crystallization, is one of the most common techniques used in industry for recovery of dissolved solids. Evaporation is a process where a more volatile component is removed by vaporization. The product from evaporation is a more concentrated liquid or in some cases dried solids although this could be considered as drying or crystallization. (Towler & Sinnott, 2013)

Many different evaporation technologies have been proposed and used in different industries. Evaporation is also a common unit operation in biofuel production processes for recovery of water or solvents. The basic evaporator types can be divided into direct-heat, long-tube, forced-circulation, wiped-film and short-tube evaporators (Towler & Sinnott, 2013).

In conventional evaporators energy tied to the vapor stream is either lost or only partially used. MVR (mechanical vapor recompression) is a technology aiming to reduce the high energy consumption of evaporation equipment. The idea of MVR is to compress the vapor that is generated during the evaporation process and to use this compressed vapor with higher boiling point temperature to heat the same unit. When this vapor condenses it re-

leases its latent heat which lowers the need for external utilities for heating. (Andritz Oy, 2018) This same technology is also in use in many conventional distillation units.

MVR-evaporator requires practically only electricity to drive the mechanical compressor. This energy consumption is often considerably lower than what is required in thermally heated evaporation units. The energy requirement of the compressor is mostly dependent on the heat exchange efficiency, pressure drops in the system as well as the product specific boiling point increase (GEA Process Engineering, 2015). A very similar system is the Thermo Vapor Recompression (TVR) which uses a steam venturi instead of a mechanical compressor to compress a fraction of the steam flow and return it back into the evaporator (SPX Corporation, 2009). A simple example of an MVR-system is show in Figure 6.

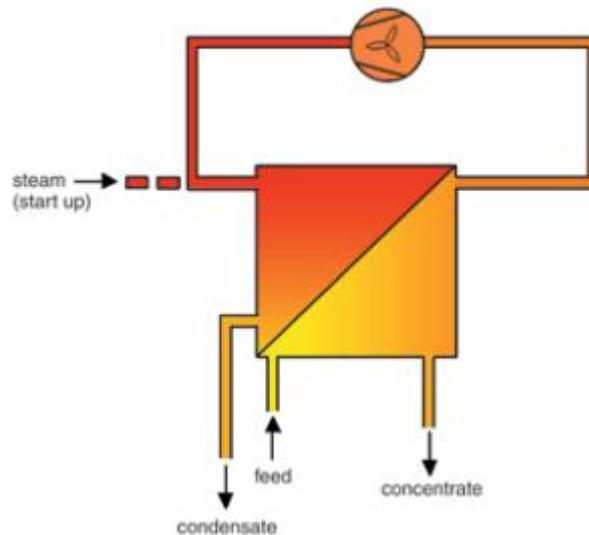


Figure 6 Basis of an MVR-system (SPX Corporation, 2009)

Another commonly used energy conservation method for evaporation is multi-effect evaporation. In this system multiple evaporation units are put in series. These units operate in different pressures so that the pressure is always lower than the next unit in the series. The vapor produced in one unit can then be used to heat up the unit before it since the temperature of the vapor is higher in the unit with higher pressure. An example of this system is shown in Figure 7.

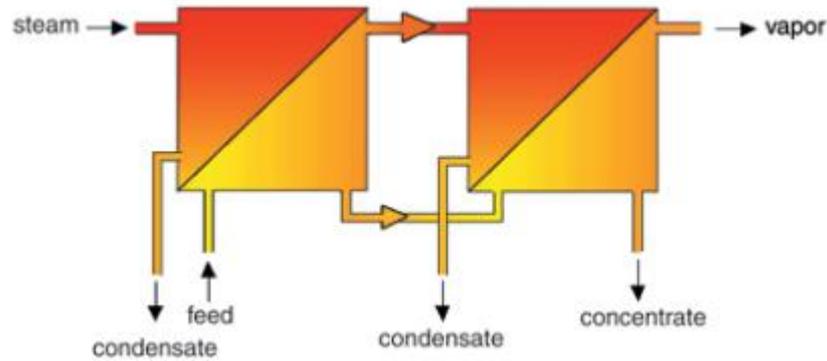


Figure 7 Multiple effect evaporator principle (SPX Corporation, 2009)

### 3.3.4. Drying

Drying is a process for removing water or other volatile liquids from solids by evaporation. The difference between evaporation and drying is in the desired end product. In drying the aim is to remove most or all the water from the solids and to produce dry product whereas in evaporation the product is more concentrated liquid. Drying is an operation that is present in almost every process where solids are the desired end product (Towler & Sinnott, 2013). This is also the case in many biorefineries. In biofuel production plants solid lignin is often obtained as a side stream to be fed into a CHP-plant or to be sold as a side product.

Drying is a very energy-intensive process. It accounts for about 15% of industrial energy consumption (Atuonwu et al., 2011). Thermal drying, which is the most common type, uses hot air as the heating and mass transfer medium. If there are concerns about flammability, a carrying gas, such as nitrogen or flue gas, can also be used. Gas is heated using a burner either directly or indirectly. Many types of fuels can be used for the burner such as oil, gas or biomass (Towler & Sinnott, 2013).

The energy efficiency of a drying operation is dependent on the solids being dried and the type of dryer being used. In many processes where heat sensitive solids are being dried, the overall energy efficiency can be low due to the low drying temperature used. A common way to improve energy efficiency in the drying process is to preheat the dryer input air using exhaust air from the same process. This is suitable for some processes but processes

where the drying temperature is relatively low, this might be thermodynamically infeasible. (Atuonwu et al., 2011)

A more novel approach to energy efficient drying of solids is drying air dehumidification using adsorbents. In these processes moisture is removed from the inlet air using different types of adsorbents such as zeolite. The main energy input to this type of process is for the adsorbent regeneration which is done using hot air. This presents some integration opportunities since the regenerator exhausts have high energy content. This technology is suitable especially for low temperature air drying processes. (Atuonwu et al., 2011)

### **3.4. Case studies on biofuel energy balance**

#### **3.4.1. Bioethanol**

Biofuel production is a competitive scene. Many countries have their own policies for biofuel production and usage and the demand for biofuels is growing all the time due to environmental demands (Meihui et al., 2014). Because of these demands it is expected that biofuels will provide around 27% of the transportation fuels by 2050 (Morales et al., 2015). The newest EU target for renewable energy by 2030 is 32 % (Keating & Simon, 2018). Bioethanol is the most produced biofuel with around 90% share of all the biofuel production (Meihui et al., 2014). It has great flexibility and potential as a transport fuel. It can be used as a mixture with fossil fuels in existing vehicles without a need for engine modifications as well as a non-mixture in specially designed engines (Morales et al., 2015).

Bioethanol is being produced as both first generation and second-generation biofuel. Energy balance of these processes can differ greatly. In this chapter, a literature review of different case studies on bioethanol plants and their overall energy efficiencies is made.

Bioethanol production plants are evaluated based on their energy balance, also called energy ratio. It is defined as the heat content ratio of the produced fuel (J/kg) divided by the non-renewable energy that is needed to produce one kilogram of that fuel. It depends mainly on the performance of the process and the raw material, which can differ greatly between plants. The value of this ratio can be lower or higher than one and theoretically approach infinity if the plant only uses renewable energy for its process. (Morales et al., 2015)

Morales et al. (2015) compiled sixty case studies available from literature where different lignocellulosic raw materials were used for bioethanol production. The energy balance of these cases varied between 0,5 and 13. Morales et al. (2015) clarify that the only cases where the energy balance was lower than 1 were cases where no electricity cogeneration was done using leftover biomass. This shows that use of side and waste products for energy generation is an important parameter when designing bioethanol production plants. This is also the reason why second-generation fuels often have higher energy efficiency than the first generation fuels. (Morales et al., 2015)

Wang et al. (2014) analyzed a plant producing bioethanol from sweet sorghum stem which is a fast growing, non-food feedstock crop and has gained a lot of attention especially in China for its good yield and low cost as a raw material for bioethanol. Energy balance of this plant was found to be 1,56. The low energy balance can be contributed to the large quantity of steam required by the process (around 65% of the consumed fossil energy). Steam is mainly generated using coal combustion in China. Other big energy demand is the plant cultivation unit. The different stages and units present in the process and the required utilities and raw materials are shown in Figure 8.

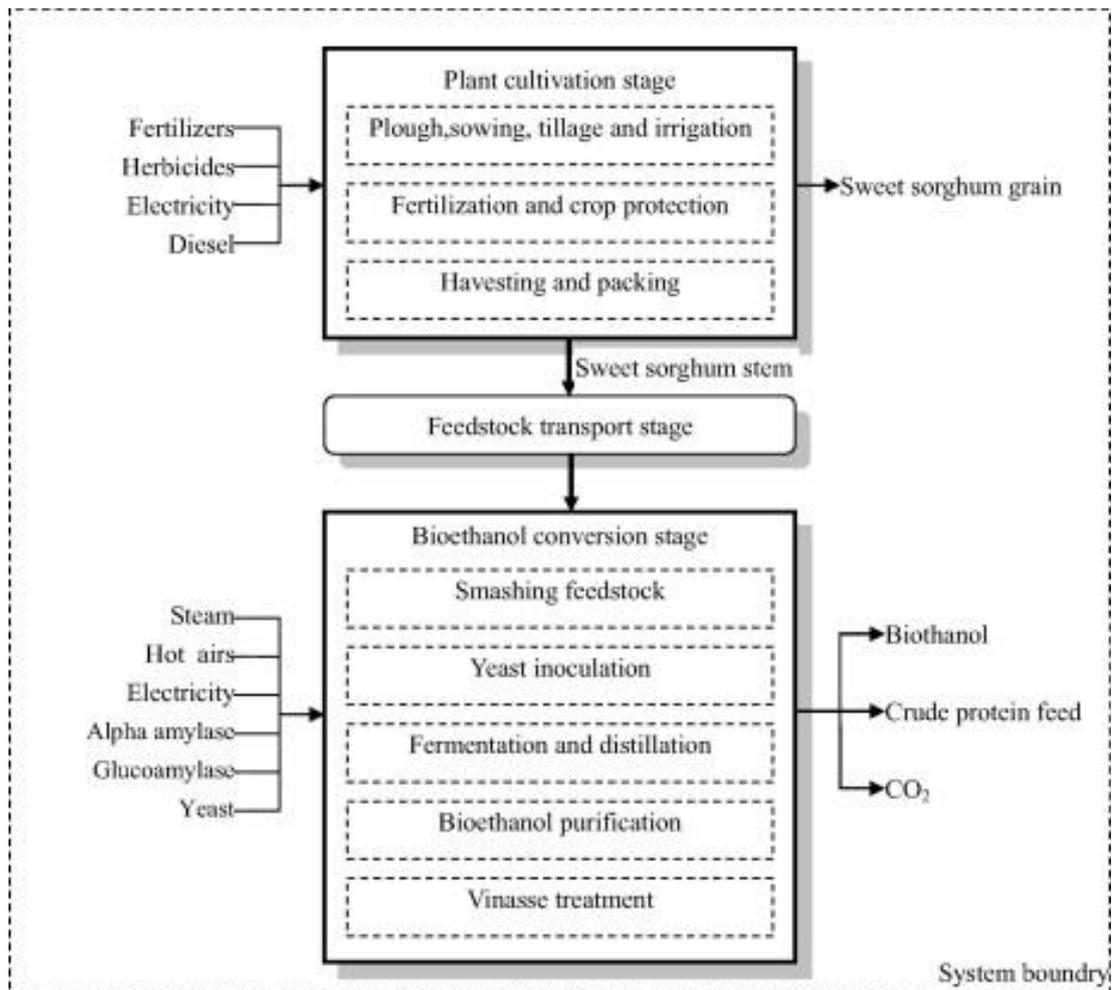


Figure 8 Bioethanol production process stages and units from the study of Wang et al. (2014)

First generation biofuel production from sweet potato was studied by Zhang et al. (2017). In this study they used three different plant production modes: one without any cogeneration, one with cogeneration from distillation waste and one with extended recycling of by-product and wastes such as CO<sub>2</sub> and solids. As expected, cogeneration increased the energy balance of the process. Without any recycling and co-production, a 1,23 energy balance was achieved. With improved cogeneration energy balance was increased to 2,23. Zhang et al. also studied the environmental impact of the process and it was noted that the highest environmental impact category for this type of process was eutrophication. Toxicity to humans and global warming potential were also in the high impact category. Increase in cogeneration decreased the environmental impact of the plant. The processing steps of this plant along with the different production modes studied are presented in Figure 9.

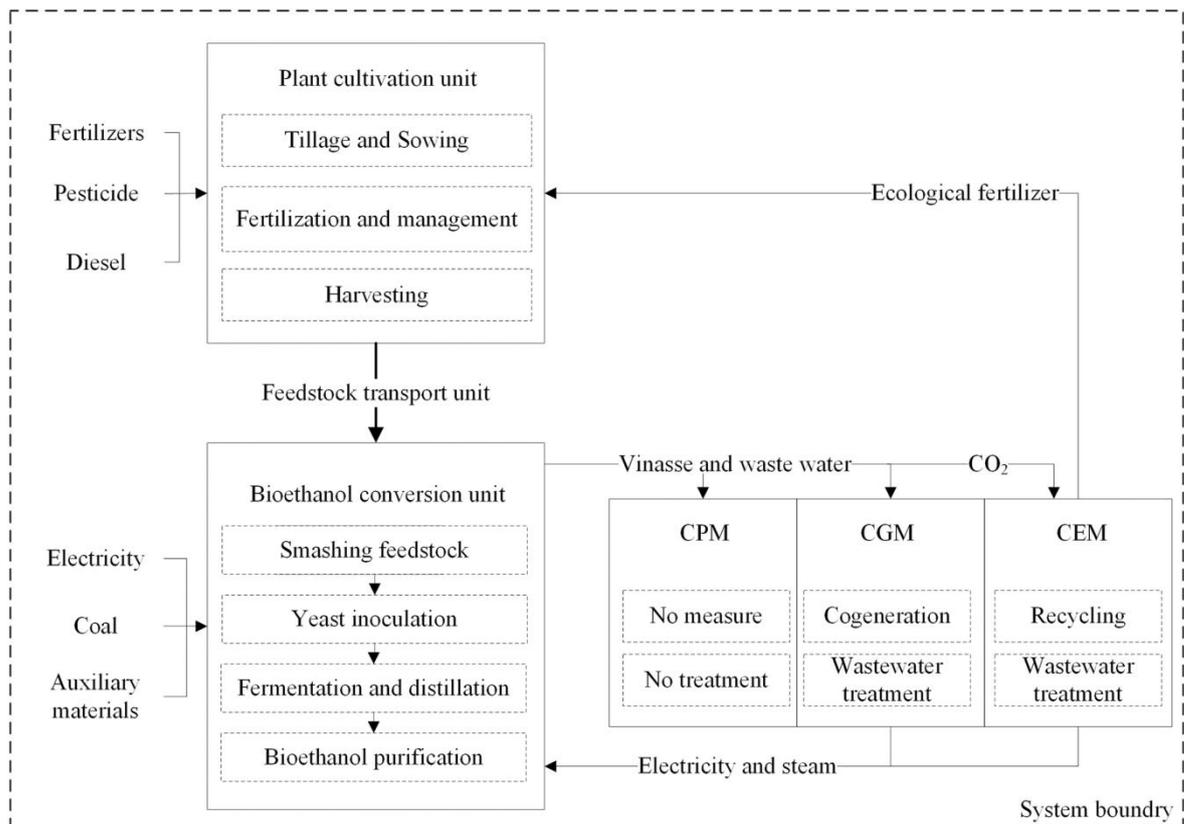


Figure 9 Bioethanol production plant with different operation modes as presented by Zhang et al. (2017). CPM: Conventional production mode, CGM: Cogeneration mode, CEM: Circular economy mode.

Abdullah et al. (2016) made a preliminary case study on a bioethanol production plant using oil palm frond as the raw material. This is a side product of the palm oil industry with very high nutritional and energy content. It is the biggest generated oil palm biomass, but its utilization is still in the early stages (Ooi et al., 2017). The process concept was developed based on literature on the current bioethanol technologies. The process consists of sterilization, fermentation, centrifugation, distillation, rectification and dehydration steps. This plant also includes a cogeneration system where leftover biomass fiber is used as a burning fuel. An energy balance of 7,48 was estimated for this plant concept which is a very good value for bioethanol production. A flow diagram of this process showing different process steps is shown in Figure 10.

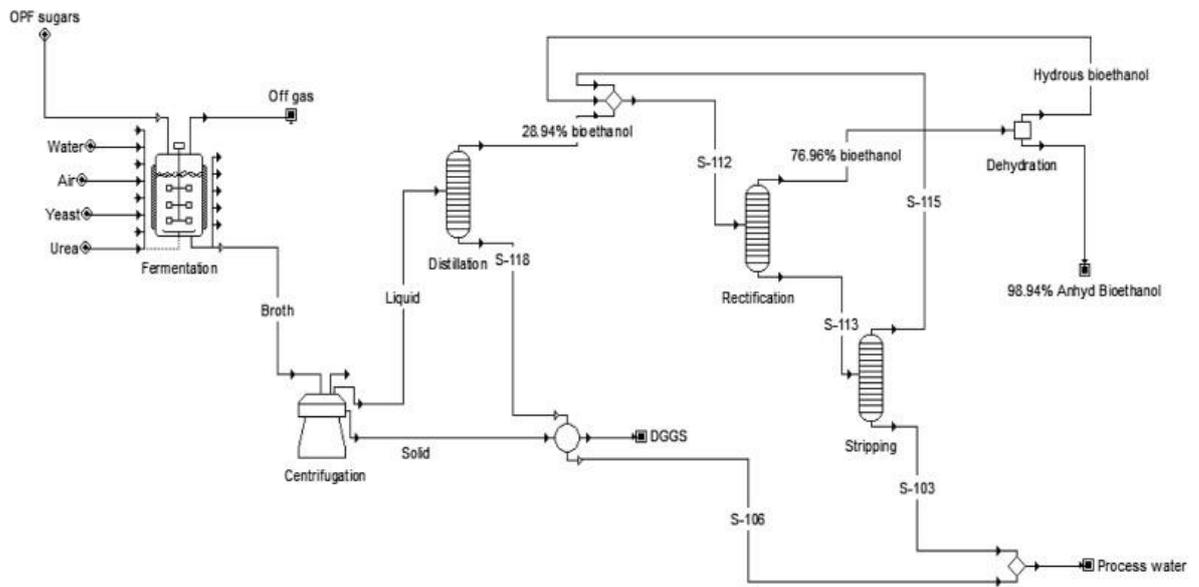


Figure 10 Process flow diagram for the palm biomass bioethanol process from Abdullah et al. 2016

A techno-economic evaluation for bamboo-based bioethanol production was made by Littlewood et al. (2013). Although they did not do an energy balance analysis for the project, it was determined that production of bioethanol from bamboo feedstock could be profitable. They used a liquid hot water extraction technology to enhance sugar release from the bamboo lignocellulose. As with previous case studies shown this plant also included co-generation of electricity by burning residual biomass. It was observed that the lowest ethanol selling price for this process was 0,484 \$/L.

An evaluation of first generation biofuels made from corn grain and soybean was made by Hill et al. (2006). They observed positive net energy balances for all processes. Out of all the studied raw materials, soybean had the highest energy balance when producing biodiesel. An energy balance of 1,25 was observed for bioethanol made from corn.

Bioethanol production was also studied by Pimentel & Patzek (2005). They observed that although corn-based ethanol production has seen support from many corporations, the net energy balance of such processes is often negative. Ethanol made from corn also has the first-generation bioethanol problems such as ethical and economic issues. A comparison to switchgrass and wood-based bioethanol was also made. According to this study both second generation bioethanol processes have even more negative energy balance than that of corn-based bioethanol. Bioethanol made from corn had an energy balance of 0,77 whereas

ethanol made from switchgrass and wood had energy balances of 0,69 and 0,63 respectively. These results are very low compared to many other case studies. This study has seen some criticism for example from Van Gerpen & Shrestha (2005).

Switchgrass-based ethanol was also studied by Schmer et al. (2007). According to them switchgrass-based bioethanol appeared to have high energy balance of 13,1. However this is also much higher than any other switchgrass-based processes that were compiled by Morales et al. (2015). The switchgrass energy balance case studies seem to go as low as 1. No mention was made on cogeneration in the process.

The case studies show that most bioethanol production plants work on a positive energy balance which is to be expected. However, there are large differences between different processes but also some criticism made. Most often second-generation biofuel production plants have higher energy efficiency than the first generation plants. It can also be seen that co-generation of energy by is an important part of increasing the plant energy efficiency. Usually this is done by burning leftover biomass and using the energy acquired to cover the need of the plant. A summary of the previous case studies is shown in Table II.

Table II Summary of bioethanol production case studies.

Source	Biomass	Energy Balance	Production price
Wang et al. (2014)	Sweet sorgum stem	1,56	-
Zhang et al. (2017)	Sweet potato	1,23-2,23	-
Abdullah et al. (2016)	Oil palm frond	7,48	0,52 \$/L
Littlewood et al. (2013)	Bamboo	-	0,484 \$/L
Hill et al. (2006)	Corn grain & soybean	1,25 (corn) 1,93 (soybean)	0,46 \$/L (corn) 0,55 \$/L (soybean)
Schmer et al. (2007)	Switchgrass	13,1	-
Pimentel & Patzek (2005)	Corn, switchgrass & wood	0,77 (corn) 0,69 (switchgrass) 0,63 (wood)	0,45 \$/L (corn) 0,54 \$/L (switchgrass) 0,58 \$/L (wood)

### 3.4.2. Other biofuels

Biofuels such as biodiesel have seen an increase in production along with bioethanol and their production is predicted to grow along with the increase in demand for renewable fuels. Biodiesel is traditionally made by using the transesterification process where oils such as vegetable oils, animal fats and microbial oils are used as raw material (Zhang et al., 2016). Vegetable and animal-based oils once used as a cooking oil are usually an unwanted waste product which is why their recycling for biofuel production is desirable (Varanda & Martins, 2011). Other more novel bio diesel processes also exist such as hydrotreating of waste oils. Other bio-based fuels are for example biogas, syngas, bio-gasoline and other bioalcohols.

