THE ANALYSIS OF AN AMMONIA/WATER HYBRID HEAT PUMP IN THE ETHANOL PRODUCTION PROCESS

By

Pieter J.J. Visagie, B.Eng.

Dissertation submitted in partial fulfilment of the degree

Master of Engineering

In the

School of Mechanical Engineering,

Faculty of Engineering

At the

North West University, Potchefstroom Campus

Promoter: Mr. P.W. Jordaan

POTCHEFSTROOM

November 2008

ACKNOWLEDGEMENTS

Firstly I would like to thank my heavenly Father:

"For the Lord gives wisdom, and from his mouth comes knowledge and understanding." Proverbs 2:6

Thanks to Mr. Pietman Jordaan, for all your guidance and enthusiasm during the past two years. Thanks for your ongoing interest in my work.

I would also like to thank Ethanol Fuel Technologies, for giving me the opportunity to conduct this study. Thanks to Anka Oberholzer, Fanie Bester and Michael Beckly for your advice, help and assistance with the evaluation and market knowledge needed in my project.

Thanks to my parents, who carried me through the duration of my studies. Thanks for always believing in me.

Lastly, but most important, to my wife Dorinda, thanks for all you love and support during the past two years. I really love you.

ABSTRACT

Title : The analysis of an ammonia/water hybrid heat pump in the ethanol
production process
Author : Pieter Johannes Jacobus Visagie
Promoter : Mr. P.W. Jordaan
School : Mechanical Engineering
Degree : Master of Engineering

Ethanol is a renewable energy source that could decrease society's dependence on fossil fuels, while reducing greenhouse gas emissions. Producing ethanol on a small scale on South African farms could provide farmers with the capability of increasing their profits by reducing their input cost. Ethanol can be directly used as fuel and could supply alternative products to their market.

This study evaluated the feasibility of using an ammonia/water hybrid heat pump in the ethanol production process. A model for the material and energy balance of a small scale ethanol plant was simulated, to obtain the requirements to which the hybrid heat pump had to adhere.

A *two stage hybrid heat pump* (TSHHP) was then modelled. It is capable of operating at high temperatures and it has high temperature lift capabilities, which are suitable in the production of ethanol. The results from the model demonstrated that the TSHHP could operate at an average temperature lift of 106℃ with a maximum temperature of heat delivery as high as 142℃ and cooling as low as 9℃. Simultaneous heating and cooling demand in the ethanol production process can be met with the TSHHP. For the TSHHP model, 120 kW of heating and 65 kW of cooling is supplied while maintaining a COP of 2.1. The model accuracy was also verified against another simulation program.

Implementation of the TSHHP into the ethanol plant was then discussed, as well as methods to optimize production by energy management. When compared to conventional heating and cooling systems, it was found that the TSHHP provides a more cost effective and energy efficient way of producing ethanol. The economic evaluation demonstrated that the installation cost of the TSHHP would only be 63% of the price of a conventional system. The main advantage is that the TSHHP uses only 38% of the energy used in a conventional system.

Keywords: heat pump, hybrid, refrigerant, zeotropic mixture, ethanol plant.

OPSOMMING

Titel	:	Die analise van ‘n ammoniak/water hibriede hittepomp in die etanol vervaardigingsproses.
Outeur	:	Pieter Johannes Jacobus Visagie
Promotor	:	Mr. P.W. Jordaan
Skool	:	Meganiese Ingenieurswese
Graad	:	Meesters in Ingenieurswese

Etanol is ‘n hernubare bron van energie wat die samelewing se afhanklikheid aan fossielbrandstowwe kan verlaag, terwyl dit terselfdertyd kweekhuis-gasvrystelling beperk. Die vervaardiging van etanol op klein skaal op Suid-Afrikaanse plase kan boere die vaardigheid gee om hul winste te verhoog deur ‘n verlaging in hul insetkoste. Etanol kan direk as brandstof gebruik word terwyl dit ook alternatiewe produkte kan lewer vir die boere se mark.

Hierdie studie het die moontlikheid vir die gebruik van ‘n ammoniak/water hibriede hittepomp in die etanol vervaardigings proses geëvalueer. ‘n Materiaal- en energiebalans vir ‘n kleinskaalse etanolaanleg is gesimuleer om die vereistes te bepaal waaraan die hibriede hittepomp moes voldoen.

‘n *Tweestadium hibriede hittepomp* (TSHHP) was toe gemodelleer. Dit het die vemoë om teen hoë temperature te werk, terwyl dit ‘n hoë temperatuur styging verskaf en is daarom geskik vir die vervaardiging van etanol. Die resultate van die model het gedemonstreer dat die TSHHP kan werk teen ‘n gemiddelde temperatuur styging van 106℃, met ‘n maksimum hitte-leweringstemperatuur so hoog as 142℃ en verkoeling so laag as 9℃. Gelyktydige verhitting en verkoeling kan gedoen word met die TSHHP. Vir die TSHHP model kan 120 kW se verhitting en 65 kW se verkoeling gelewer word terwyl ‘n COP van 2.1 gehandhaaf word. Die akkuraatheid van die model is ook geverifieer teen ‘n ander simulasie program.