Crude glycerol has been researched as a raw material for biodiesel, hydrogen and biogas production. Glycerol is a byproduct of biodiesel production which is usually either used by the cosmetic industry or burned for energy production. Conversion of crude glycerol into biofuels is usually done by biological means using microbial activity. Biodiesel made from

crude glycerol has been reported to have a positive net energy balance of 1.16 whereas hydrogen and biogas production have much lower energy balances of 0,22 and 0,27 respectively. (Zhang et al., 2016)

Pimentel & Patzek (2005) reported low energy balance for biodiesel production from soybean and sunflower oil. Soybean based biodiesel was reported to have an energy balance of 0,79 whereas sunflower based biodiesel had an energy balance of only 0,46. According to these results biodiesel production is not energy efficient. However, this paper was criticized by Van Gerpen & Shrestha (2005). Their conclusion is that the energy balance of biodiesel production from soybean should be closer to 2,8 which is a good balance for biodiesel production.

A very detailed life cycle analysis of biodiesel made from soybean was made by Sheehan et al. (1998) According to this study biodiesel energy balance is 3,2 which supports the renewable nature of biodiesel. Biodiesel was also observed to have much lower net CO<sub>2</sub> emissions compared to petroleum diesel. This study was later revisited by Pradhan et al. (2011) which includes newer data from biodiesel plants build after 2002. This updated paper reports that biodiesel energy balance has increased to 5,54. This increase can be contributed to better soybean yields as well as more energy efficient plants. Biodiesel production from soybean was also analyzed by Hill et al. (2006) who report energy balance of 1,93 which, although lower, still makes biodiesel production net energy positive.

Gas based biofuels have also been of interest in the recent years. Methane production from energy crops has shown promise in this field. This process is based on anaerobic digestion. When using lignocellulosic biomass as the raw material this process requires pretreatment technologies like the bioethanol process which requires additional energy input. However pretreated raw material can also increase the efficiency of the digestion process which provides higher yields of methane. High energy balances, up to 13,1 have been reported for this type of process. (Uellendahl et al., 2008).

Overall other biofuels besides bioethanol seem to achieve a positive energy balance which supports the idea of renewable and environmental energy source. A summary of the studies is shown in Table III.

Table III Summary of biofuel production energy balances

Source	Type of fuel	Raw material	Energy balance
Zhang (2016)	Biodiesel		1,16
	Hydrogen	Crude glycerol	0,22
	Biogas		0,27
Pimentel & Patzek (2005)	Biodiesel	Soybean	0,79
Van Gerpen & Shrestsah (2005) (correction)		Sunflower oil	0,46
			2,8
Sheehan (1998)	Biodiesel	Soybean	3,2
Pradhan (revisit) (2011)			5,54
Hill et al. (2006)	Biodiesel	Soybean	1,93
Uellendahl et al. (2008)	Biomethane	1 <sup>st</sup> & 2 <sup>nd</sup> generation energy crops	6,8-13,1

#### 4. METHODS FOR ANALYZING AND IMPROVING ENERGY EFFICIENCY

There are many different ways to optimize a process towards more energy efficient design. Inefficiencies in a process can be contributed to use of process heat and utilities, inefficient unit operation design and inefficient use or raw materials and waste streams in the process. Few of the methods used find and improve these inefficiencies are reviewed in this chapter.

##### 4.1. Pinch analysis

###### 4.1.1. Introduction to pinch analysis

Reducing resource consumption and increasing energy efficiency in process industry can be achieved by recycling and re-using energy and material streams. Pinch analysis is a method invented for this purpose and was formulated by Linhoff et al. in the 70's (Kemp et al., 2007; Klemeš & Kravanja, 2013). Heat integration based on pinch-analysis is used to examine and optimize the heat exchange between cold and hot process stream and to lower the consumption of external heating or cooling utilities. This procedure has a profitable effect on process costs and economics. (Klemeš & Kravanja, 2013)

The basic principle of pinch-analysis is to find heat exchanger targets that define the minimum heating and cooling utilities needed for the process. For this so-called energy targeting a minimum temperature difference  $\Delta T_{\min}$  has to be defined. The temperature difference between hot stream being cooled and cold stream being heated cannot be lower than this determined value. (Kemp et al., 2007)

Besides heat integration, pinch-analysis has found use in many other integration problems. It has been used in integration of separation columns, reactors, compressors and expanders, boilers and heat pumps (Towler & Sinnott, 2013). It can also be adapted for mass integration for example for reducing waste water effluents and to reduce the fresh water intake to the process (Wang & Smith, 1994). Pinch analysis can also be combined with other methodologies used for process integration. Combination of pinch analysis and exergy analysis has been used to examine the energy efficiency of a power plant (Feng & Zhu, 1997) and this combination has been said to be an effective method for optimizing low temperature processes (Correa & Gundersen, 2016).

Pinch analysis implements classical thermodynamics in a practical way and does so with an approach that is largely non-mathematical (Kemp et al., 2007). This makes Pinch analysis a tool that is efficient and easy to understand for heat integration and process optimization.

Pinch-analysis is often associated with its graphical representation of composite curves and the grand composite curve. Composite curves are constructed by calculating heat loads or enthalpies for each cold and hot stream and drawing them into the same plot at the correct temperature intervals. Enthalpy of a process flow is defined as: (Kemp et al., 2007)

$$\Delta H = C_p \dot{m} \Delta T \quad (1)$$

Where	$\Delta H$	Enthalphy change of the process stream, kW
	$C_p$	Specific heat capacity, kJ/kgK
	$\dot{m}$	mass flow, kg/s
	$\Delta T$	Temperature change of the stream, K

Streams in the process can be divided into two categories: streams that require heating and streams that require cooling. Streams that require heating are called cold streams as their

starting temperature is cooler than their target temperature whereas streams that require cooling are called hot streams.

The stream temperature and enthalpy are plotted into a T-H diagram. Temperature ranges where same types of streams (cold or hot) overlap the enthalpies of the streams are combined and added together. This way two curves are created: one for the hot composite and one for the cold composite. These curves are positioned no closer than the chosen minimum temperature interval  $\Delta T_{\min}$ . A lot of parallels between this method and the McCabe-Thiele method used for designing distillation columns can be found (Seider et al., 2009). An example of construction of a hot composite curve is shown in Figure 11.

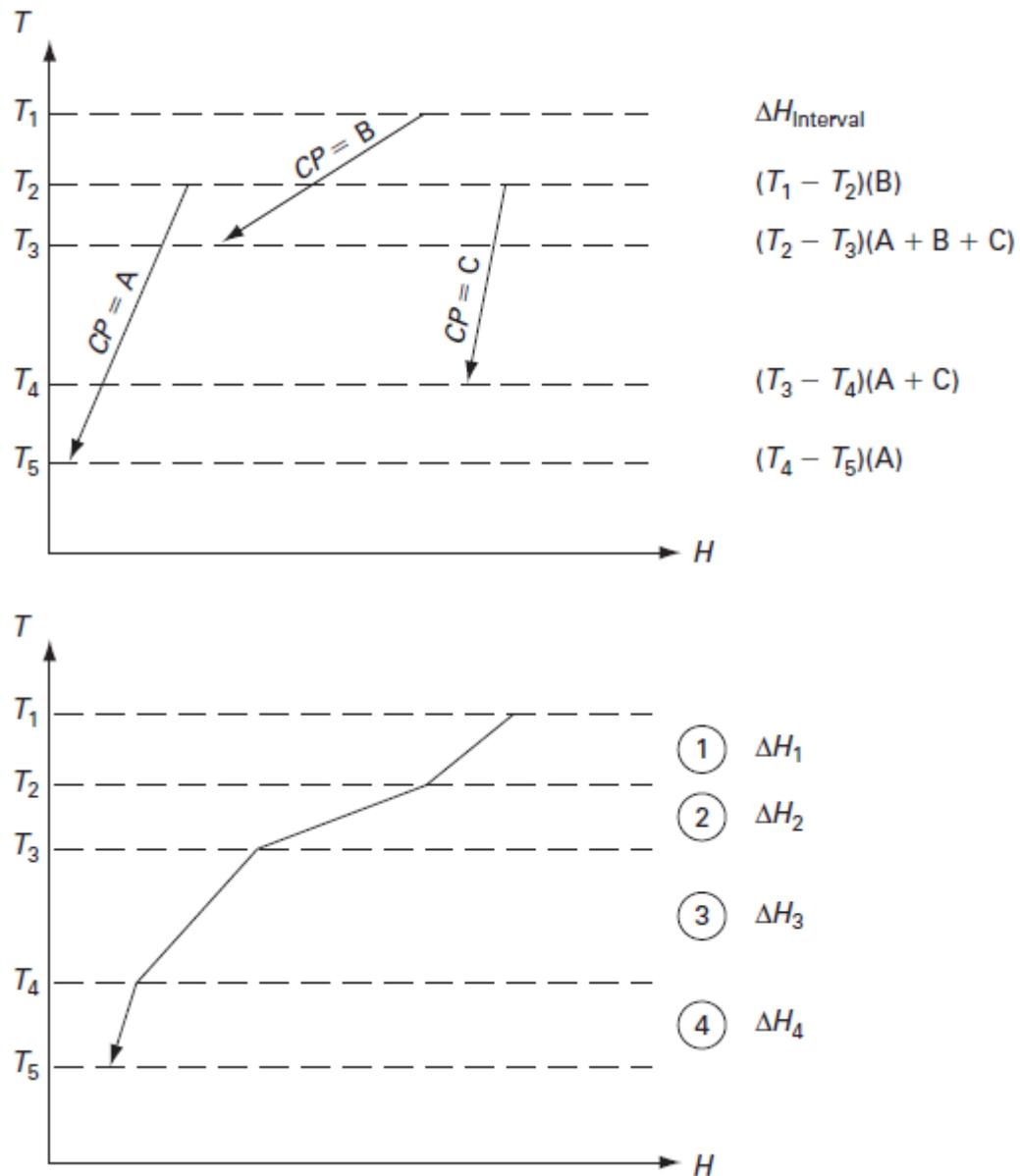


Figure 11 Construction of a hot composite curve with three process streams (Kemp et al., 2007)

Hot and cold composite curves are plotted into the same figure so that the hot composite is above the cold composite. The point where the temperature difference between the two curves is at its smallest is called the pinch point. This temperature difference is the same as the chosen  $\Delta T_{\text{min}}$  and can be adjusted by moving the composite curves along the H-axis.

The overlap between the two composite curves represents the possible heat recovery of the process. The required external cooling or heating needed for the process can be observed from the “overshoot” at the top and at the bottom of the graph where the two composite

curves don't overlap. The needed heating and cooling duties can be easily read from the H-axis. An example of four-stream composite curves and the determination of heat recovery and needed heating and cooling duty is shown in Figure 12. (Kemp et al., 2007)

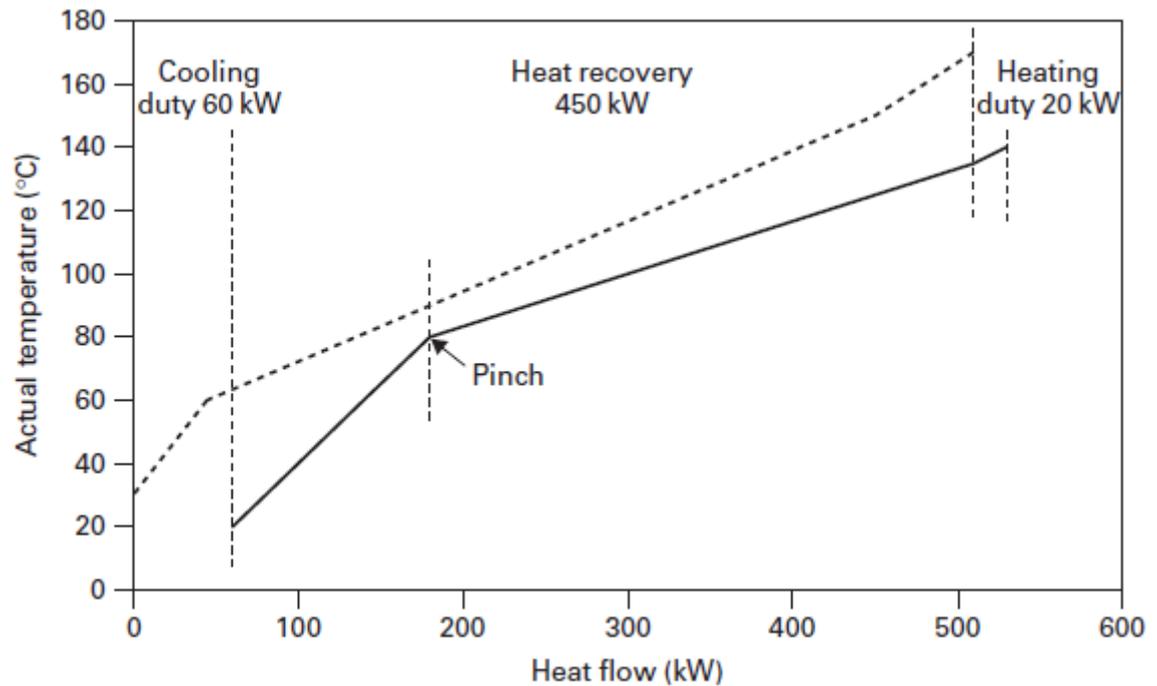


Figure 12 Hot and cold composite curves and the determination of available heat recovery and needed heating and cooling duties (Kemp et al., 2007)

Another way of representing Pinch is with grand composite curve. This is created by shifting both the temperatures of both the hot and the cold composite curves by  $\frac{1}{2}\Delta T_{\min}$ . Cold curve is shifted upwards and hot curve is shifted downwards. These temperatures are called shifted temperatures. After this the two composite curves touch each other at the Pinch point. The grand composite curve is constructed by taking the enthalpy difference between the two curves at each temperature and plotting this into a new T-H plot. An example construction of grand composite curve is shown in Figure 13. (Kemp et al., 2007)

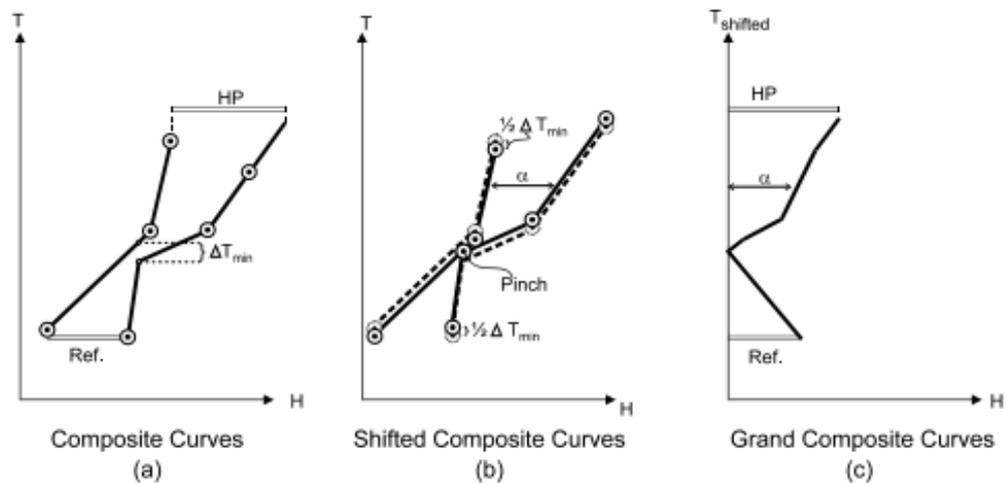


Figure 13 Construction of grand composite curve. (Linnhoff March, 1998). HP stands for High Pressure steam and Ref. stands for Refrigerant

The grand composite curve is an especially useful tool for targeting multiple utility levels. The amount of heating or cooling duty needed for each temperature can be read straight from the grand composite curve which makes setting utility targets easy. (Linnhoff March, 1998)

Choosing the right  $\Delta T_{\min}$  for the process is an important step when conducting pinch analysis. Although a low value for  $\Delta T_{\min}$  means lower utility consumption it comes with drawback of higher heat exchanger area. The heat exchanger area is roughly inversely proportional to the  $\Delta T_{\min}$  and the area increases to infinity when  $\Delta T_{\min}$  is 0 (Kemp et al., 2007). This creates an obvious parallel between minimum temperature difference and the capital cost of heat exchange network. Higher heat exchanger area means higher investment costs. A balance between capital cost and energy efficiency is often one of the main targets in pinch analysis.

Besides the composite curves, pinch analysis can be conducted by constructing so called problem tables. In these tables the stream temperature intervals and enthalpy changes are presented in table form. This is an effective way to conduct pinch analysis with simple tools such as spreadsheets. The construction of a problem table is presented in more detail for example in the book by Kemp et al. (2007).

#### 4.1.2. Heat exchanger networks

Heat exchanger network (HEN) design is a key design aspect in most chemical engineering applications. Large amount of energy is used by heating and cooling utilities and an efficiently designed HEN can lead up to 20-30% energy savings (Hindmarsh, 1983).

Heat exchanger networks and their optimization is one of the most studied design problem in chemical engineering. They are very strongly related to the energy efficiency of the process. The purpose of HENs is to integrate hot and cold streams of the process and to reduce the amount of heating or cooling utilities needed. Even though the optimization of HENs is of great importance, its implementation is not always simple, and a lot of work has been made in order to create methods to overcome these problems. (Escobar & Trierweiler, 2013)

Heat exchangers used in chemical processes can be divided into three families: shell-and-tube, plate-and-frame and recuperative exchangers. Shell-and-tube type exchangers are often used for liquid process streams but can also include gasses or condensing/boiling streams. In these exchangers the liquid flows through a set of tubes and exchanges heat with the fluid flowing outside the tubes. (Kemp et al., 2007)

Plate-and-frame exchangers consist of large number of plates pressed together and the fluid flows through narrow channels between each plate. A large heat transfer area can be achieved with this setup, but these types of exchangers are often susceptible to fouling. Also, the narrow passages tend to create high pressure drops. Modifiability one of the advantages of these exchangers, plates can often be added or removed to change the heat exchange area. (Kemp et al., 2007)

Recuperative exchangers are mainly used to exchange heat between gas streams. There are many different variants of recuperative heat exchangers, but they often have extended heat surface areas such as fins to make up for the low heat transfer coefficients of gasses. (Kemp et al., 2007)

Heat exchanger network consists of multiple heat exchangers that are used to transfer heat between process streams and utilities. With pinch analysis the placement of these heat exchangers can be optimized so that maximum amount of energy is recovered. Pinch analysis

can also be used as a basis for designing heat exchangers and estimating heat exchange areas.

The simplest method for designing and representing a heat exchanger network is the grid diagram. In grid diagram the hot and cold streams are drawn as horizontal line with high temperature on the left side and the cold temperatures on the right side. Usually the hot streams are drawn above the cold streams. The heat exchanger matches are drawn as two circles on the matched streams connected by a vertical line. The diagram can also show the heat duties of each heat exchanger as well as the temperature of the process stream after each unit. An example of a grid diagram of a distillation system is shown in Figure 14. (Kemp et al., 2007)

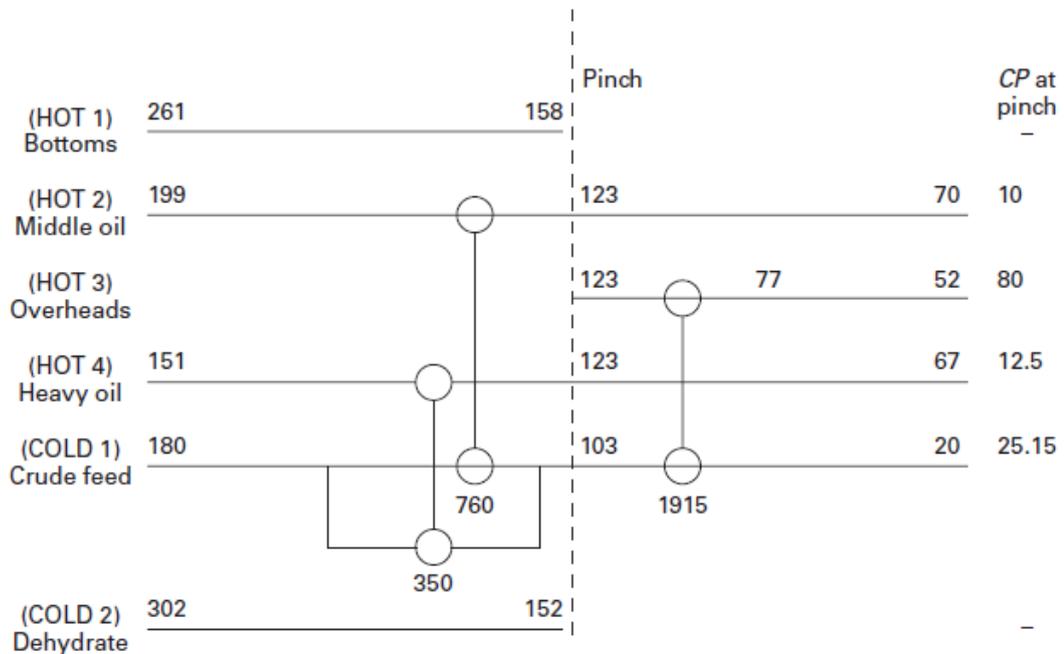


Figure 14 A heat network grid diagram for a distillation system (Kemp et al., 2007)

As can be seen from Figure 14 the grid diagram can also be used to easily present the process pinch point. With this presentation it is also simple to design heat exchanger networks that do not transfer heat across the pinch.

#### 4.1.3. Significance and use of pinch analysis

In the region above the pinch, hot composite transfers all its heat into the cold composite. This means that only heating utility is needed, and this area is called the net heat sink. In the area below the Pinch only cooling utility is required and this is called the net heat source. This definition creates two thermodynamically separate regions. If heat is transferred from above the pinch where there is already a heat deficit, the need for external heating increases by the same amount. At the same time below the pinch where there is already excess heat the need for cooling is increased by the amount heat transferred over the pinch. For this reason, the most thermodynamically efficient process can be designed by not transferring any heat over the pinch. (Kemp et al., 2007)

The advantage of pinch analysis is that it gives clear and easy to understand results of how much external heating or cooling is required and at which part of the process these utilities are required. Pinch analysis can also be adapted to many unit operations such as distillation and evaporation. Reboiler and condenser duties in distillation columns operate either above or below the pinch just like any other heating or cooling duties in the process. This means that a distillation unit can be placed ineffectively across the pinch so that the reboiler duty operates above the pinch and the condenser duty operates below the pinch. The appropriate placement of the column should be either completely above or completely below the pinch. Changing the placement of the column in relation to the pinch is usually not so simple since it might require change of operating pressure or different column arrangements such as double-effect-distillation or intermediate condenser. (Smith, 2005)

Pinch-analysis can also be used for integration of heat engines and heat pumps to the process. A heat engine can be used effectively above the pinch where it can provide heat to the process while also providing work. A heat pump on the other hand operates most efficiently across the pinch where it takes heat from below the pinch and rejects it at a temperature above the pinch. This saves on both cold and hot utilities. Of course, the economic savings obtained from the heat pump depend on the amount of heat saved compared to the total operation and capital cost of the heat pump. A presentation of heat pump placement in regard to the pinch point is shown in Figure 15 (Linnhoff March, 1998)

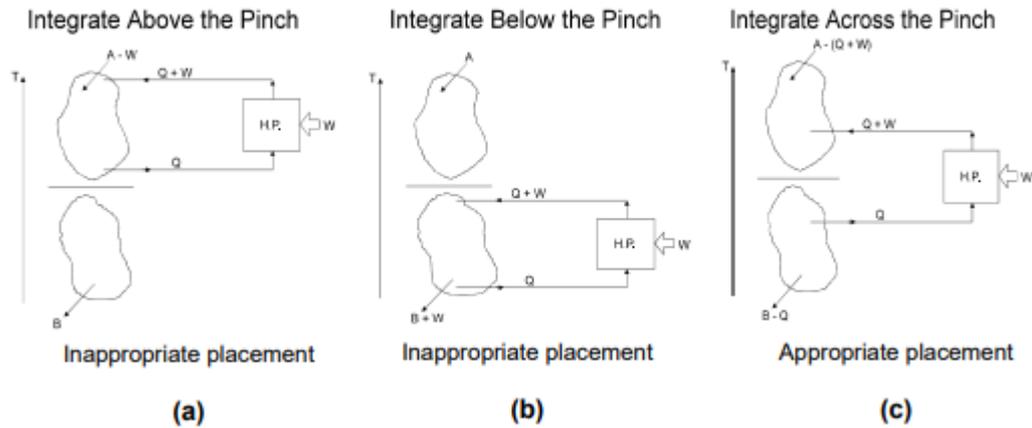


Figure 15 The appropriate and inappropriate placement of a heat pump in relation to the pinch (Linnhoff March, 1998)

For applications such as distillation, evaporation, heat engines and heat pumps the grand composite curve can be modified and used to find the integration possibilities easily (Smith, 2005).

The right use of pinch can significantly reduce the amount of heating and cooling utilities needed. This has an immediate effect not only to process economy but inherent safety as well. Lower usage of high-temperature and high-pressure utilities lowers risk of the process. However, not all process streams should be used for heat integration. Many chemical species can cause problems when coming to contact with each other and special care should be taken when using these streams in heat exchangers. There are typical safety issues associated with HEN-design such as contamination, leakage, runaway reactions and explosion (Chan et al., 2014). Since pinch analysis is a heat integration and efficiency optimization tool, it doesn't naturally consider safety of the process. Work has been done for example by Chan et al. (2014) to modify Pinch analysis to consider inherent safety when designing a process.

Many studies regarding the possible energy savings obtained by using Pinch-analysis has been made. Depending on the process type and the initial conditions of energy integration of the studied plant both energy and economic savings can be significant. Some of these findings released in different papers are shown in Table IV.

Table IV Case studies on pinch analysis on different processes

Source	Process	Energy Saving
Fenwicks et al. (2014)	Sulphonation process	0,316 MW 96,6 % cooling demand save 11,4 % heating demand save
Gunnarsson & Magnusson (2011)	Oil refinery, retrofit	4,7 MW 37 % cooling demand save 42 % heating demand save
Matsuda et al. (2009)	Industrial area consisting of different types of chemical plants using “Area-wide pinch technology”	Up to 780 MW

#### 4.1.4. Methods used for pinch-analysis

Pinch analysis is a simple method for evaluating and improving process energy efficiency. Construction of composite curves and their analysis doesn't require complex mathematics or graphical methods. For this reason, pinch analysis can be conducted with simple tools such as worksheets. However, there are commercial and non-commercial tools that make pinch analysis fast and efficient. Many of these tools don't only calculate and construct composite curves but can also design complete heat exchanger networks with just the basic stream information of the process.

Software for conducting and automating pinch analysis have been created since the early stages of pinch analysis. Early examples such as TARGET and PROTAB were developed quickly but were simple in their operation. Later, software such as Supertarget and Aspen Pinch (also known as Aspen HX-Net, now known as Aspen Energy Analyzer) were created. These were much more sophisticated and use complex targeting procedures. They can also create automated HENs but still allow the user to create their own designs. (Kemp et al., 2007)

When conducting pinch analysis, the most efficient method is to start the design at the pinch point and separate the problem into two different areas. The pinch point is the most constrained area in the design and often has very restricted matches for the suitable heat exchanger networks. Quite often there is an essential match that needs to be made in order to come up with the most efficient solution. Starting the design from either the hot or the cold side can often lead to excessive amount of heat exchanger units needed. (Linnhoff & Hindmarsh, 1983)

Following the rules created by Linnhoff & Hindmarsh (1983) a MER-network (minimum energy requirement/maximum energy recovery) can be achieved:

1. Divide the problem at the pinch, design each part separately
2. Start the design from the Pinch
3. Right above the pinch  $mC_p(\text{hot}) \leq mC_p(\text{cold})$
4. Right below the pinch  $mC_p(\text{hot}) \geq mC_p(\text{cold})$
5. Maximize the heat exchanger loads
6. Use heating utilities only above the pinch and cooling utilities only below the pinch

Following these rules it can be made sure that no heat is exchanged across the pinch. Sometimes methods such as stream splitting need to be applied in order to meet the 3. and 4. criteria at the pinch. Also, the optimal design might not always be achievable or cross pinch exchange might sometimes be allowable when the optimal ratio between energy efficiency and amount of heat exchanger units is optimized. (Kemp et al., 2007)

## **4.2. Exergy analysis**

Exergy analysis is a tool that can predict the thermodynamic performance of an energy system and can be used to increase the efficiency of said systems by determining the exergy generation and losses (Kwak et al., 2003; Hajjaji et al., 2012). Exergy analysis can reveal the possibilities of implementing more efficient process systems and how much the implementation will benefit the process economically and environmentally.

### **4.2.1. Basics of exergy**

In chemical industry there are few basic methods for improving energy efficiency of the process. Traditional techniques can be divided into two approaches: the use of energetic

balances and calculation of performance indexes. The use of energetic balances is based on the first law of thermodynamic, whereas the index approach also incorporates the use of the second law of thermodynamics. It can be said that the use of second law gives much more valuable information because the energetic balance calculations often don't distinguish between different types of energy involved in the process. (Araújo et al., 2007)

Different quality of energy is used in different processes. The quality of energy is related to the capacity which a given form of energy can cause a change in the process. This quality can be divided based on the type of energy: ordered and disordered type of energy. Ordered form of energy has no variance in quality and is fully convertible through work to other forms of energy and it consists of potential and kinetic energy. Disordered type of energy has a variable quality. The quality of disordered energy is dependent on the parameters of the energy carrier and of the environment. Examples of disordered energy are internal energy, thermal radiation and chemical energy. (Araújo et al., 2007)

Exergy establishes a standard for the quality of disordered energy (Araújo et al., 2007). Exergy is defined as the maximum available work when a stream of substance is brought from its initial state to the state of the surrounding environment (Choi et al., 2005). One major difference between energy and exergy is that energy is always conserved and can only change form as per the first law of thermodynamics. Exergy however can also be destroyed by irreversible processes.

Exergy losses are always a caused by irreversibilities in the process. Some major reasons for exergy losses are (Aspirion et al., 2011):

- Pressure drop
- Mixing
- Heat transfer

The basic mathematical expression for exergy is defined as (Hinderick et al., 1996):

$$E = \Delta H - T_0 \Delta S \quad (2)$$

Where	$E$	Exergy, kJ
	$T_0$	Reference temperature, K
	$\Delta S$	Entropy, kJ/K

Total exergy of a stream can be expressed as (Araújo et al., 2007):

$$E_{tot} = E_K + E_P + E_{PH} + E_{CH} \quad (3)$$

Where	$E_{tot}$	Total exergy of a stream, kJ
	$E_K$	Kinetic exergy, kJ
	$E_P$	Potential exergy, kJ
	$E_{PH}$	Physical exergy, kJ
	$E_{CH}$	Chemical exergy, kJ

Kinetic and potential exergy are ordered forms of exergy which can be represented with standard equation for kinetic and potential energy. In chemical processes these terms are usually negligible and can be ignored (Hinderick et al., 1996). Physical exergy is defined as the maximum amount of work that is obtainable when a stream is reversibly taken from its initial state to the environment state and it can be derived from the basic exergy equation (Araújo et al., 2007)

$$E_{PH} = (H_1 - T_0 S_1) - (H_0 - T_0 S_0) \quad (4)$$

Where	$H_0$	Enthalpy of the stream at initial state, kJ
	$H_1$	Enthalpy of the stream at environment state, kJ
	$S_0$	Entropy of the stream at initial state, kJ/K
	$S_1$	Entropy of the stream at environment state, kJ/K

Chemical exergy is the amount of work obtainable when a stream is changing state reversibly from its initial state to dead state. Dead state means that all the components are in equilibrium in the environment conditions. There are different methods for calculating chemical exergy. One way for multiphase stream exergy calculation is proposed by Hinderick et al. (1996)

$$E_{CH} = L_0 \sum_{i=1}^n x_{0,i} E_{0,i}^{0l} + V_0 \sum_{i=1}^n y_{0,i} E_{0,i}^{0v} + E_{mix} \quad (5)$$

Where	$L_0$	Liquid fraction in reference conditions, -
	$V_0$	Vapor fraction in reference conditions, -
	$E_{0,i}^{0l}$	Standard exergy for liquid fraction, kJ

$E_{0,i}^{0v}$	Standard exergy for vapor fraction, kJ
$x_0$	Molar fraction in liquid phase in standard conditions, -
$y_0$	Molar fraction in vapor phase in standard conditions, -

The standard exergies of species in different phases can be obtained for example from literature sources. The mixing term in equation 5 results from isothermal and isobaric mixing of the pure process components at the actual process conditions. This mixing term has a negative value in relation the pure components. The exergy of mixing can be calculated using a general expression for exergy as shown in equation 2. The enthalpy and entropy of the mixture can be calculated using the property change of mixing described as (Hinderick et al., 1996):

$$\Delta_{mix}M = x(M^l - \sum_{i=1}^n x_i M_i^l) + y(M^v - \sum_{i=1}^n y_i M_i^v) \quad (6)$$

Where	$\Delta_{mix}M$	Property change of mixing, kJ/mol
	$M^l$	Thermodynamic property of a mixture in liquid phase
	$M^v$	Thermodynamic property of a mixture in vapor phase
	x	Liquid mole fraction, -
	y	Vapor mole fraction, -

Total chemical exergy can be obtained by adding the chemical and mixing exergy calculations together. This way of calculating chemical exergy is efficient when working with process simulation software which can give the needed thermodynamic properties of the stream.

#### 4.2.2. Efficiency criteria

The main purpose of exergy analysis is to find the inefficiencies in the process. For this, basic criteria are established. Cornelissen (1997) presented basic efficiency criteria for a process

Simple efficiency

$$\eta_e = \frac{E_{out}}{E_{in}} \quad (7)$$

Where  $\eta_e$  Simple efficiency, -  
 $E_{Out}$  Exergy going out of the system, kJ  
 $E_{in}$  Exergy going into the system, kJ

Rational efficiency

$$\psi = \frac{\Delta E_{Out}}{\Delta E_{in}} \quad (8)$$

Where  $\psi$  Rational efficiency, -  
 $\Delta E_{in}$  Required exergy change in the system, kJ  
 $\Delta E_{Out}$  Desired exergy output from the system, kJ

$\Delta E_{out}$  in equation 8 is determined by examining the system. It can be described as the exergy that is desired to be obtained from the process. It can consist for example from chemical and thermal exergy increase in the system or only from the chemical exergy increase. It must be determined on case by case basis. (Cornelissen, 1997)

Efficiency with transiting exergy

$$\chi = \frac{E_{out} - E_{TR}}{E_{in} - E_{TR}} \quad (9)$$

Where  $\chi$  Efficiency with transiting energy, -  
 $E_{TR}$  Transiting exergy, kJ

Transiting exergy is the exergy that passes through the process without taking any part in the mechanical, thermal or chemical changes in the system (Cornelissen, 1997).

These efficiency criteria can be used to determine the need for improvements in the process. Obviously 100% efficiency is not realistically possible in most processes, but very low efficiencies often indicate that there is a room for improvement. The choice of criteria is based on the application. For basic analysis simple efficiency criteria is often good

enough but for more accurate findings either rational or transiting efficiency should be used.

Exergy analysis has been used in many applications. It can be used to optimize single process unit operations or whole processes. It has been proven effective for finding new configurations for example in distillation columns (Araújo et al., 2007).

#### 4.2.3. Usage of exergy analysis

Many studies show that exergy analysis is a useful tool for designing improvements for many types of production plants. Most papers on the subject focus on specific parts of the process such as co-generation systems or water reduction and recycling. Often exergy analysis is made on thermochemical pathways whereas exergy analysis of biochemical pathways sees less research. (Kang & Tan, 2015)

Exergy analysis can be used in multitude of ways. A basic example of exergy loss due to pressure drop and a proposed improvement to the process is shown in Figure 16.

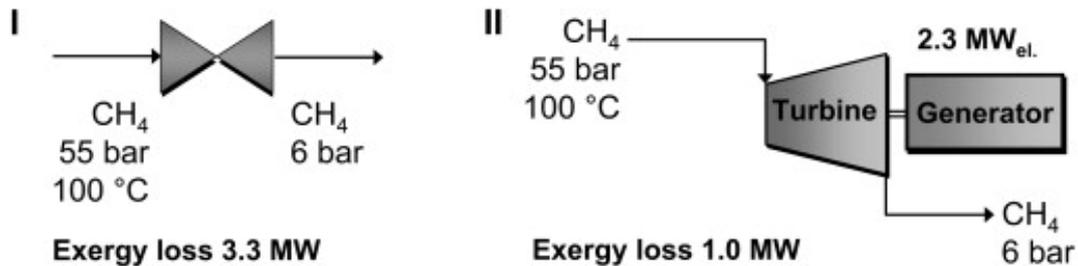


Figure 16 Exergy loss due to pressure drop and an improvement to the process. (Aspirion et al., 2011)

In Figure 16 a basic exergy loss due to a pressure drop in a let-down valve is presented. By installing a turbine instead of a valve, the exergy loss can be reduced to 1 MW and 2.3MW of electrical power is generated. (Aspirion et al., 2011)

Exergy analysis is an especially useful tool for optimizing thermodynamic equipment such as distillation columns (Choi et al., 2005; Araújo et al., 2007). An example of an improvement to a distillation column due to exergy analysis is shown in Figure 17.

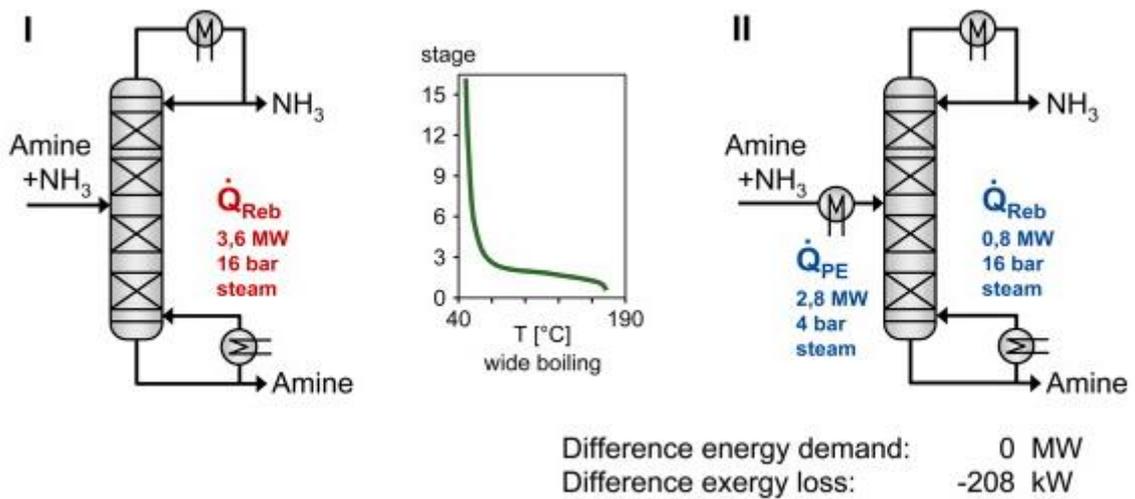


Figure 17 Improvements for a distillation column based on the exergy analysis. (Aspirion et al., 2011)

In Figure 17 an exergy analysis for a distillation column processing a wide boiling mixture is made. In the conventional process the whole heat duty of 3.6 MW is supplied by 16 bar high pressure steam. By adding a pre-evaporator 2.8 MW could be supplied with 4 bar steam. Adding a pre-evaporator to the column doesn't decrease the energy usage but lowers the exergy loss and in turn reduces the reboiler duty. The higher investment cost will be paid back by the reduced need of high pressure steam. (Aspirion et al., 2011)

Exergy analysis has been used for example in justifying the feasibility of a second-generation bioethanol plant and to make comparisons between different types of raw materials in bioethanol production (Tan et al., 2010). Exergy analysis was also combined with pinch-analysis by Modarressi et al. (2012) for a bioethanol and biomethane plant. When the external utilities are first reduced by pinch analysis without changes to the feedstocks or products, exergy analysis can then be used to supposedly increase process efficiency even more effectively. Using pinch analysis reduction hot and cold utility demand in the bioethanol and biomethane plant could be decreased by 40%. Exergy analysis showed that bioethanol production process has a high exergy efficiency.

Tarigahaleslami et al. (2012) conducted a study on evaluating crude oil distillation column exergy losses and proposed retrofit options based on these findings to yield energy savings. Using simulation software, they could determine the exergy losses for each individual stage of the distillation column. A reduction in exergy losses of 17,16% could be achieved

as well as a fuel consumption reduction of 3,6%. This shows that simulation-based exergy analysis has possibilities in increasing process efficiencies. However, chemical exergy of the process was not considered in these calculations which may cause inaccuracies.

Like pinch analysis, exergy analysis observes the efficiency of the process from an energy point of view. Unlike pinch analysis however, exergy analysis doesn't give straight solutions or optimization results. Pinch analysis can be adapted to create HENs that are more economic than energy efficient or vice versa. Exergy analysis only finds the inefficiencies of the process where irreversibilities are present but doesn't give straight answers how to improve upon them. Finding an actual solution to increase energy efficiency requires engineering knowledge.

Exergy analysis has been combined with other methods in order to optimize processes from many perspectives. Li et al. (2011) combined exergy analysis to inherent safety index method in order to take into account process safety. So called exergoeconomic and exergoenvironmental analysis have also been in use in process design. These methods combine exergy analysis with economic and environmental analysis methods respectively. When the exergy losses have been pinpointed, their effects on the process economics and environmental impact can be estimated. Options for improving the process can be observed based on these findings. (Petraokopoulou et al., 2011)

There is one important rule for exergy: Exergy losses can be accepted but only with a good justification based on economic and environmental perspectives. This shows that process design is not a single objective process and often conflicting objectives exist. (Aspirion et al., 2011)

### **4.3. Benchmarking**

One approach to lowering energy consumption and increasing energy efficiency is energy benchmarking. Benchmarking is a process where the performance of a plant is compared to other similar plants in the same industry. This process can be used to estimate energy conservation potential of the plant. (Yang et al., 2016) Energy benchmarks can be applied on a sector, country or process level. The choice of level also affects the extent of how much structural differences between the optimized plant and the plants being compared to influences the energy improvement potential (Lurijssen et al., 2013).