Die implementasie van TSHHP in ‘n etanol aanleg was toe bespreek, sowel as maniere om die bestuur van energie te optimiseer. Wanneer die TSHHP vergelyk is teen konvensionele verhitting en verkoeling sisteme, is dit gevind dat TSHHP ‘n meer koste effektiewe en energiedoeltreffende manier verskaf om etanol te vervaardig. Die ekonomiese evaluasie het getoon dat die installasiekoste van ‘n TSHHP slegs 63% van die prys van ‘n konvensionele sisteem sal wees. Die grootste voordeel van die TSHHP is dat dit slegs 38% van die energie van ‘n konvensionele sisteem gebruik.

Sleutelwoorde: hittepomp, hibried, werksvloeier, zeotropiese mengsel, etanolaanleg.

SCOPE OF THE STUDY

A thermodynamic model of an ammonia/water hybrid heat pump implementation into a small scale ethanol plant was developed for the company Ethanol Fuel Technologies(EFT).

The following goals were achieved:

- Literature survey on the ethanol production process was conducted.
- With this a mass and energy balance was calculated to obtain a measure of the energy required in the small ethanol plant proposed by EFT.
- An extensive literature survey was conducted on existing hybrid heat pump technology for high temperature applications.
- A model for a high temperature hybrid heat pump was developed. The model can be used to obtain parameters that will help with the detail design of the components in the cycle. Parameters like pressures, concentration of the binary mixture, temperatures and heat transfer throughout the cycle.
- A method of implementation of the hybrid heat pump into the ethanol plant was then discussed.
- The economic analysis provided the probability of future investment into detail design for the application of heat pumps in ethanol plants.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

NOMENCLATURE

A : Area [m^2]

C_p : Specific heat [kJ/kJ.K]

h : Enthalpy [kJ/kg] / Time [hours]

m : Mass [kg]

$\dot{m}$: Mass flow rate [kg/s]

P : Pressure [bar]

Q : Heat transfer [kW]

q : Quality of vapour mass fraction [kg vapour/kg mixture]

s : Entropy [kJ/kg-K]

T : Absolute temperature [K] [°C]

T : Temperature [K]

u : Internal energy [kJ/kg]

U : Overall heat transfer coefficient [W/m^{2}K]

v : Specific volume [m^3/kg]

V : Volumetric flow rate [m^3/s]

W : Compressor power [kW]

x : Ammonia mass fraction [kg ammonia/kg mixture]

SUBSCRIPTS

c : cool stream

e : exit condition

h : hot stream

i : initial condition

is : isentropic

GREEK SYMBOLS

Δ : difference

ε : heat exchanger effectiveness

η : efficiency

ρ : density [kg/m^3]

ABBREVIATIONS

AHP	Absorption Heat Pumps
AHT	Absorption Heat Transformer
CFC	Chlorofluorocarbons
COP	Coefficient of Performance
DDGS	Dried Distillers Grain Solubles
EES	Engineering Equation Solver
EFT	Ethanol Fuel Technologies
FFV	Flexible Fuel Vehicles
GWP	Global Warming Potential
HCFC	Hydrochlorofluorocarbons

HHP	Hybrid Heat Pump
HST	Heat Storage Tank
HT	High Temperature
HTF	Heat Transfer Fluid
LMTD	Log Mean Temperature Difference
LT	Low Temperature
NPSH	Net Positive Suction Head
NTU	Number of Transfer Units
ODP	Ozone Depletion Potential
OP	Operating Point
TSHHP	Two Stage Hybrid Heat Pump
VCHP	Vapour Compression Heat Pump

Chapter 1 – An Introduction

1.1 Introduction

Energy is essential for sustainable development of the modern society, and thus there is a great dependence on it. The main source of this energy is released with the combustion of fossil fuels such as coal, crude oil and natural gas. According to EIA (2008), fossil fuels contributes to 86% of the worldwide energy consumption. The demand and consumption of liquid fuels is also increasing annually due to economic growth worldwide and is projected to increase by 50% from 2005 to 2030.

The combustion of fossil fuels affects our environment in numerous ways, the largest environmental problem being the generation of carbon dioxide and other greenhouse gases. Several studies have also indicated that fossil fuel reserves, like crude oil, will near an end between 2050 and 2075. (Walsh, 2000)

The depletion of fossil fuel deposits and increased emissions of greenhouse gases is the main reasons why renewable sources of energy become more attractive. Utilizing our natural energy sources in more efficient ways is a necessity for society. The high cost of crude oil is also a major contributing factor in finding a replacement for fossil fuels with alternative energy sources. Renewable energy can be seen as such a replacement.