Benchmarking can be divided into two general groups: process based and product-based benchmarking. Process based benchmarking is often preferred in complex industrial process systems. It is an efficient tool for identifying and improving energy efficiency of the plant. However, it also often requires a lot of effort to implement because of the complexity of these processes. (Ke et al., 2013)

Product based benchmarking is often simple in terms of methodology compared to process-based benchmarking. It is simpler and has higher applicability in many industrial areas. In exchange for this simplicity, product-based benchmarking also has lower accuracy and it is often hard to pinpoint the energy inefficiencies to a certain part of the process. This makes the improvement of efficiency harder than with process-based benchmarking. (Ke et al., 2013)

Laurijssen et al. (2013) did an energy benchmark comparison of 23 Dutch paper mills. They found some significant energy efficiency improvement opportunities in certain parts of the process. However, in many parts of the processes energy improvements could not be made without interfering with the product quality. This study shows that although benchmarking is in use in many industries, it can be challenging to apply. This is especially true in chemical industry where processes are often very energy intensive and the process is sensitive to variables in operation.

A simulation-based benchmarking technique was proposed by Yang et al. (2016). First a basic system is created using process simulation software. Using methods such as sensitivity analysis on raw materials, pinch analysis etc. this simulation is improved upon. Eventually so-called benchmark system is created. The energy efficiency of this system can then be used as a basis when comparing or designing other systems with the same products. A diagram showing the generation of this benchmark system is shown in Figure 18. Yang et al. conclude that this method can overcome many difficulties that are often associated with benchmarking techniques. Significant reduction in energy consumption could be achieved with proper usage of this technique.

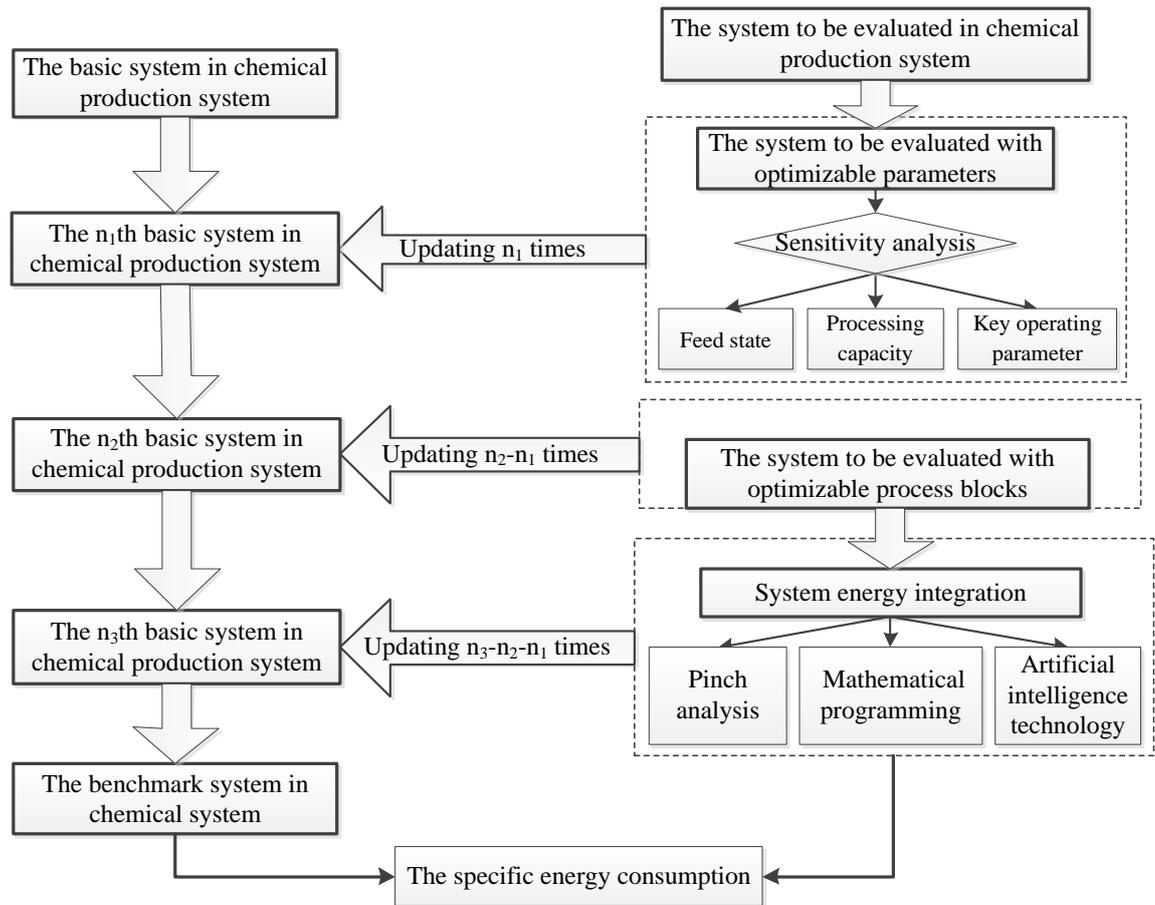


Figure 18 Steps when creating a benchmark system using simulation software. (Yang et al., 2016)

Benchmarking is a simple method, but it also has some issues and challenges that need to be taken into account. Some of these challenges include the size of the reasonable benchmark population, process confidentiality, data validation, choice of peak or annual energy efficiency and understandability vs. sophistication questions. (Birchfield, 2000)

Saygin et al, (2011) conducted an energy benchmarking study on 17 different industry sectors in both industrialized and developing countries. The most energy-intensive sectors were petroleum refineries, iron and steel, non-ferrous metals, non-metallic minerals, chemicals and petrochemicals and pulp and paper. Together these sectors have an energy saving potential of 20,9 EJ/a (exajoules). This means there is a lot of energy saving to be obtained from optimization of processes. However, achieving these savings would require a lot of work.

## 5. THERMODYNAMIC MODELS FOR NON-IDEAL SYSTEMS

Process simulation is an important part when designing any kind of chemical process. A proper process simulation can give the mass and energy balances of the whole process before any experimental data is available. This is also important when considering the energy efficiency of the process. The possible inefficiencies of the plant can be found using the created simulation and a preliminary energy analysis of the process can be made using the simulation environment.

The accuracy of a process simulation is often limited and can be affected by the choice of thermodynamic property methods. Many processes, especially biorefinery processes, include chemical and physical phenomena which cannot be represented using ideal equations. The raw materials and products of these processes consist of many different complex organic compounds. For this reason, multitudes of different thermodynamic calculation methods have been proposed. The choice of these methods depends on the chemical species and physical phases that are present in the process.

An overall outlook on how thermodynamic methods are chosen for biorefinery process simulations for different systems is made in the following chapter. This information is also used later in the practical part of thesis to optimize a bioethanol process simulation to obtain accurate mass and energy balances and to improve the energy efficiency of the process.

Simulation software such as Aspen Plus have an extensive documentation with help for choosing the right property method for each chemical process. There are four factors which need to be taken into account when choosing the property method (Calrson, 1996):

- The nature of properties of interest
- The composition of the mixture
- The pressure and temperature range
- The availability of parameters

When these factors are known, a simple way of choosing the right methods is to use so called decision trees. These are often available from literature or the simulation software

itself. They are very simplified but show the basic steps of decision making. (Carlson, 1996) An example of such decision tree is shown in Figure 19.

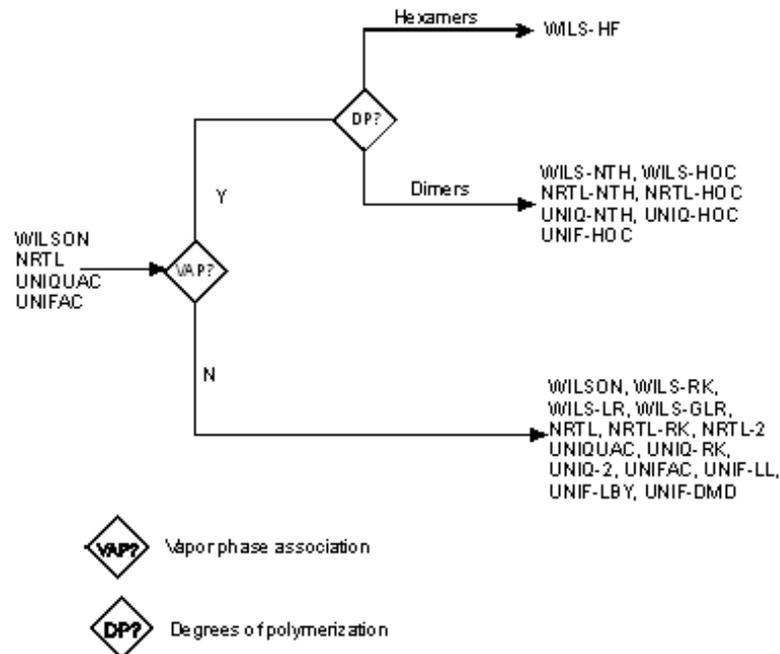


Figure 19 Decision tree for choosing an activity coefficient method. (AspenTech, 2016)

Biorefineries almost always include unit operations such as distillation and evaporation. When simulating these, an important consideration is the vapor-liquid equilibrium. Since these process steps include both vapor phase and a liquid phase and chemical equilibrium exists in both phases the choice of right method is imperative. Depending on the process liquid-liquid equilibrium might also be present which is often important to consider when choosing the right property method.

One of the common non-ideality causing functional groups present in biofuel processes are alcohols and carboxylic acids. Carboxylic acids are a by-product of most biomass pre-treatment methods (Jönsson & Martín, 2016) and they are often used in the chemical pre-treatment of biomass. The non-ideality caused by carboxylic acids can be contributed to their tendency to create hydrogen bonds and form oligomers in both vapor and liquid phases although often in literature only the formation of different dimers in the vapor phase is considered (Ferreira et al., 2003; Yushu et al., 2012; Carolina dos Ramos et al., 2011). This

interaction between molecules like carboxylic acids and alcohols and the tendency to create oligomers due to hydrogen bonding is called association. The non-ideal interactions between associating species creates a challenge for modelling these processes. For this reason, equation of state models designed to model associating compounds are given special emphasis in this chapter.

There are two types of thermodynamic property methods available for process simulation: Equation of State (EOS) and Activity Coefficient methods. It is common for these to be combined so that activity coefficient models are used for predicting liquid phase behavior and equation of state models are used for the vapor phase. An overview of different methods presented in this work is shown in Table V.

Table V Thermodynamic models focused on in this work

Model	Reason for inclusion
PC-SAFT	EOS-method for associating species, good results according to literature
CPA	EOS-method for associating species, good results according to literature
HOC	Association, proposed model by the Aspen Plus decision tree for carboxylic acids containing systems
Nothnagel	For associating systems proposed by Aspen Plus
NRTL	Flexible and proven model for many non-ideal systems
UNIQUAC	Suitable model for many non-ideal systems
UNIFAC	Useful model for preliminary estimation using group contributions
Wilson	Used in many systems where alcohols are present

### 5.1. Equation of state models

The first type of property methods available in commercial simulation software are equation of state methods. Equation of state is a thermodynamic equation that creates a relationship between pressure, volume and temperature and describes the state of a matter under given physical conditions. They are semi-empirical and are often developed for pure substances and need additional variables and mixing rules in order to model mixtures. (Ramdharee et al., 2013)

Equations of state tie the vapor and liquid fugacities to fugacity coefficients. EOS can be used to solve these fugacity coefficients which can then be used to determine the phase equilibrium conditions as shown in equations 10-12:

$$f_i^v = f_i^l \quad (10)$$

$$f_i^v = \varphi_i^v y_i p \quad (11)$$

$$f_i^l = \varphi_i^l x_i p \quad (12)$$

Where	$f_i^l$	Liquid phase fugacity, Pa
	$f_i^v$	Vapor phase fugacity, Pa
	$\varphi_i^l$	Liquid phase fugacity coefficient, -
	$\varphi_i^v$	Vapor phase fugacity coefficient, -

Equation 10 shows the basic relationship between two phases in the system at equilibrium and equations 11 and 12 explain how these fugacities can be presented in terms of fugacity coefficients and molar fractions of phases.

Fugacity presents the tendency of vaporization. It behaves very similarly to the partial pressure in a perfect gas mixture. In an ideal mixture the activity coefficient equals 1 and the fugacity of the mixture is the same as the partial pressure of the component. (Myint et al., 2015)

EOS-models are not often presented as equations for solving fugacity coefficients. Instead they describe the pressure, volume and temperature behavior of a system. Common way is

to describe the system using pressure. From this the fugacity coefficient can be determined using the following equation: (AspenTech, 2016)

$$\ln \phi_i^a = -\frac{1}{RT} \int_{\infty}^{V_a} \left[ \left( \frac{\partial p}{\partial n_i} \right)_{T,V,n_{iej}} - \frac{RT}{V} \right] dV - \ln Z_m^a \quad (13)$$

Where	$p$	pressure, Pa
	$R$	Ideal gas constant, J/molK
	$n$	Amount of substance, mol
	$V$	Volume, m <sup>3</sup>
	$Z$	Compressibility factor, -

Thermodynamic properties such as enthalpy can be calculated using departure functions as shown in

$$H_m = H_m^{ig} + (H_m - H_m^{ig}) \quad (14)$$

Where	$H_m$	Mixture enthalpy, kJ
	$H_m^{ig}$	Mixture ideal gas enthalpy, kJ

The enthalpy departure can be related to other properties through fundamental thermodynamic equation:

$$(H_m - H_m^{ig}) = - \int_{\infty}^V \left( p - \frac{RT}{V} \right) dV - RT \ln \left( \frac{V}{V^{ig}} \right) + T(S_m - S_m^{ig}) + RT(Z_m - 1) \quad (15)$$

$$(S_m - S_m^{ig}) = - \int_{\infty}^V \left[ \left( \frac{\partial p}{\partial T} \right)_V - \frac{R}{V} \right] dV + R \ln \left( \frac{V}{V^{ig}} \right) \quad (16)$$

Where	$S_m$	Mixture entropy, kJ/K
	$S_m^{ig}$	Mixture ideal gas entropy, kJ/K

In equation 15 the pressure is obtained by applying a suitable EOS.

Two EOS property methods widely used in industry are The Peng-Robinson and Soave-Redlich-Kwong equations. They are especially applicable in petroleum applications. The Reidlich-Kwong equations can be employed for fugacity, enthalpy and entropy calcula-

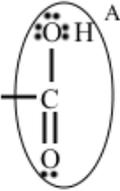
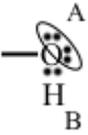
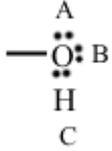
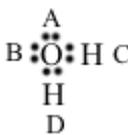
tions and gas-phase properties. However, it is poor at predicting liquid phase properties but gives good prediction of polar systems. The Peng-Robinson equation performs well in gas and condensate systems. (Ramdharee et al., 2013)

### **5.1.1. SAFT-models**

The SAFT (statistical associating fluid theory) EOS and its derivatives have been used to describe vapor-liquid equilibria of carboxylic acid containing systems. In SAFT models molecules are described as chains of monomer segments and the association interactions inside and between the molecules which can be described independently. SAFT-models have been used extensively for modelling polymer systems whereas their application for cross associating systems such as alcohol and organic acid mixtures has been lesser but has gained more interest recently. (Yushu et al., 2012; Carolina dos Ramos et al., 2011; Kontogeorgis et al., 2006b).

For association modelling with SAFT-type EOS so called association parameter is required for each associating component present in the system (Kontogeorgis et al., 2006a). This parameter is dependent on the type of association. Eight different association schemes have been classified. Four of the most commonly used are shown in Table VI.

Table VI Different association schemes that affect the EOS-association parameters. Letters A, B, C and D represent the association sites (Modified from source (Kontogeorgis et al., 2006a))

Compunds	Formula	Sites	Type
Acids		1 donor/acceptor	1A
Alcohols		1 donor, 1 acceptor	2B
Ammonia, alcohols		2 donors, 1 acceptor	3B
Water, glycols		2 donors, 2 acceptors	4C

As can be seen from Table VI one type of compound for example alcohols, can be represented with multiple association schemes. The choice of association scheme is based on the type of system where the component is. For example, water is usually considered to have 4 association sites where it can form hydrogen bonds: two at the unbounded electron pairs and two at the hydrogen atoms. Some results show however that in some systems water can only form hydrogen bonds on three sites due to steric hindrance (Perakis et al., 2007). For this reason, different association options should be investigated when using the SAFT or CPA type EOS.

Another issue that affects the modelling accuracy of association EOS is the choice of so called combining rule. Two binary parameters present in these models, the association energy ( $\epsilon_{ij}$ ) and volume ( $\beta_{ij}$ ), are far from trivial to obtain from experimental data. However, these parameters can be approximated using so called combining rule which tie the cross association parameters to the pure component parameters (Gross & Sadowski, 2002). Many methods for this have been proposed and the right choice depends on the application. However, two models, so called CR1 and ECR models have been said to be successful in many applications (Kontogeorgis et al., 2006a) as well as model proposed by Wolbach & Sandler (1998).

Mathematically SAFT is based on the equation for the residual Helmholtz free energy per mole (Economou, 2002; AspenTech, 2016):

$$A^{res}(T, V, N) = A(T, V, N) - A^{ideal}(T, V, N) \quad (17)$$

Where	$A$	Helmholtz free energy, kJ/mol
	$A^{res}$	Residual Helmholtz free energy, kJ/mol
	$A^{ideal}$	Ideal-gas Helmholtz free energy, kJ/mol

In SAFT the residual Helmholtz free energy is divided into four contributors:

$$A^{res} = \alpha^{hs} + \alpha^{disp} + \alpha^{assoc} + \alpha^{chain} \quad (18)$$

Where	$\alpha^{hs}$	Hard sphere contribution parameter, kJ/mol
	$\alpha^{disp}$	Dispersion contribution parameter, kJ/mol
	$\alpha^{assoc}$	Association contribution parameter, kJ/mol
	$\alpha^{chain}$	Chain contribution parameter, kJ/mol

These contributors present the different interactions between and inside molecules: the hard sphere interactions, the dispersion interactions, the association interactions and the chain interactions. A schematic representation of the SAFT-model is shown in Figure 20.

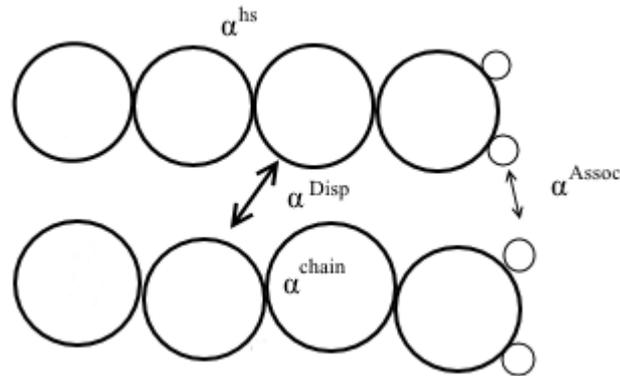


Figure 20 A model showing the interactions between and inside the molecules in the SAFT-model. (Modified from source Kleiner et al. (2009))

The hard sphere contribution can be expressed as:

$$\frac{\alpha^{hs}}{RT} = m \frac{4\eta - 3\eta^2}{(1-\eta)^2} \quad (19)$$

$$\eta = 0,74048\rho m v^0 \quad (20)$$

$$v^0 = v^{00} \left[ 1 - C e^{\left(\frac{-3u^0}{kt}\right)} \right]^3 \quad (21)$$

Where	$m$	The number of spherical segments per molecule, -
	$\eta$	Reduced density, kg/mol
	$\rho$	Density of the fluid, kg/m <sup>3</sup>
	$v^0$	Close-packed hard-core volume of the fluid, cm <sup>3</sup> /mol
	$v^{00}$	Temperature independent soft-core volume of the fluid, cm <sup>3</sup> /mol
	$C$	Constant, 0,12
	$u^0/k$	Dispersion energy parameter, -

The chain contribution parameter represents the Helmholtz free energy increment due to formation of covalent bonds and is based on Wertheim's thermodynamic theory of polymerization. It can be expressed as:

$$\frac{\alpha^{chain}}{RT} = (1 - m) \ln \frac{1-0,5\eta}{(1-\eta)^3} \quad (22)$$

The dispersion interaction in SAFT is presented by the calculating an average dispersion energy between hard chains (Soo, 2011). The dispersion interaction contribution can be

calculated using few different methods that are presented for example in the article made by Economou (2002). One expression for dispersion interaction is:

$$\frac{\alpha^{disp}}{RT} = \sum_i \sum_j D_{ij} \left[ \frac{u}{kT} \right]^i \left[ \frac{\eta}{0,74048} \right]^j \quad (23)$$

$$u = u^0 \left[ 1 + \frac{e}{kT} \right] \quad (24)$$

Where  $D_{ij}$  Dispersion constant, -  
 $u$  Dispersion energy of interaction, -  
 $e/k$  constant, -

The association contribution can be expressed as: (Economou, 2002)

$$\frac{a^{assoc}}{RT} = \sum_{A=1}^M \left[ \ln X^A - \frac{X^A}{2} \right] + 0,5M \quad (25)$$

$$X^A = \left( 1 + \sum_{B=1}^M \rho X^B \Delta^{AB} \right)^{-1} \quad (26)$$

$$\Delta^{AB} = \sqrt{2} v^0 \frac{1-0,5\eta}{(1-\eta)^3} \left[ e^{\frac{\epsilon^{AB}}{kT}} - 1 \right] \kappa^{AB} \quad (27)$$

Where  $M$  Number of association site per molecule, -  
 $X^A$  Mole fraction of molecules not bonded at site A  
 $\Delta^{AB}$  Association strength,  
 $\epsilon^{AB}/k$  Energy of association,  
 $\kappa^{AB}$  Volume of association,

These equations apply for pure components. For component mixtures the SAFT-model can be extended by adding mixing rules to the dispersion contribution. These extended rules are presented by Huang & Radosz (1990), Chapman et al. (1990) and Mansoori et al. (1971). Using these rules, the SAFT-model requires only one binary parameter.

PC-SAFT (perturbed chain-statistical associating fluid theory) model applied for modelling mixture containing carboxylic acids was studied by Yushu et al. (2012) PC-SAFT is an enhanced version of the original SAFT with better accuracy. Yushu et al. found the accuracy of PC-SAFT model to be good for estimating both pure and mixtures of carboxylic acids.

A derivative of SAFT, GC-SAFT-VR (group contribution statistical associating fluid theory variable range) application for various associating systems was studied by Carolina dos

Ramos et al. (2011) This is a version of SAFT that includes group contribution (GC) type of schemes. In group contribution models a system is described as different functional groups and it is assumed that the thermodynamic behavior of the molecule can be described with parameters individual to each functional group. This is also the basis of the UNIFAC-method presented in later chapter. In GC-SAFT-VR molecules are described as chains that are composed of segments with different size and/or energy and these segments represent each functional group in the molecule (Peng et al., 2010). Carolina dos Ramos et al. concluded that this method provides good prediction of fluid and phase behavior of associating compounds.

### 5.1.2. Hayden-O'Connell EOS

The Hayden-O'Connell (HOC) EOS is based on the virial equation of state. This equation relates the compressibility factor to other state variables: temperature and pressure or density. In the HOC correlation the virial equation is terminated at the second coefficient which represents the deviation from the ideal gas law. Because of this the compressibility factor in a mixture of N components can be expressed as:

$$Z = \frac{pV_m}{RT} = 1 + \frac{Bp}{RT} \quad (28)$$

$$B = \sum_{i=1}^N \sum_{j=1}^N z_i z_j B_{i,j}(T) \quad (29)$$

Where	$Z$	Compressibility factor, -
	$z_i$	Mole fraction of a substance in a mixture, -
	$p$	Pressure, Pa
	$R$	The ideal gas constant, J/molK
	$T$	Temperature, K
	$B$	The overall virial coefficient, cm <sup>3</sup> /g mol
	$B_{i,j}$	The 2 <sup>nd</sup> virial coefficient, cm <sup>3</sup> /g mol
	$V_m$	Molar volume, cm <sup>3</sup> /g mol

The virial equation is not valid for components with strong association such as carboxylic acids. However, the Hayden-O'Connell correlation takes this into account by implementing the chemical theory of non-ideality into the equation. (Hayden & O'Connell, 1975).

Molecular configurations of the species affect the way molecule pairs can collide. These pair collisions can be represented with three configurations: free, metastable and bound pairs. The HOC-model then presents the second virial coefficient as the sum of these three pair interactions as shown in equation 30 (Hayden & O'Connell, 1975).

$$B_{i,j} = B_{free} + B_{metastable} + B_{bound} + B_{chem} \quad (30)$$

Where	$B_{free}$	Free pair interaction parameter
	$B_{metastable}$	Metastable pair interaction parameter
	$B_{bound}$	Bound pair interaction parameter
	$B_{chem}$	Chemical pair interaction parameter

The last parameter  $B_{chem}$  is required for associating substances such as carboxylic acids. For a pure material this correlation requires data for critical temperature, critical pressure, dipole moment and radius of gyration. (Stein & Miller, 1980; Hayden & O'Connell, 1975).

The HOC-correlation is suitable for many vapor-liquid equilibrium systems that contain associating species and it can be much more accurate than other methods for more complex systems. It can also be used without the need for experimental data. It is recommended by many simulation software documentation for modelling vapor phase association. However, it is not suitable for high pressure applications. (Hayden & O'Connell, 1975)

### 5.1.3. Nothnagel-EOS

The Nothnagel equation of state is another way to solve vapor phase non-idealities. It is in some ways similar to the HOC-correlation that it uses the chemical theory of dimerization to account strong association and solvation effects which makes it a suitable method for carboxylic acid containing processes. It cannot be used to calculate liquid phase equilibriums. (AspenTech, 2016)

The Nothnagel EOS is expressed as:

$$P = \frac{RT}{V_m + b_v} \quad (31)$$

Where  $b_v$  The excluded volume,  $m^3$

The excluded volume  $b_v$  in equation 31 is a nonadjustable parameter that is described by Nothnagel et al. (1973) as “the inaccessibility of some parts of space owing to the finite size of the molecules”. This parameter is used to describe the deviations from the ideal gas behavior. It is proportional to the actual volume of the molecule and it can be calculated using different correlations (Nothnagel et al., 1973). Nothnagel EOS is the suggested method along with HOC by Aspen Plus property guide for carboxylic acid containing mixtures.

#### 5.1.4. CPA

Cubic-Plus-Association (CPA) method is another type of EOS that has been used to model associating and polar components. It is based on the SRK-model with the addition of Wertheim and lattice-fluid theories that are identical to those from the SAFT-model. CPA was originally created for the use of oil and gas industry with special emphasis on compounds such as methanol and glycols. Later acids were included due to the rising interest of some oil and gas companies. (Kontogeorgis et al., 2006a)

CPA has shown promise in systems containing all kinds of associating and non-associating groups. It has an advantage over the classical SRK and PR-models for modelling highly immiscible system which means it is suitable for modelling many LLE-systems. (Kontogeorgis et al., 2006a)

The mathematical presentation of CPA is constructed by combining the SRK-EOS with an association term presented for example in paper by Michelsen & Hendriks (2001). The CPA model expressed in terms of pressure is expressed as:

$$p = \frac{RT}{V_m - b} - \frac{\beta(T)}{V_m(V_m + b)} - \frac{1}{2} \left( \frac{RT}{V_m} \right) \left( 1 + \frac{1}{V_m} \frac{\partial \ln g}{\partial \left( \frac{1}{V_m} \right)} \right) \sum_i x_i \sum_{A_i} (1 - X_{A_i}) \quad (32)$$

$$X_{A_i} = \frac{1}{1 + \frac{1}{V_m} \sum_j x_j \sum_{B_j} X_{B_j} \Delta^{A_i B_j}} \quad (33)$$

$$\Delta^{A_i B_j} = g(V_m)^{ref} \left[ e^{\frac{\epsilon^{A_i B_j}}{RT}} - 1 \right] b_{ij} \beta^{A_i B_j} \quad (34)$$

Where  $g$  The radial distribution function, -  
 $\beta$  The SRK energy term, bar/L mol<sup>2</sup>  
 $\Delta^{A_i B_j}$  Associating strength, -

$\epsilon^{A_i B_j}$	Associating energy, bar/L mol
$\beta^{A_i B_j}$	Association volume parameter, -

The expression shown in equation 32 consists of the basic SRK EOS with added contribution of association term. The thorough derivation of the CPA-model is reviewed by Kontogeorgis et al. (2006a).

CPA has been used to model both LLE and VLE systems. Applications include components such as alcohols, hydrocarbons, organic acids and water (Kontogeorgis et al., 2006a). CPA was applied for water/alcohol/alkane systems for example by Voutsas et al. (1999). Satisfactory results were obtained for these systems although the choice of combining rules was critical for accurate results. Derawi et al. (2004) researched the accuracy of CPA to systems containing formic, acetic and propanoic acid. Best results were obtained using one-site association scheme and excellent binary VLE results were obtained for carboxylic acid-alkane systems along with acceptable LLE results.

## 5.2. Activity coefficient models

The activity coefficient methods are based on using activity coefficients which describe the departure from ideal thermodynamic properties of a mixture. An ideal mixture can be described with chemical potential as shown in equation 35 (Myint et al., 2015; Saville, 2011):

$$\mu_i(P, T, n) - \mu_i^0(T, P) = RT \ln z_i \quad (35)$$

Where  $\mu_i$  Pure component ideal gas chemical potential, kJ/mol

$\mu_i^0$  Chemical potential of component i in ideal gas mixture, kJ/mol

For a real mixture the activity coefficient is added to model the non-ideal behavior:

$$\mu_i(P, T, n) - \mu_i^0(T, P) = RT \ln(z_i \gamma_i) \quad (36)$$

Where  $\gamma_i$  Activity coefficient, -

Activity coefficients can be used for both liquid and vapor phases. However, activity coefficients are often used to determine the liquid phase fugacity and the vapor phase is solved using EOS. Liquid phase fugacity can then be expressed as:

$$f_i^l(P, T, n) = z_i \gamma_i f_i(T, P) \quad (37)$$

Equation 37 is comparable to equation 12 in equation of state methods. This way the Vapor-Liquid equilibrium can be represented by using Activity coefficients in the liquid phase and EOS in the vapor phase and assuming these two equations equal in equilibrium condition.

The enthalpy of a liquid mixture can be calculated using equation

$$H_m^l = \sum_i x_i (H_i^{*,v} - \Delta_{vap} H_i^*) + H_m^{E,l} \quad (38)$$

$$H_m^{E,l} = -RT^2 \sum_i x_i \frac{\partial \ln \gamma_i}{\partial T} \quad (39)$$

Where  $H^{E,l}$  Excess liquid enthalpy, kJ  
 $H^{*,v}$  Pure component vapor enthalpy, kJ  
 $\Delta_{vap} H^*$  Component vaporization enthalpy, kJ

### 5.2.1. NRTL

The Non-Random Two Liquid (NRTL) model is a flexible activity coefficient model. It can be used for many types of processes and can model highly non-ideal systems. It can be used for both VLE and LLE applications. NRTL is widely used in for equilibrium calculations for many different applications. The activity coefficients in NRTL can be mathematically described for mixtures as (AspenTech, 2016; Renon & Praunitz, 1968):

$$\ln \gamma_i = \frac{\sum_j x_j \tau_{ji} G_{ij}}{\sum_k x_k G_{ki}} + \sum_j \frac{x_j G_{ij}}{x_k G_{kj}} \left( \tau_{ij} - \frac{\sum_m x_m \tau_{mj} G_{mj}}{\sum_k x_k G_{kj}} \right) \quad (40)$$

$$G_{ij} = e^{-\alpha_{ij} \tau_{ij}} \quad (41)$$

Where  $G$  NRTL parameter, -  
 $\tau$  Interaction parameter, -

The parameters  $\tau_i$  and  $G$  can be expressed in temperature dependent form as shown in equations 42 and 43

$$\tau_{ij} = \alpha_{ij} + \frac{b_{ij}}{T} + e_{ij} \ln T + c_{ij} T \quad (42)$$

$$a_{ij} = c_{ij} + d_{ij} (T - 273.15K) \quad (43)$$

Where	$\alpha$	Non-randomness parameter, -
	$b$	NRTL parameter, -
	$e$	NRTL parameter, -
	$d$	NRTL parameter, -
	$c$	NRTL parameter, -

Most parameters in equations 40-43 are determined by VLE and LLE data regression but many binary parameters are available in most simulation software databases. NRTL is used for calculating liquid activity coefficients, for vapor phase equilibrium the ideal gas model or EOS-models such as RK and HOC can be combined together with NRTL.

NRTL-method is suitable for many different applications. It has been successfully applied for applications such as presenting LLE-equilibrium of glycerol + ethanol + ethylic biodiesel system (Basso et al., 2013). NRTL along with Soave-Redlich-Kwong method for vapor phase estimation has also been effectively used for simulating processing and distillation with energy integration of bioethanol made from sugarcane (Dias et al., 2011).

### 5.2.2. UNIQUAC

The NRTL-model suffers from its requirement of three binary parameters ( $G$ ,  $\tau$ ,  $\alpha$ ) that can be hard to obtain because the experimental data for typical binary systems is often not plentiful enough for a precise acquisition of these parameters. For this reason the UNIQUAC(Universal Quasi-Chemical) -model was proposed. This model is based on the idea that an equilibrium state can be described with two terms: one for the entropic contribution called the combinatorial part and one for the intermolecular forces that are responsible for enthalpy of mixing called the residual part. With this assumption the Gibbs free energy equation is expressed as (Prausnitz et al., 1998):

$$\frac{G^E}{RT} = \left(\frac{G^E}{RT}\right)_{combinatorial} + \left(\frac{G^E}{RT}\right)_{residual} \quad (44)$$

Where  $G^E$  Excess Gibbs energy, kJ/mol

The activity coefficients are expressed as (AspenTech, 2016):

$$\ln \gamma_i = \ln \frac{\phi_i}{x_i} + \frac{z}{2} q_i \ln \frac{\theta_i}{\phi_i} - q'_i \ln t'_i - q'_i \sum_j \frac{\theta'_j \tau_{ij}}{t'_j} + l_i + q'_i - \frac{\phi_i}{x_i} \sum_j x_j l_j \quad (45)$$

Where	$\phi, \phi'$	Segment fractions
	$\theta, \theta'$	Area fractions, -
	$q, q'$	Molecular structure constant, -
	$l$	Constant, -

UNIQUAC-model has two adjustable unary parameters that are present in the residual part of equation 44. In binary systems there are two adjustable parameters  $\tau_{ij}$  and  $\tau_{ji}$  in equation 45.

Dias et al. (2011) compared different thermodynamic models for a bioethanol plant process simulation. It was observed that UNIQUAC did not give reliable results for an extractive distillation process that was employed for ethanol dehydration. Pla-Franco et al. (2014) did similar tests between the UNIQUAC model and NRTL-model for simulation of ethanol distillation. The UNIQUAC-model proved more reliable than the NRTL-model for VLE and VLLE estimation. In other research this model proved to be more accurate of predicting VLE and azeotropic composition of a water-ethanol system compared to NRTL and WILSON models (Voutsas et al., 2011). These studies show that UNIQUAC can perform well in many systems, but the applicability of the thermodynamic model is very dependent on the process conditions as well as parameters used.

### 5.2.3. UNIFAC

The UNIFAC (UNIQUAC Functional-group Activity Coefficients) model is a group-contribution model that can estimate activity coefficients in liquid mixtures. This method requires the knowledge of the molecular structure of every participating component in the mixture and the parameters that are associated to each functional group present. However, this model was developed as a combination of the UNIQUAC model. This method, like UNIQUAC separates the model into combinatorial and residual part. The activity coefficient can then be expressed as: (AspenTech, 2016)

$$\ln \gamma = \ln \gamma_i^c + \ln \gamma_i^r \quad (46)$$

$$\ln \gamma_i^c = \ln \left( \frac{\phi_i}{x_i} \right) + 1 - \frac{\phi_i}{x_i} - \frac{z}{2} \left[ \ln \frac{\phi_i}{\theta_i} + 1 - \frac{\phi_i}{\theta_i} \right] \quad (47)$$

$$\ln \gamma_i^r = \sum_k^{ng} v_{ki} [\ln \Gamma_k - \ln \Gamma_k^i] \quad (48)$$

Where  $\Gamma$  Group residual activity coefficient, -

$v_k$  The number of groups of type k

The group residual activity coefficients represent the deviation from the ideal model due to the group interactions.

Group contribution methods such as UNIFAC are based on the idea that physical properties of a compound are made up of contributions of each atom, group and bonds (Towler & Sinnott, 2013). UNIFAC doesn't require any experimental data or prior knowledge of the chemical mechanics which makes it useful for preliminary screening of a process. It has been used for estimating both vapor-liquid and liquid-liquid equilibrium. However, it does require group-interaction parameters that might not be available for all components. A lot of work has however been made to determine these missing parameters and quite comprehensive databases are available. Since UNIFAC is more predictive than most other activity coefficient models, it should not be used for more accurate analysis. (González et al., 2007)

#### 5.2.4. WILSON

An expression for excess Gibbs free energy was presented by Wilson (1964):

$$\frac{G^E}{RT} = - \sum_i x_i \ln(1 - \sum_j x_j A_{ij}) \quad (49)$$

Where  $A_{ij}$  Wilson parameter, -

The activity coefficients for each component can then be defined as:

$$\ln \gamma_i = 1 - \ln \left( \sum_j A_{ij} x_j \right) - \sum_j \frac{A_{ji} x_j}{\sum_k A_{jk} x_k} \quad (50)$$

This model is called the Wilson activity coefficient model. It was created to model highly non-ideal systems and for polycomponent systems. In equation 50 there are two adjustable parameters  $A_{ij}$  and  $A_{ji}$ . These variables are related to the pure component molar volumes and characteristic energy differences.

There are two disadvantages in the Wilson equation. It is not useful for systems where the logarithm of the activity coefficient when plotted against  $x$ , shows a maxima or minima. This is not a problem in most common systems. The other problem is that WILSON-equation is not capable of predict limited miscibility i.e. systems where two distinct liquid phases exist. This makes it unsuitable for LLE estimation. (Gomes de Azevedo, 1998)

The Wilson model has been used especially in alcohol containing systems (AspenTech, 2016). It has been shown to give good prediction of VLE and azeotropic composition in ethanol-water mixtures compared to NRTL and UNIQUAC methods but at the same time poor prediction of excess enthalpy of this system (Voutsas et al., 2011). For ternary mixtures found in distillation processes of wine the Wilson model has shown to give fairly reliable results (Faúndez & Valderrama, 2009). However, some poor results for ethanol-water system have also been reported (Hadrich & Kechaou, 2010). The mixed results can probably be contributed to the choice of unary and binary parameters of the model as well as the process conditions.

### **5.3. Verifying the choice of right method**

When choosing the right thermodynamic method for a simulation application a verification of the method suitability is required. Quite often when modelling a conventional process knowledge and expertise of previous similar simulation cases can be used for estimating the model suitability. However, using previous cases as a reference doesn't always ensure the model accuracy for new applications. Different components and process conditions can lower the accuracy of previously accurate model. To obtain accurate results from process simulation, the thermodynamic methods should be verified on case by case basis.

The basis of model verification is comparing experimental data with the calculated results. The data being observed depends on the application and the interest of the designer. For example, vapor-liquid equilibrium data is often used to verify model application in binary systems where the equilibrium between the two phases is of importance. For example, in unit operations such as distillation this equilibrium plays probably the most important role. This data is also used to fit binary parameters in most thermodynamic models. (Carlson 1996; O'Connell et al., 2009)

When doing property validation each component should be validated separately to see the performance of the model on the grand scale (Calrson, 1996). Often properties such as pure component vapor pressure, density and heat capacity are fitted to data, but these properties can be chosen on the case by case basis. If experimental data on mixture properties is available those can also be tested. Often discrepancies in mixture properties can be traced to single pure component properties (Calrson, 1996).

#### **5.4. Conclusions on thermodynamic models**

For accurate simulation the choice of the right thermodynamic methods is of great importance. As seen in the earlier chapters certain methods perform better than others in different systems. The choice should be reviewed for each unit operation independently to obtain the most reliable results. An overview of different methods and their applicability for different systems is shown in Table VII.

Table VII Overview of different thermodynamic method discussed in this work

Method	Applicable	Non-applicable	Comments
PC-SAFT	Associating species, pure liquid polymers & polymer solutions, hydrocarbon systems	Electrolyte systems	-
CPA	Associating species	Electrolyte systems	-
HOC	Associating species, vapor phase	Liquid phase, high pressures	-
NOTHNAGEL	Associating species, vapor phase	Liquid phase. High pressures	-
NRTL	Ideal & non-ideal applications, heterogeneous azeotropes	Vapor phase, >10 bar	-
UNIQUAC	Polar & nonpolar liquid mixtures, ideal & non-ideal, heterogeneous azeotropes	Vapor phase, >10 bar	-
UNIFAC	Non-ideal systems with two liquid phases, Heterogeneous azeotropes	Vapor phase, >10 bar	Group contribution prediction. For preliminary estimation
WILSON	Alcohols, Non-ideal solutions, Homogeneous azeotropes	Vapor phase, >10 bar, Heterogeneous azeotropes	-



As can be seen from Figure 21 this process includes many of the energy intensive process steps discussed in the theoretical part of this thesis. This makes it into a good candidate for energy optimization work using pinch analysis.

## 6. PROCESS SIMULATION

The process simulation for this process was completely build using Aspen Plus V9.0. Some initial guesses and process parameters were obtained from simulation results made before this thesis work with many different commercial simulation software. The aim was to observe the effectiveness of combining process simulation and energy analysis software made by AspenTech for this type of process design.

For energy integration and Pinch analysis Aspen Energy Analyzer V9.0 was used. The analysis was based on the process simulation made with Aspen Plus using the import feature. This way the stream information and heat exchanger duties could easily be transferred for energy analysis.

The chemical components present in the simulation were mostly obtained from Aspen Plus database. Certain components that were not available were modelled using similar components with possible changes to certain physical properties. An overview of these is shown in Table VIII.

Table VIII Representation of components not available in Aspen Plus databases

Component	Modelled as	Changes
Cellulose	Solid	Heat of formation Heat Capacity Molar volume (Wooley & Putsche, 1996)
Lignin	Dextrose	-
Hemicellulose	Arabinose	-

## 6.1. Thermodynamic methods

The appropriate thermodynamic method was chosen among the methods presented in the theoretical part of this thesis. The model verification was done by comparing experimental data available from literature to the ones predicted by the model.

Parameters for different models were obtained from Aspen Plus database, literature and data regression runs. The PC-SAFT and CPA EOS methods did not have parameters for all components in the Aspen database and these had to be obtained using different methods. Regressed parameters were obtained by using the build in regression mode in Aspen Plus with the maximum likelihood method. The experimental data was obtained from Aspen Plus NIST database. Pure component parameters were regressed using experimental data of pure component vapor pressure and density. An overview of the parameters obtained for each model is shown in Table IX.

Table IX Parameter acquisition methods

Model	Parameters obtained from
PC-SAFT	Data regression
	Literature
CPA	Data regression
	Literature
HOC	Aspen database
Nothnagel	Aspen database
NRTL	Aspen database
UNIQUAC	Aspen database
WILSON	Aspen database

### 6.1.1. Binary data validation

The validation of different thermodynamic methods for the chemical systems present in the process simulation was done by comparing experimental VLE-data of different components obtained from literature to the estimated models. The comparison was made comparing weighted sum of squares and residual root mean square error calculated between the

model and experimental data by Aspen Plus estimation tool. The weighted sum of squares is expressed as (AspenTech, 2016):

$$S = \sum_{o=1}^t w_o \left[ \sum_{i=1}^k \sum_{j=1}^m \left( \frac{Z_{ij} - ZM_{ij}}{\sigma_{ij}} \right)^2 \right] \quad 51$$

Where	$S$	Weighted sum of squares, -
	$ZM_{ij}$	Measured value, -
	$Z_{ij}$	Calculated value, -
	$\sigma$	Standard deviation, -
	$w$	Weighting factor for data group, -
	$o$	data group number in regression case, -
	$t$	Total number of data groups used, -
	$i$	Data point number within a data group, -
	$k$	Total number of points in a data group, -
	$j$	Measured variable for data point, -
	$m$	Number of measured variables for a data point, -

The root mean square error is expressed as:

$$S_E = \frac{\sqrt{S}}{h-t} \quad (52)$$

Where	$S_E$	The root mean square error, -
	$h$	Number of parameters, -

The chosen experimental VLE data used for comparison were obtained from NIST database integrated into the Aspen Plus. Four different chemical systems present in the process were used for the data validation. The results of these estimation runs are shown in Table X.

Table X Sum of squares comparison between binary VLE data and predicted model

Method	Square root error			
	System A	System B	System C	System D
NRTL-HOC	14	24	4	51
UNIQUAC-HOC	12	22	4	59
WILSON-HOC	13	25	4	56
PC-SAFT	28	33	25	107
CPA	26	31	23	66

The parameters and association schemes for PC-SAFT and CPA methods were chosen based on the “best case” scenario where the smallest sum of squares was obtained. Even with this assumption the two EOS-methods performed worse by themselves than the activity coefficient + HOC methods. Nothnagel method for vapor phase was also investigated but results for this were overall worse for all chemical systems compared to HOC.

Based on all the verification tests the most accurate method for this type of process was UNIQUAC-HOC. However, all three activity coefficient + HOC methods give similar results and they all could be suitable for simulation purposes. The less frequently used models PC-SAFT and CPA didn't perform very well. This was not completely unexpected since the application of these methods is more in the field of other associating hydrocarbon systems such as alcohols, alkanes and glycols. The interest in using these methods for carboxylic acid containing systems has only increased in recent years. These results could also be contributed to poor parameter regression although even with parameters obtained from literature the results weren't satisfactory.

## 6.2. Simulation construction

The process simulation was made using Aspen Plus V.9.0. The main aim of this simulation was to obtain accurate stream compositions and flowrates as well as required heat exchanger duties that could then be used for the pinch analysis.

Most emphasis on the simulation was made on the more energy intensive unit operations such as evaporation and distillation. The process already includes many energy efficient

unit operations such as MVR- and MEE-evaporators and heat integrated distillation columns. The simulation process flowsheet is shown in Appendix I and the flowchart is presented in Appendix II. For the MVR- and MEE-evaporators there is no ready to use model available in the Aspen Plus. These unit operations were constructed by using combination of flash-blocks, heat exchangers and compressors. An example of an MVR-evaporator constructed in the simulation environment is shown in Figure 22 and an example of an MEE-evaporator is shown in Figure 23

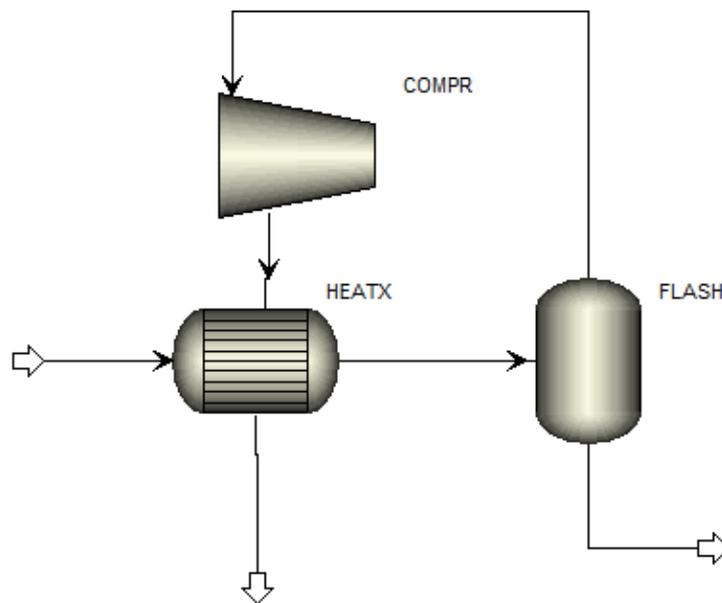


Figure 22 An example of an MVR-evaporator build with Aspen Plus

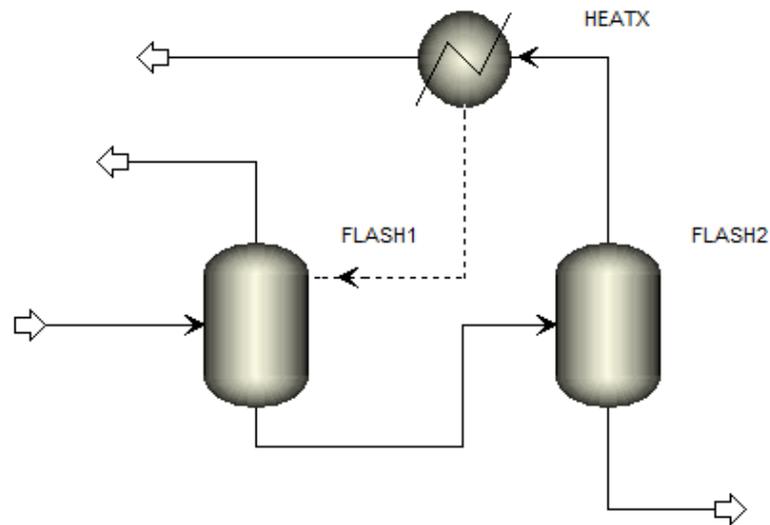


Figure 23 An example of a 2-unit MEE-evaporator build with Aspen Plus

Many tear streams in the process propose a challenge to the simulation convergence. As can be seen from the process block diagram this process has a large amount of tear streams. To acquire good convergence, the amount of tear streams was limited compared to the real process and replaced with estimated feed streams. This was done mainly because the simulation import feature from Aspen Plus to Aspen Energy Analyzer requires an errorless final convergence run. The results from the simulation were still observed to be accurate.

### 6.2.1. The effect of thermodynamic method on the simulation results

Although the most suitable thermodynamic method was already chosen based on initial verification with binary and ternary data, it was interesting to observe the effect of these methods to the results of the simulation especially in terms of pinch analysis.

When comparing NRTL-HOC, UNIQUAC-HOC and WILSON-HOC the overall effect of the liquid phase activity coefficient method on the estimated process total energy consumption was not very significant, only around 0,5% between the highest and lowest energy consumption. Some local differences between single heater duty estimates were up to 5%. This was to be expected based on the method verification results. The small differences between the methods can probably be contributed to different estimates for activity coefficients for each component. Differences in activity coefficient causes different vapor frac-

tions in many unit operations such as distillation and evaporation which causes difference in stream composition. Also, the excess liquid enthalpy is calculated using activity coefficient as show in Equation 39 which means that changes in activity coefficient changes the required heating and cooling duties.

The results of the chosen models were also compared to case were the vapor phase was assumed ideal i.e. regular UNIQUAC or NRTL models. This demonstrates the importance of choosing the right method to model the non-ideal gas phase behavior of the system. Results of choice of method on energy consumption of some process equipment is shown in Figure 24.

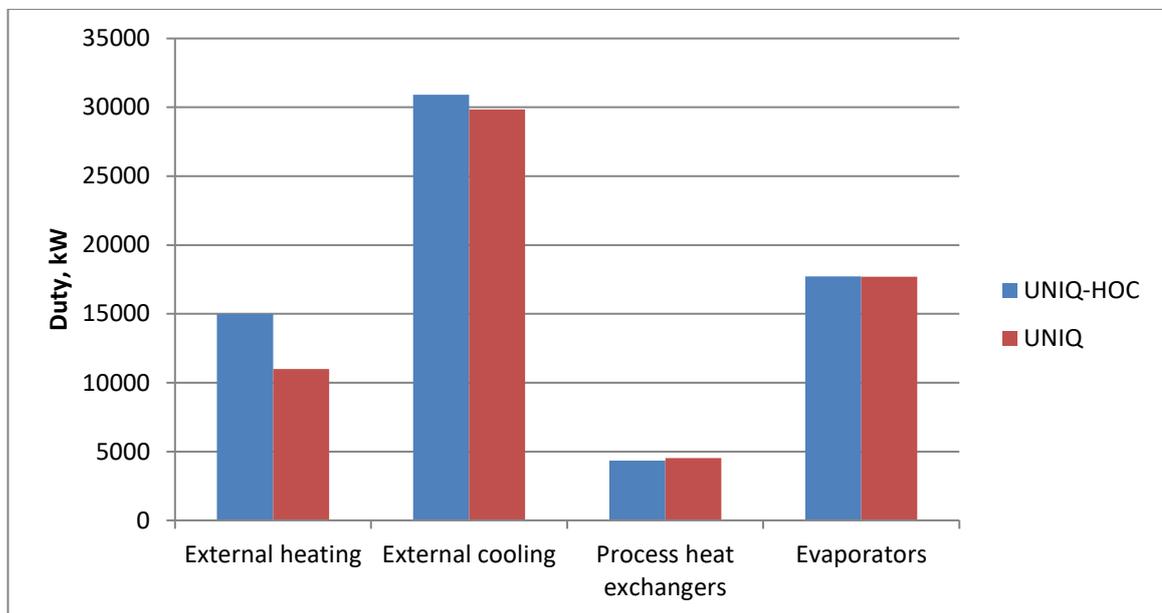


Figure 24 The effect of vapor phase non-ideality model to the required energy consumption of the process.

Looking at the comparison in Figure 24 the UNIQUAC method surprisingly estimates fairly similar overall energy consumption to the UNIQUAC-HOC method. However, there is a significant difference in external heating requirement. When looking at individual heater duties the difference between two estimates can be up to 70%. This error can cause insufficiently sized heat exchangers. The different energy requirement also has a direct effect on the composite curves of the process which would also change the pinch temperatures and heat integration possibilities.

## 7. PINCH ANALYSIS OF THE PROCESS

### 7.1. Simulation import

Pinch analysis for the process was made using the import feature from Aspen Plus simulation to Aspen Energy Analysis. This import feature automatically determines all the heat sources and sinks of the process based on the defined heat exchangers and stream temperatures.

This pinch analysis study was made for the whole bioethanol process. Another approach would have been to do the analysis separately for each part of the process based on the plant layout. This way the heat integration would be easier to physically accomplish but the total energy savings potential would be lower.

Many streams in the process go through phase changes during vaporization or condensation which causes drastic changes in the heat capacity of these streams during heat exchange. Aspen Energy Analyzer can take this into account when importing simulation case from Aspen Plus. These streams are separated into segments of temperature intervals with different heat capacity values which affects the shape of the composite curves. This option allows for a more accurate look on the energy integration possibilities of the process.

Certain streams that could not be accurately modelled with the simulation software were added manually as heat sources or sinks based on existing process documentation.

### 7.2. Composite curves

The  $DT_{\min}$  (minimum temperature approach) for the process was chosen based on targeting the minimum total cost index. The principle of this analysis is to observe the effect of chosen  $DT_{\min}$  on the yearly cost of the plant when the capital cost is divided over a time period, often the plant payback time. Increase in  $DT_{\min}$  lowers the required heat exchange area while increasing the required utilities. Often a global minimum for this yearly cost can be found. Aspen Energy Analyzer default of 5 years was used for this. The results of this analysis are shown in Figure 25.

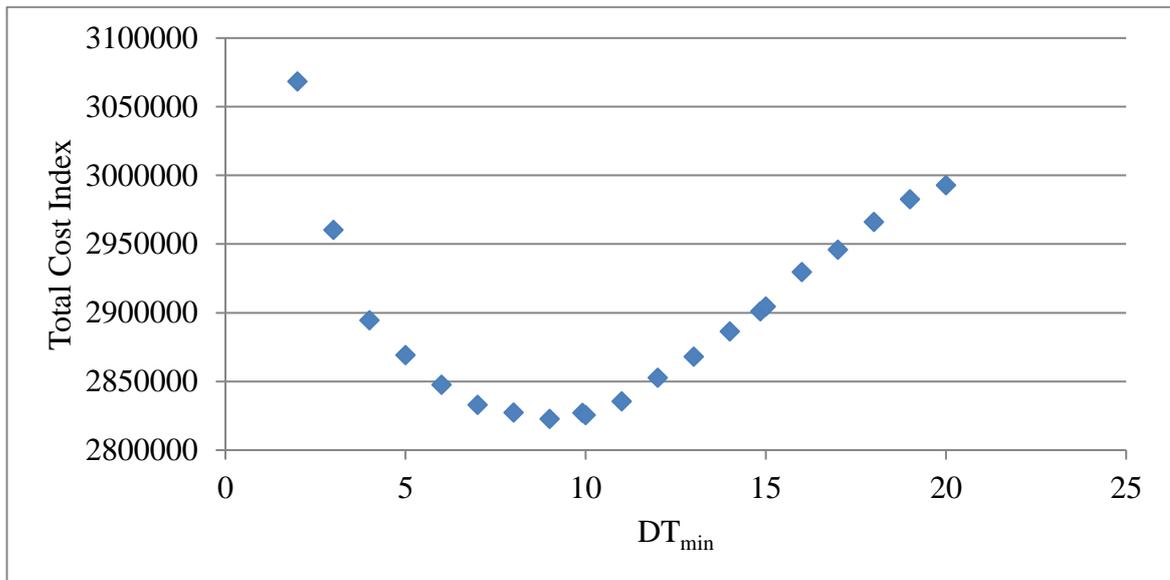


Figure 25 The effect of chosen  $DT_{min}$  on the total cost of the process

It can be seen from Figure 25 that the minimum total cost is obtained when the  $DT_{min}$  value is set to be around 9. This value was used for the pinch analysis as it's not far from  $10\text{ }^{\circ}\text{C}$  which is often used for initial estimation for  $DT_{min}$  in many processes.

The composite curves were constructed for most of the process excluding certain parts. Besides heat exchangers also required evaporator heat duties were included in the pinch analysis. The constructed composite curves are shown in Figure 26.

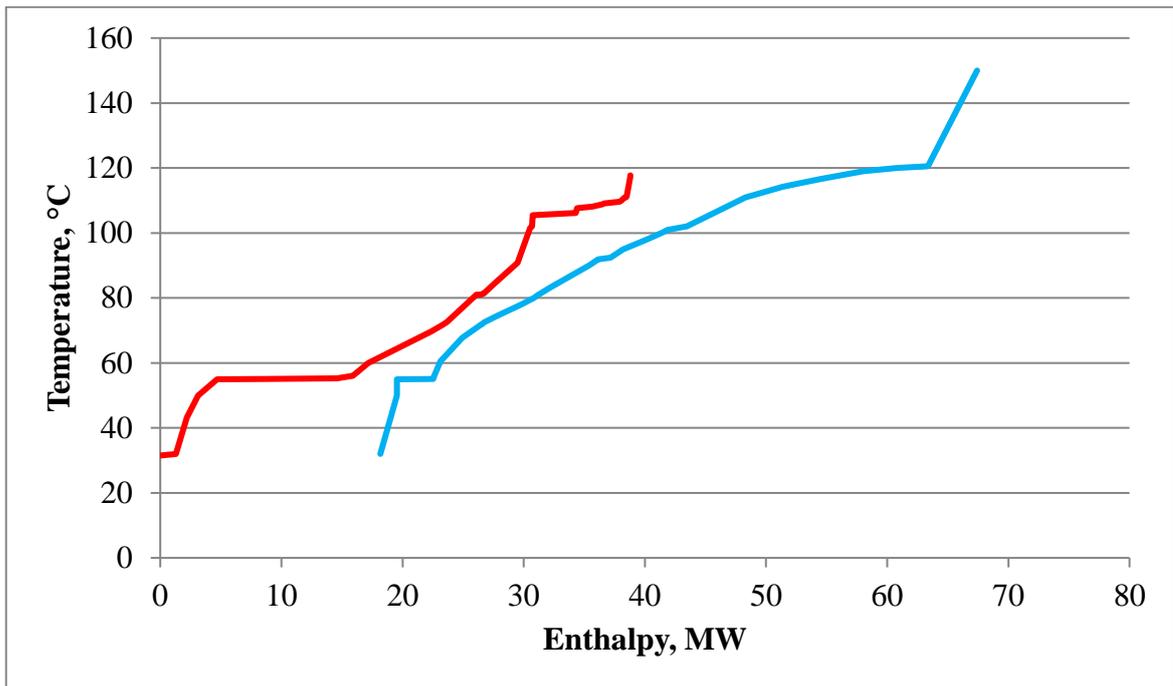


Figure 26 Composite curves for the process

It can be seen from Figure 26 that there are heat integration possibilities in the process. However, still around 29 MW of external heating and 18 MW of external cooling will be required. The pinch temperatures of this process were 81,3 °C for hot streams and 72,3 °C for cold streams and the process pinch is at 76,8 °C.  $\Delta T$  stays very constant near both sides of the pinch which creates so called “pinch region”. This requires more care when designing the heat exchanger network. This is shown very clearly in the grand composite curve of the process:

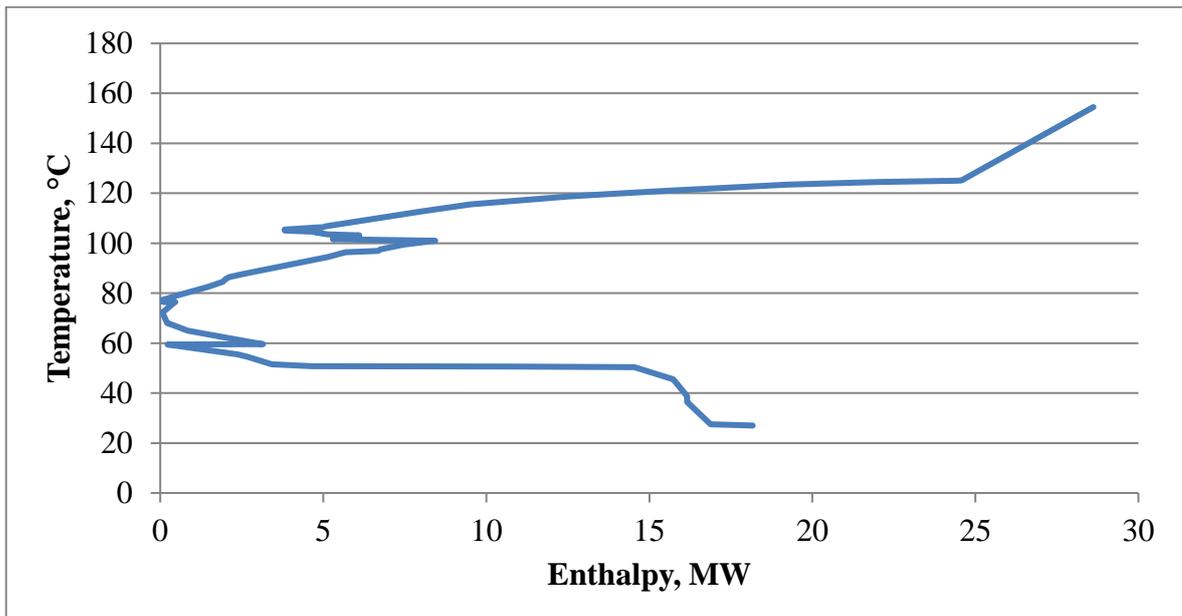


Figure 27 Grand composite curve for the process

The GCC reveals the real situation and shows multiple pinches. However, the other pinch points are only a “near pinches”. These near pinches can be treated as real pinch points but relaxing them and allowing heat exchange over them will still reach the overall energy target (Kemp et al., 2007). In order to keep the heat exchanger network as simple as possible these near pinches weren’t given any special attention.

### 7.3. Results

The results obtained from the pinch analysis show significant energy integration possibilities. Compared to the original base case heat exchanger network a quite large amount of heating and cooling utilities could be saved by redesigning the HEN according to the principles of pinch analysis. The results of required heating and cooling duties for both of these cases are shown in Figure 28:

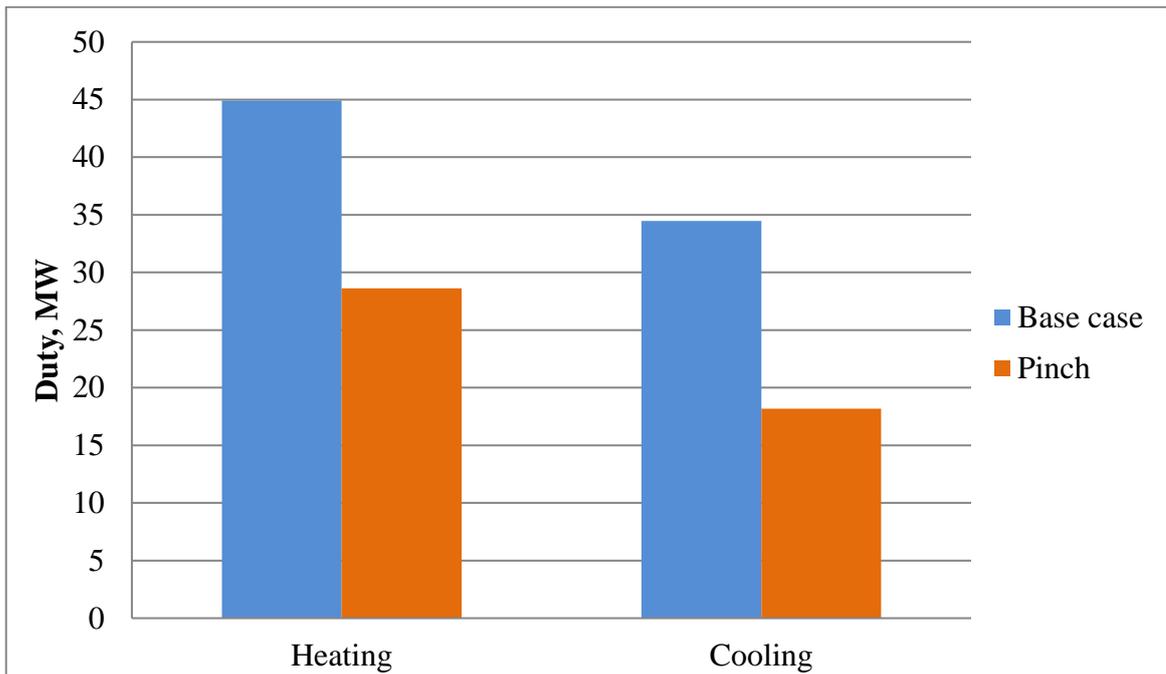


Figure 28 Heating and cooling requirement difference between the base case and pinch network

Figure 28 shows that over 16 MW of heating (36 %) and 16 MW (47%) of cooling could be saved.

The simulation shows that there is large amount of cross-pinch heat exchange happening in the original simulation model. Many hot streams above the pinch are cooled with utility water and many cold streams below the pinch are heated with utility steam. Some cross-pinch heat exchange between process streams is also happening. This causes the large energy requirement compared to the pinch design

In order to construct a heat exchange network according to the pinch principle some stream splitting had to be done. This was because the rule of  $mCp(\text{cold}) > mCp(\text{hot})$  right above the pinch and  $mCp(\text{cold}) < mCp(\text{hot})$  right below the pinch was not obtainable with the original stream flowrates. As with most pinch problems stream splitting also has multiple possible answers which leads to the same energy integration possibilities.

Comparison between the features of the optimal pinch design network and the base case are shown in Table XI:

Table XI Amount of heat exchangers and total heat exchanger area for base case and the pinch network

	Base case	Optimum pinch network
Number of heat exchangers	39	46
Heat exchange area, m <sup>2</sup>	4522	7628

Table XI shows that the optimum pinch network requires a larger capital investment. This optimum pinch network is based on a theoretical “vertical” heat exchange between the cold and hot composite curves. It should be possible to achieve this target when the process is still being designed but in a retrofit situation this might not be possible.

Aspen Energy Analyzer can also propose HENs based on non-linear programming. These networks are not based on the pinch principle and just aim for the right balance between energy efficiency and capital cost. Unfortunately, the software was not able to find any answers for this HEN problem, perhaps because the stream data was too complicated. This shows the limitations of this type of software.

## 8. CONCLUSIONS

In this work a process simulation for a bioethanol process was constructed with Aspen Plus. The thermodynamic method used for this simulation was chosen based on comparing VLE data available from literature to the modelled VLE-results. The results from the process simulation were imported to Aspen Energy Analyzer software which was used to conduct a pinch analysis study for the process. The aim was to find the energy saving potential of the process if the heat exchanger network was constructed based on the pinch principle.

Thermodynamic method choice also affected the results of pinch-analysis. Although the difference between the different activity coefficient+HOC methods weren't significant, the difference compared to ideal vapor phase models was much larger. This shows that it is important to use right type of method to model non-ideal behavior of different species not only for accurate stream composition results but also for energy consumption results.

The pinch analysis made for the biorefinery process shows high energy integration possibilities. Up to 36 % of heating and 47 % of cooling utility usage could be saved by constructing the heat exchange network according to pinch principles.

The program used to conduct the pinch analysis was not able to find answers to the HEN-problem automatically although this is one of the properties of the software. All the networks had to be constructed by hand. This shows that there are limitations in this type of software and that in many cases constructing an efficient heat exchanger network requires engineering knowledge and understanding of the basic principles of pinch.

Although the optimum pinch network could be, in theory, constructed based on this work it would not be a simple task to build a plant wide heat integration network. Instead the pinch analysis could be conducted for each part of the process separately. This would result in smaller energy savings but significantly simplify the HEN. It would be especially interesting to conduct pinch analysis on the MEE-evaporators in the process to see if any of the effects in the evaporator trains crosses the pinch causing energy losses. With the approach used in this work this could not be properly evaluated. Other challenges in the pinch network that should be researched in the future include process startup, semi batch process heat integration and the optimization of  $DT_{\min}$  value based on actual process economics.

## REFERENCES

- Abdullah, S. et al., 2016. Case study: Preliminary assessment of integrated palm biomass biorefinery for bioethanol production utilizing non-food sugars from oil palm frond petiole. *Energy Conversion and Management*, 108(1), pp. 233-242.
- ACS Presidential Roundtable on Sustainable Manufacturing, 2009. *Technology Area 2: Energy Efficiency*, Washington: ACS.
- Alakangas, E. & Flyktman, M., 2001. *Biomass CHP technologies*, Jyväskylä: VTT Energy.
- Ali Mandegari, M., Farzad, S. & Görgens, J., 2017. Economic and environmental assessment of cellulosic ethanol production scenarios annexed to a typical sugar mill. *Bioresource Technology*, 224(1), pp. 314-326.
- Alvira, P., Tomás-Pejó, E., Ballesteros, M. & Negro, M., 2010. Pretreatment technologies for an efficient bioethanol production process based on enzymatic hydrolysis: A review. *Bioresource Technology*, 101(1), pp. 4851-4861.
- Andritz Oy, 2018. *ANDRITZ Mechanical Vapor Recompression (MVR) evaporator*. [Online] Available at: <https://www.andritz.com/products-en/group/pulp-and-paper/pulp-production/kraft-pulp/evaporation-plants/mvr-evaporators> [Accessed 21 February 2018].
- Araújo, A., Brito, R. & Vasconcelos, L., 2007. Exergetic analysis of distillation processes - A case study. *Energy*, 32(7), pp. 1187-1193.
- Aristovich, Y., Lutugina, N., Malenko, Y. & Morachevskii, A., 1960. Liquid-vapor equilibrium in the process of rectification of the ternary system water + formic acid + acetic acid. *Zh. Prikl. Khim*, 33(1), p. 2693.
- AspenTech, 2016. *Aspen Plus V9 Help*, Bedford: AspenTech.
- Aspirion, N. & Kaibel, G., 2010. Dividing wall columns: Fundamentals and recent advances. *Chemical Engineering and Processing: Process Intensification*, 49(2), pp. 139-146.

Aspirion, N., Rumpf, B. & Gritsch, A., 2011. Work flow in process development for energy efficient processes. *Applied Thermal Engineering*, 31(13), pp. 2067-2072.

Atuonwu, J., Van Straten, G. & Van Deventer, H., 2011. Optimizing Energy Efficiency in Low Temperature Drying by Zeolite Adsorption and Process Integration. *Chemical Engineering Transactions*, 25(1), pp. 111-116.

Basso, R. et al., 2013. LLE experimental data, thermodynamic modeling and sensitivity analysis in the ethyl biodiesel from macauba oil settling step. *Bioresource Technology*, 131(1), pp. 468-475.

Biofuel.org.uk, 2010. *First Generation Biofuels*. [Online] Available at: <http://biofuel.org.uk/first-generation-biofuel.html> [Accessed 19 January 2018].

Biofuels.org.uk, 2010. *Second Generation Biofuels*. [Online] Available at: <http://biofuel.org.uk/second-generation-biofuels.html> [Accessed 19 January 2018].

Biofuels.org.uk, 2010. *Third Generation Biofuels*. [Online] Available at: <http://biofuel.org.uk/third-generation-biofuels.html> [Accessed 22 January 2018].

Birchfield, G., 2000. Issues and Challenges In Energy Benchmarking. *Energy Engineering*, 98(2), pp. 38-51.

Calrson, E., 1996. Don't Gamble With Physical Properties For Simulations. *Chemical Engineering Progress*, 10(1996), pp. 35-46.

Carolina dos Ramos, M., Haley, J., Westwood, J. & McCabe, C., 2011. Extending the GC-SAFT-VR approach to associating functional groups: Alcohols, aldehydes, amines and carboxylic acids. *Fluid Phase Equilibria*, 306(1), pp. 97-111.

Cefic aisbl, 2013. *European Chemistry for Growth; Unlocking a competitive, low carbon and energy efficient future*, Brussels: Cefic aisbl.

- Chalov, N. & Aleksandrova, O., 1957. Liquid-vapor Phase Equilibrium of Formic Acid-water At Normal and Low Pressures. *Gidroliz. Loskhim. Prom-st*, 10(3), pp. 15-17.
- Chan, I. et al., 2014. Heat Exchanger Network Design Considering Inherent Safety. *Energy Procedia*, 61(1), pp. 2469-2473.
- Chapman, W., Gubbins, K., Jackson, D. & Radosz, M., 1990. A New Reference Equation of State for Associating Liquids. *Industrial & Engineering Chemistry Research*, 29(1), p. 1709.
- Choi, H.-S., Lee, T.-J., Kim, Y.-G. & Song, S.-L., 2005. Performance improvement of multiple-effect distiller with thermal vapor compression system by exergy analysis. *Desalination*, 182(1-3), pp. 239-249.
- Cornelissen, R., 1997. *Thermodynamics and sustainable development*, Enschede: Universiteit Twente.
- Correa, D. & Gundersen, T., 2016. Process design methodology for energy-efficient processes operating below and across ambient temperature. *AIChE Journal*, 62(7), pp. 2324-2340.
- Derawi, S. et al., 2004. Application of the CPA equation of state to organic acids. *Fluid Phase Equilibria*, 225(1), pp. 107-113.
- Dias, M. et al., 2009. Production of bioethanol and other bio-based materials from sugarcane bagasse: Integration to conventional bioethanol production process. *Chemical Engineering Research and Design*, 87(1), pp. 1206-1216.
- Dias, M. et al., 2011. Improving bioethanol production from sugarcane: evaluation of distillation, thermal integration and cogeneration system. *Energy*, 36(6), pp. 3691-3703.
- Economou, I., 2002. Statistical Associating Fluid Theory: A Successful Model for the Calculation of Thermodynamic and Phase Equilibrium Properties of Complex Fluid Mixtures. *Industrial & Engineering Chemistry Research*, 41(1), pp. 953-962.

- Einstein, D., Worrel, E. & Khurshch, M., 2001. *Steam Systems in Industry: Energy Use and Energy Efficiency Improvement Potentials*, Berkeley: Lawrence Berkeley National Laboratory.
- Escobar, M. & Trierweiler, J., 2013. Optimal heat exchange network synthesis: A case study comparison. *Applied Thermal Engineering*, 51(1-2), pp. 801-826.
- Faúndez, C. & Valderrama, J., 2009. Activity Coefficient Models to Describe Vapor-Liquid Equilibrium in Ternary Hydro-Alcoholic Solutions. *Chinese Journal of Chemical Engineering*, 17(2), pp. 259-267.
- Feng, X. & Zhu, X., 1997. Combining pinch and exergy analysis for process modifications. *Applied Thermal Engineering*, 17(3), pp. 249-261.
- Fenwicks, M., Robert, K. & Alex, A., 2014. Energy Efficiency Analysis Using Pinch Technology: A Case Study of Orbit Chemicals Industry. *IOSR Journal of Mechanical and Civil Engineering*, 11(3), pp. 44-53.
- Ferreira, O., Fornari, T., Brignole, E. & Bottini, S., 2003. Modelling of association effects in mixtures of carboxylic acids with associating and non-associating components. *Latin America Applied Research*, 33(1), pp. 307-312.
- GEA Process Engineering, 2015. *Evaporation Technology Using Mechanical Vapour Recompression - Technology and Applications*, Ettlingen: GEA Wiegand GmbH.
- Gomes de Azevedo, E., 1998. *Molecular Thermodynamics of Fluid-Phase Equilibria*. 3rd ed. Upper Saddle River: Prentice Hall.
- González, H., Abildskov, J. & Gani, R., 2007. A Method for Prediction of UNIFAC Group Interaction Parameters. *AIChE Journal*, 53(6), pp. 1620-1632.
- Gross, J. & Sadowski, G., 2002. Application of the Perturbed-Chain SAFT Equation of State to Associating Systems. *Industrial & Engineering Chemistry Research*, 41(1), pp. 5510-5515.
- Gunnarsson, A. & Magnusson, C., 2011. *Pinch analysis of Nynas refinery*, Göteborg: Chalmers University of Technology.

- Hadrich, B. & Kechaou, N., 2010. Identification of Best Model for Equilibrium Data of Ethanol-Water Mixture. *Journal of Chemistry and Chemical Engineering*, 4(6), pp. 46-48.
- Hajjaji, N., Pons, M.-N., Houas, A. & Renaudin, V., 2012. Exergy analysis: An efficient tool for understanding and improving hydrogen production via the steam methane reforming process. *Energy Policy*, 42(1), pp. 392-399.
- Halvorsen, I. & Skogestad, S., 2011. Energy efficient distillation. *Journal of Natural Gas Science and Engineering*, 3(4), pp. 571-580.
- Hayden, J. & O'Connell, P., 1975. A Generalized Method for Predicting Second Virial Coefficients. *Industrial & Engineering Chemistry Process Design and Development*, 14(3), pp. 209-216.
- Heikkilä, I. et al., 2008. *Teollisuuden energiatehokkuus*, Helsinki: Suomen Ympäristökeskus.
- Hill, J. et al., 2006. Environmental, economic and energetic costs and benefits of biodiesel and ethanol fuels. *Proceeding of the National Academy of Science of United States of America*, 103(30), pp. 11206-11210.
- Hinderick, A. et al., 1996. Exergy analysis with a flowsheeting simulator-I Theory; calculating exergies of material streams. *Chemical Engineering Science*, 51(20), pp. 4693-4700.
- Hindmarsh, E., 1983. The Pinch Design Method For Heat Exchanger Networks. *Chemical Engineering Science*, 38(5), pp. 745-763.
- Huang, S. & Radosz, M., 1990. Equation of State for Small, Large, Polydisperse, and Associating Molecules. *Industrial & Engineering Chemistry Research*, 29(1), p. 2284.
- Humbird, D. et al., 2011. *Process Design and Economics for Biochemical Conversion of Lignocellulosic Biomass to Ethanol*, Colorado: National Renewable Energy Laboratory.
- Jönsson, L. & Martín, C., 2016. Pretreatment of lignocellulose: Formation of inhibitory by-products and strategies for minimizing their effects. *Biosource Technology*, 199(1), pp. 103-112.

Kang, Q. & Tan, T., 2015. Exergy and CO<sub>2</sub> Analysis as Key Tools for the Evaluation of Bio-Ethanol Production. *Sustainability*, 8(1), p. 76.

Keating, D. & Simon, F., 2018. *EU strikes deal on 32% renewable energy target and palm oil ban after all-night session.* [Online] Available at: <https://www.euractiv.com/section/energy/news/eu-strikes-deal-on-32-renewable-energy-target-and-palm-oil-ban-after-all-night-session/> [Accessed 25 June 2018].

Ke, J., Price, L., McNeil, M. & Khanna, N. Z. N., 2013. Analysis and practises of energy benchmarking for industry from the perspective of system engineering. *Energy*, 51(1), pp. 32-44.

Kemp, I. et al., 2007. *Pinch Analysis and Process Integration - A user guide on process integration for the efficient use of energy.* 2nd ed. Oxford: Butterworth-Heinemann.

Kleiner, M., Tumakaka, F. & Sadowski, G., 2009. Thermodynamic Modelling of Complex Systems. In: Berlin, ed. *Molecular Thermodynamics of Complex Systems.* Heidelberg: Springer-Verlag Berling Heidelberg, pp. 76-108.

Klemeš, J. & Kravanja, Z., 2013. Forty years of Heat Integration: Pinch Analysis (PA) and Mathematical Programmin (MP). *Current Opinion in Chemical Engineering*, 2(4), pp. 461-474.

Kontogeorgis, G. et al., 2006a. Ten Years with the CPA (Cubic-Plus-Association) Equation of State. Part 1. Pure Compounds and Self-Associating Systems. *Industrial & Engineering Chemistry Research*, 45(1), pp. 4855-4868.

Kontogeorgis, G. et al., 2006b. Ten Years with the CPA (Cupic-Plus-Association) Equation of State. Part 2. Cross-Associating and Multicomponent Systems. *Industrial Engineering & Chemistry Research*, 45(1), pp. 4869-4878.

Kwak, H.-Y., Kim, D.-J. & Jeon, J.-S., 2003. Exergetic and thermoeconomic analyses of power plants. *Energy*, 28(4), pp. 343-360.

Laurijssen, J., Faaij, A. & Worrel, E., 2013. Benchmarking energy use in the paper industry: a benchamrking study on process unit level. *Energy Efficiency*, 6(1), pp. 49-63.

- Linnhoff March, 1998. *Introduction to Pinch Technology*, Northwich: Linnhoff March.
- Linnhoff, B. & Hindmarsh, E., 1983. The Pinch Design Method For Heat Exchanger Networks. *Chemical Engineering Science*, 38(5), pp. 745-763.
- Littlewood, J., Wang, L., Turnbull, C. & Murphy, R., 2013. Techno-economical potential for bioethanol from bamboo in China. *Biotechnology for Biofuels*, 6(173), pp. 1-13.
- Li, X. et al., 2011. Incorporating Exergy Analysis and Inherent Safety Analysis for Sustainability Assessment of Biofuels. *Industria & Engineering Chemistry Research*, 50(1), pp. 2981-2993.
- Lurijsen, J., Faaij, A. & Worrell, E., 2013. Benchmarking energy use in the paper industry: a benchmarking study on process unit level. *Energy Efficiency*, 6(1), pp. 49-63.
- Mains, G., 1922. -. *Chem. Metall. Eng.*, 26(1), pp. 779-784.
- Mansoori, G., Carnahan, N., Starling, K. & Leland, T., 1971. Equilibrium Thermodynamic Properties of the Mixture of Hard Spheres. *The Journal of Chemical Physics*, 54(1), p. 1523.
- Mathias, P., 2017. Guideline for the Analysis of Vapor-Liquid Equilibrium Data. *Journal of chemical & engineering data*, 62(1), pp. 2231-2233.
- Matsuda, K., Hirochi, Y., Tatsumi, H. & Shire, T., 2009. Applying heat integration total site based pinch technology to a large industrial area in Japan to further improve performance of highly efficient process plants. *Energy*, 34(10), pp. 1687-1692.
- Meihui, S. et al., 2014. A Multi-Yeast Analysis of the Energy Balance, Green Gas Emissions, and Production Costs of First and Second Generation Bioethanol. *International Journal of Green Energy*, 12(1), pp. 168-184.
- Michelsen, M. & Hendriks, E., 2001. Physical properties from association models. *Fluid Phase Equilibria*, 180(1-2), pp. 165-174.
- Modarresi, A., Kravanja, P. & Friedl, A., 2012. Pinch and exergy analysis of lignocellulosic ethanol, biomethane, heat and power production from straw. *Applied Thermal Engineering*, 43(1), pp. 20-28.

- Moncada, J., El-Halwagi, M. & Cardona, C., 2013. Techno-economic analysis for a sugarcane biorefinery: Colombian case. *Bioresource Technology*, 135(1), pp. 533-543.
- Morales, M., Quintero, J., Conejeros, R. & Aroca, G., 2015. Life cycle assesment of lignocellulosic bioethanol: Environmental impacts and energy balance. *Renewable and Sustainable Energy Reviews*, 42(1), pp. 1349-1361.
- Myint, P., Hao, Y. & Firoozabadi, A., 2015. *The CPA Equation of State and an Activity Coefficient Model for Accurate Molar Enthalpy Calculations of Mixtures with Carbon Dioxide and Water/Brine*, Livermore: Lawrence Livermore National Laboratory.
- Nothnagel, K., Abrams, D. & Praunitz, J., 1973. Generalized Correlation for Fugacity Coefficients in Miztures at Moderate Pressures. *Industrial & Engineering Chemistry Process Design and Development*, 12(1), pp. 25-35.
- O'Connell, J. et al., 2009. Thermodynamic Property Modeling for Chemical Process and Products Engineering: Some Perspectives. *Industrial & Engineering Chemistry Research*, 48(10), pp. 4619-4637.
- Ooi, Z., Teoh, Y., Kunasundari, B. & Shuit, S., 2017. Oil palm frond as a sustainable and promising biomass source in Malasya: A review. *Evironmental Progress & Sustainable Energy*, 36(6), pp. 1864-1874.
- Pascal, P., Dupuy, E. & Garnier, M., 1921. Study of Binary and Ternary Mixtures Found in the Manufacture of Synthetic Acetic Acid. *Bull. Soc. Chim. Fr*, 21(1), pp. 9-21.
- Peng, Y., Goff, K., Carolina Dos Ramos, M. & McCabe, C., 2010. Predicting the Phase Behavior of Polymer Systems with the GC-SAFT-VR Approach. *Industrial & Engineering Chemistry Research*, 49(3), pp. 1378-1394.
- Perakis, C., Voutsas, E., Magoulas, K. & Tassios, D., 2007. Thermodynamic Modeling of the Water + Acetic Acid + CO<sub>2</sub> System: The Importance of the Number of Association Sites of Water and of the Nonassociation Contribution for the CPA and SAFT-Type Models. *Industrial & Engineering Chemistry Research*, 46(3), pp. 932-938.

- Petrakopoulou, F., Boyano, A., Cabrera, M. & Tsatsaronis, G., 2011. Exergoeconomic and exergoenvironmental analyses of a combined cycle power plant with chemical looping technology. *International Journal of Greenhouse Gas Control*, 5(3), pp. 475-482.
- Pimentel, D. & Patzek, T., 2005. Ethanol Production Using Corn, Switchgrass, and Wood; Biodiesel Production Using Soybean and Sunflower. *Natural Resources Research*, 14(1), pp. 65-76.
- Pla-Franco, J., Lladosa, E., Loras, S. & Montón, J., 2014. Thermodynamic Analysis and Process Simulation of Ethanol Dehydration via Heterogeneous Azeotropic Distillation. *Industrial & Engineering Chemistry Research*, 53(14), pp. 6084-6093.
- Pradhan, A. et al., 2011. Energy Life-Cycle Assessment of Soybean Biodiesel Revisited. *American Society of Agricultural and Biological Engineers*, 54(3), pp. 1031-1039.
- Prausnitz, J., Lichtenthaler, R. & Gomes de Azevedo, E., 1998. *Molecular Thermodynamics of Fluid-Phase Equilibria*. 3rd ed. Upper Saddle River: Prentice Hall PTR.
- Ramdharee, S., Muzenda, E. & Belaid, M., 2013. *A Review of the Equation of State and Their Applicability in Phase Equilibrium Modelling*. Johannesburg, ICBE.
- Renon, H. & Prausnitz, J., 1968. Local Composition in Thermodynamic Excess Functions for Liquid Mixtures. *AIChE Journal*, 14(1), pp. 135-144.
- Saville, G., 2011. *Thermopedia - Activity coefficient*. [Online] Available at: <http://thermopedia.com/content/288/> [Accessed 13 February 2018].
- Saygin, D., Worrel, E., Patel, M. & Gielen, D., 2011. Benchmarking the energy use of energy-intensive industries in industrialized and in developing countries. *Energy*, 36(11), pp. 6661-6673.
- Schmer, M., Voge, K., Mitchell, R. & Perrin, R., 2007. Net energy of cellulosic ethanol from switchgrass. *Proceedings of the National Academy of Sciences of the United States of America*, 105(2), pp. 464-469.

- Seider, W., Seader, J., Lewin, D. & Widago, S., 2009. *Product and Process Design Principles - Synthesis, Analysis and Evaluation*. 3rd ed. Hoboken NJ: John Wiley & Sons, Inc.
- Sheehan, J. et al., 1998. *Life Cycle Inventory of Biodiesel and Petroleum Diesel for Use in an Urban Bus*, Colorado: National Renewable Energy Laboratory.
- Sindhu, R., Binod, P. & Pandey, A., 2016. Biological pretreatment of lignocellulosic biomass - An overview. *Bioresource Technology*, 199(1), pp. 76-82.
- Smith, R., 2005. *Chemical Process Design and Integration*. 1 ed. Chichester: John Wiley & sons Ltd..
- Soo, C.-B., 2011. *Experimental thermodynamic measurements of biofuel-related associating compounds and modeling using the PC-SAFT equation of state*, Paris: Chemican and Process Engineering. École Nationale Supérieure des Mines de Paris.
- SPX Corporation, 2009. *Evaporator Handbook*, Getzville: APV.
- Stein, F. & Miller, E., 1980. Extension of the Hayden-O'Connell Correlation to the Second Virial Coefficient of some Hydrogen-Bonding Mixtures. *Industrial & Engineering Chemistry Process Design and Development*, 19(1), pp. 123-128.
- Sun, Y. & Cheng, J., 2002. Hydrolysis of lignocellulosic materials for ethanol production: a review. *Bioresource Technology*, 83(1), pp. 1-11.
- Svensson, E. & Berntsson, T., 2014. The effect of long lead times for planning of energy efficiency and biorefinery technologies at a pulp mill. *Renewable Energy*, Volume 61, pp. 12-16.
- Tan, H., Lee, K. & Mohammed, A., 2010. Second-generation bio-ethanol (SGB) from Malaysian palm empty fruit bunch: Energy and exergy analyses. *Bioresource Technology*, 101(14), pp. 5719-5727.
- Tarighaleslami, H., Reza, O., ALi, G. & Roozbeh, H., 2012. Thermodynamic evaluation of distillation columns using exergy loss profiles: a case study on the crude oil atmospheric distillation column. *Clean Technologies and Environmental Policy*, 14(3), pp. 381-387.

Towler, G. & Sinnott, R., 2013. *Chemical Engineering Design*. 2nd ed. Waltham: Butterworth-Heinemann.

U.S Environmental Protection Agency, 2017. *Catalog of CHP Technologies*, Washington D.C.: U.S Environmental Protection Agency.

U.S. Department of Energy, 2012. *Improving Steam System Performance: A Sourcebook for Industry*. [Online] Available at: <https://energy.gov/sites/prod/files/2014/05/f15/steamsourcebook.pdf> [Accessed 20 February 2018].

Uellendahl, H. et al., 2008. Energy balance and cost-benefit analysis of biogas production from perennial energy crops pretreated by wet oxidation. *Water Science and Technology*, 58(9), pp. 1841-1847.

UNIDO, 2014. *Energy Efficiency Potentials in Industrial Steam Systems in China*, Vienna: United Nations Industrial Development Organisation.

Valdivia, M., Luis Galan, J., Laffarga, J. & Ramos, J.-L., 2016. Biofuels 2020: Biorefineries based on lignocellulosic materials. *Microbial biotechnology*, 9(5), pp. 585-594.

Van Gerpen, J. & Shrestha, D., 2005. *Biodiesel Energy Balance*, Idaho: University of Idaho - Department of Biological and Agricultural Engineering.

Wang, M. et al., 2014. Energy efficiency and environmental performance of bioethanol production from sweet sorghum stem based on life cycle analysis. *Bioresource Technology*, 163(1), pp. 74-81.

Wang, Y. & Smith, R., 1994. Wastewater minimisation. *Chemical Engineering Science*, 49(7), pp. 981-1006.

Wan, Y., Sadhukhan, J., Ng, K. & Ng, D., 2016. Techno-economic evaluations for feasibility of sago based biorefinery, Part 1: Alternative energy systems. *Chemical Engineering Research and Design*, 107(1), pp. 263-279.

- Varanda, M. P. G. & Martins, F., 2011. Life cycle analysis of biodiesel production. *Fuel Processing Technology*, 92(5), pp. 1087-1094.
- Wilson, G., 1964. A New Expression for the Excess Free Energy of Mixing. *Journal of the American Chemical Society*, 86(2), pp. 127-130.
- Wisniak, J. & Tamir, A., 1977. Vapor-Liquid Equilibria in the Ternary Systems Water-Formic Acid-Acetic Acid and Water-Acetic Acid-Propionic Acid. *Journal of Chemical Engineering Data*, 22(3), pp. 153-160.
- Wolbach, J. & Sandler, S., 1998. Using Molecular Orbital Calculations to Describe the Phase Behavior of Cross-associating Mixtures. *Industrial & Engineering Chemistry Research*, 37(1), pp. 2917-2928.
- Wooley, R. & Putsche, V., 1996. *Development of an ASPEN PLUS Physical Property Database for Biofuels Components*, Golden: National Renewable Energy Laboratory.
- Voutsas, E. C., Yakoumis, I. & Tassios, D., 1999. Prediction of phase equilibria in water/alcohol/alkane systems. *Fluid Phase Equilibria*, 158-160(1), pp. 151-168.
- Voutsas, E., Pamouktsis, C., Argyris, D. & Pappa, G., 2011. Measurements and thermodynamic modeling of the ethanol-water system with emphasis to azeotropic region. *Fluid Phase Equilibria*, 308(1), pp. 135-141.
- Yang, F., Liu, Y. & Liu, G., 2016. A process simulation based benchmarking approach for evaluation consumption of a chemical process system. *Journal of Cleaner Production*, 112(4), pp. 2730-2743.
- Yushu, C. et al., 2012. Thermodynamic Modelling of Mixtures Containing Carboxylic Acids Using the PC-SAFT Equation of State. *Industrial & Engineering Chemistry Research*, 51(1), pp. 13846-13852.
- Zhang, J. et al., 2017. Life cycle energy efficiency and environmental impact assesment of bioethanol production from sweet potato based on different production modes. *PLOS ONE*, 12(7), p. e0180685.

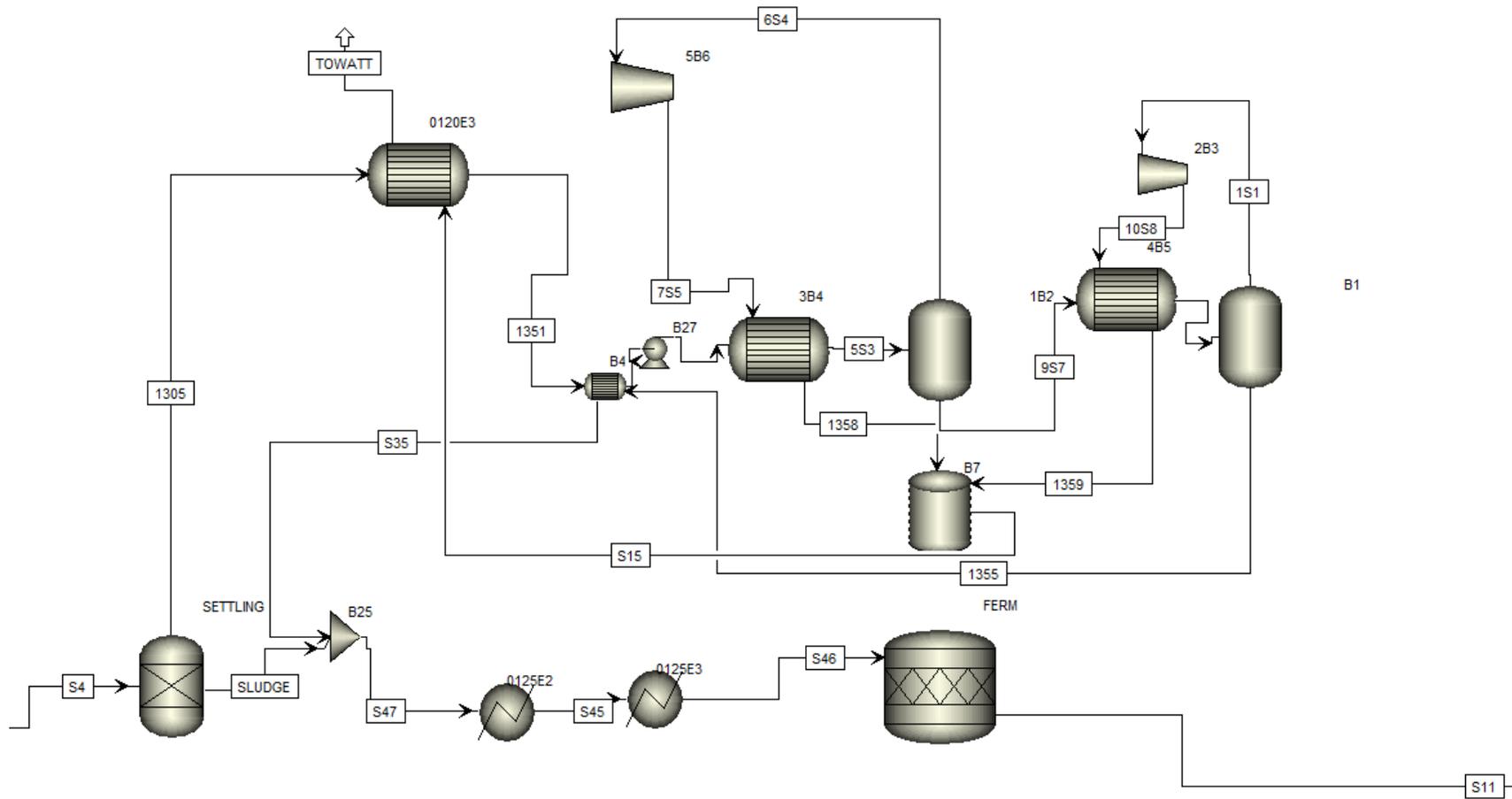
Zhang, X. Y. S., Tyagi, R., Surampalli, R. & Valéro, J., 2016. Energy balance of biofuel production from biological conversion of crude glycerol. *Journal of Environmental Management*, 170(1), pp. 169-178.

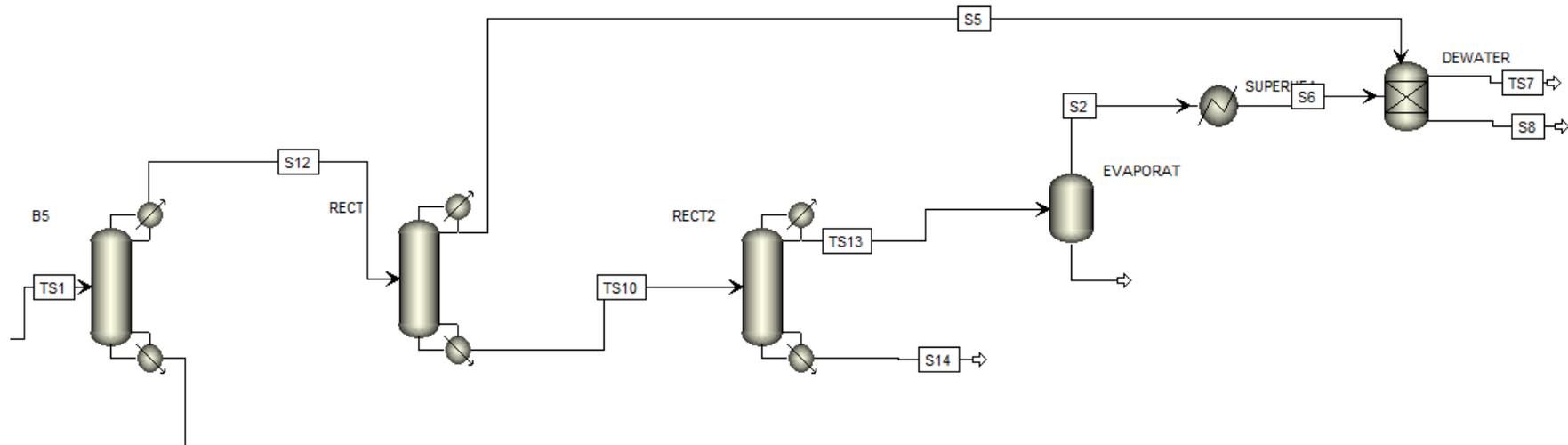
**APPENDICES**

APPENDIX I: Simulation flowsheet

APPENDIX II: Simulation flowchart

**Simulation flowsheet: Settling, fermentation and supernatant evaporation**



**Simulation flowsheet: Ethanol distillation**



**Simulation flowchart: Settling, fermentation and supernatant evaporation**

Stream name	Temperature, °C	Pressure, bar	Mass Flows, kg/h	Cellulose	Water	Dextrose	Ethanol	CO2	Hemicellulose	Lignin
1305	55	1	81654,1	0	68502,2	13151,9	0	0	0	0
1351	66	1	81654,1	0	68502,2	13151,9	0	0	0	0
S34	90	1	81654,1	0	68502,2	13151,9	0	0	0	0
S50	90	1,03	81654,1	0	68502,2	13151,9	0	0	0	0
5S3	101	1,03	81654,1	0	68502,2	13151,9	0	0	0	0
6S4	102	1	7959,18	0	7959,18	0,0002502	0	0	0	0
1358	110,8	1	7959,18	0	7959,18	0,0002502	0	0	0	0
5S3	101	1,03	81654,1	0	68502,2	13151,9	0	0	0	0
6S4	102	1	7959,18	0	7959,18	0,0002502	0	0	0	0
7S5	141	1	7959,18	0	7959,18	0,0002502	0	0	0	0
9S7	102	1	73695	0	60543	13151,9	0	0	0	0
11S9	102	1	73695	0	60543	13151,9	0	0	0	0
10S8	141	1	9031,29	0	9031,29	0,0003076	0	0	0	0
1355	102,05	1	64663,7	0	51511,7	13151,9	0	0	0	0
1359	110,8	1	9031,29	0	9031,29	0,0003076	0	0	0	0
S15	110,8	1	16990,5	0	16990,5	0,0005579	0	0	0	0
TOWATT	60	1	16990,5	0	16990,5	0,0005579	0	0	0	0
S35	72	1	64663,7	0	51511,7	13151,9	0	0	0	0
SLUDGE	55	1	11308,1	1851,57	8466,56	989 931	0	0	0	0
S45	46	1	75971,7	1851,57	59978,3	14141,9	0	0	0	0
S46	32	1	75971,7	1851,57	59978,3	14141,9	0	0	0	0
S47	70	1	75971,7	1851,57	59978,3	14141,9	0	0	0	0
S11	32	1	75971,7	1851,57	59978,3	1895,01	6263,42	5983,45	0	0

**Simulation flowchart: Ethanol distillation**

Stream name	Temperature, °C	Pressure, bar	Mass Flows, kg/h	Cellulose	Water	Dextrose	Ethanol	CO2	Hemicellulos	Lignin
TS1	50	1	69988,3	1851,57	59978,3	1895,01	6263,42	0	0	0
S12	76	0,5	15000	0	8736,87	2,95E-01	6263,15	0	0	0
TS10	104	2	12000	0	8581,77	2,95E-01	3418,24	0	0	0
TS13	92	1,7	3200	0	206 331	1,32E-143	2993,67	0	0	0
S2	92	1,7	3200	0	206 331	0	2993,67	0	0	0
S6	112	1,7	3200	0	206 331	0	2993,67	0	0	0
TS7	92	1,7	5798,26	0	180 714	0	5780,19	0	0	0
S8	92	1,7	401 743	0	343 357	0	583 857	0	0	0
S5	92	2	3000	0	155 098	1,04E-297	2844,9	0	0	0
1504	81	0,5	54988,4	1851,57	51241,3	1895	0,441726	0	0	0

**Simulation flowchart: Stillage treatment**

Stream name	Temperature, °C	Pressure, bar	Mass Flows, kg/h	Cellulose	Water	Dextrose	Ethanol	CO2	Hemicellulos	Lignin
S33	81	1	5330,93	1851,57	3024,34	455	0,022086	0	0	0
2003	81	1	49657,4	0	48217	1440	0,419639	0	0	0
S53	83	1	49657,4	0	48217	1440	0,419639	0	0	0
S54	100	1	49657,4	0	48217	1440	0,419639	0	0	0
S2U	100	1	49657,4	0	48217	1440	0,419639	0	0	0
S6U	100	1	25476,6	0	24036,6	1440	0,034007	0	0	0
S7U	101	1	25476,6	0	24036,6	1440	0,034007	0	0	0
S11U	101	1	7099,34	0	5659,34	1440	0,001142	0	0	0
S55	84	1	7099,34	0	5659,34	1440	0,001142	0	0	0
S12U	69,5	0,299097	5866,27	0	4426,27	1440	0,000336	0	0	0
S13U	83,1	0,524051	4793,52	0	3353,52	1440	9,67E+00	0	0	0
S20U	98	0,916533	3569,39	0	2129,39	1440	2,13E+00	0	0	0
S14U	98	0,916533	1224,13	0	1224,13	3,68E+00	7,54E+00	0	0	0
S15U	97	0,916533	1224,13	0	1224,13	3,68E+00	7,54E+00	0	0	0
S19U	83,1	0,524051	1072,76	0	1072,76	6,38E-01	0,000239	0	0	0
S16U	83	0,524051	1072,76	0	1072,76	6,38E-01	0,000239	0	0	0
S21U	69,5	0,299097	1233,07	0	1233,07	1,50E-01	0,000806	0	0	0
S8U	101	1	18377,3	0	18377,2	0,00053783	0,032865	0	0	0
S9U	207	2	18377,3	0	18377,2	0,00053783	0,032865	0	0	0
S10U	124	2	18377,3	0	18377,2	0,00053783	0,032865	0	0	0
S3U	100	1	24180,8	0	24180,4	0,00026572	0,385633	0	0	0
S4U	141	1	24180,8	0	24180,4	0,00026572	0,385633	0	0	0
S5U	110	1	24180,8	0	24180,4	0,00026572	0,385633	0	0	0
S56	110	1	42558,1	0	42557,7	0,00080355	0,418498	0	0	0
S57	110	1	42558,1	0	42557,7	0,00080355	0,418498	0	0	0