Renewable energy is energy that can easily and sustainably be replaced. It does not rely on fossil fuels and does not contribute to increased greenhouse gas emissions. The usage of renewable energy in the form of biofuels can have a great contribution on the environment by reducing greenhouse gas emissions. This is because renewable energy like bio-ethanol is carbon neutral. Plants absorb carbon dioxide and energy from the sun by the process called photosynthesis. When the plant material is transformed or used directly in a combustion process, energy is released and the carbon dioxide is released back into the environment. Thus the net carbon emissions for bio-fuels are zero. (Demirbas, 2004)

South Africa is a major consumer of energy, and is responsible for emitting the highest quantities of greenhouse gas on the African continent and 13th highest in the world (Wilson, et al. 2005). The Kyoto Protocol (1997) called for the reduction of greenhouse gas emissions and investing in cleaner technologies for the future. The South African government has started an initiative to decrease its global footprint on greenhouse gas emissions. The draft of Biofuel Industrial Strategy (2006) aims to get a biofuel market penetration of 4.5% into the liquid fuel (petrol and diesel) industry in South Africa by 2013. The Energy Efficiency

Strategy of South Africa (2005) also sets targets to improve the energy efficiency of the industrial sector. Voluntary agreement by the industry aims at a 15% increase in energy efficiency by 2015.

Petroleum products account for 33% of South Africa's end use of energy (Figure 1.1). With the benefit of Governmental support towards bio-fuels, bio-ethanol can be seen as a renewable source of energy that will help provide South Africa decrease its dependence on these fossil fuels. Producing bio-ethanol in energy efficient ways will also help South Africa to reach the goals set by the biofuel and energy efficiency strategies.

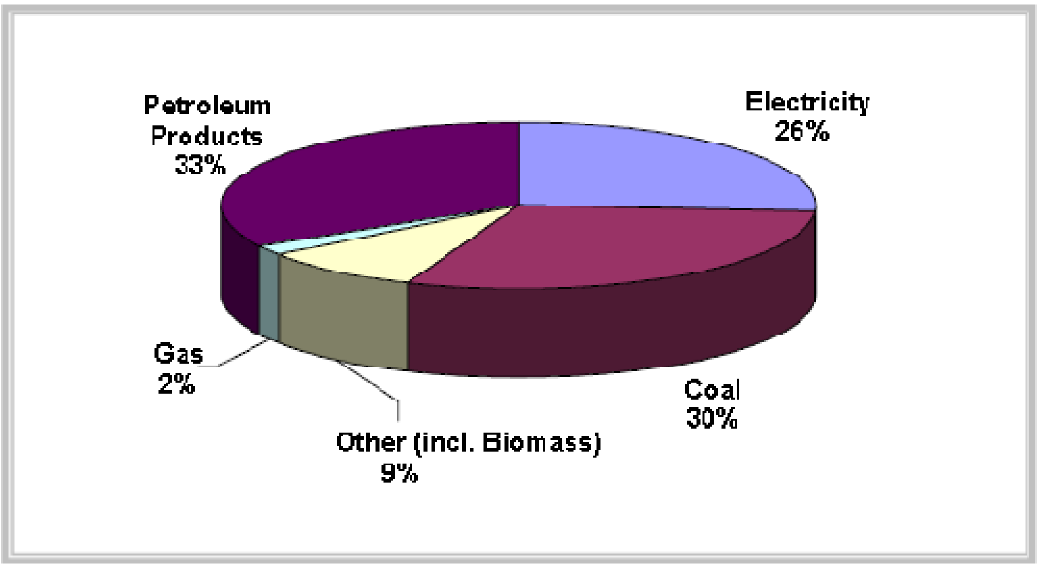

Figure 1.1 - Energy use in South Africa 2000 (DME, 2005)

Production of bio-fuel relies on the agricultural sector, to produce crops that can be converted to bio-ethanol. The South African farmer can play a significant role in producing crops that are suitable for bio-ethanol production. In the following paragraph a review of ethanol production on farms can be done by examining the situation for South African Farmers.

1.2 Ethanol production by the South African Farmer

The high cost of farming is making it near impossible for South African farmers to survive economically. Petroleum products, like diesel and petrol, is the main source of energy utilized on farms. These fuels are used to drive the machinery like tractors, generators and vehicles. The rising cost of fuel over the past few years has made it difficult for farmers to make a profit from their crops. Figure 1.2 shows the rising cost of petrol and diesel from August 1992 to August 2008.

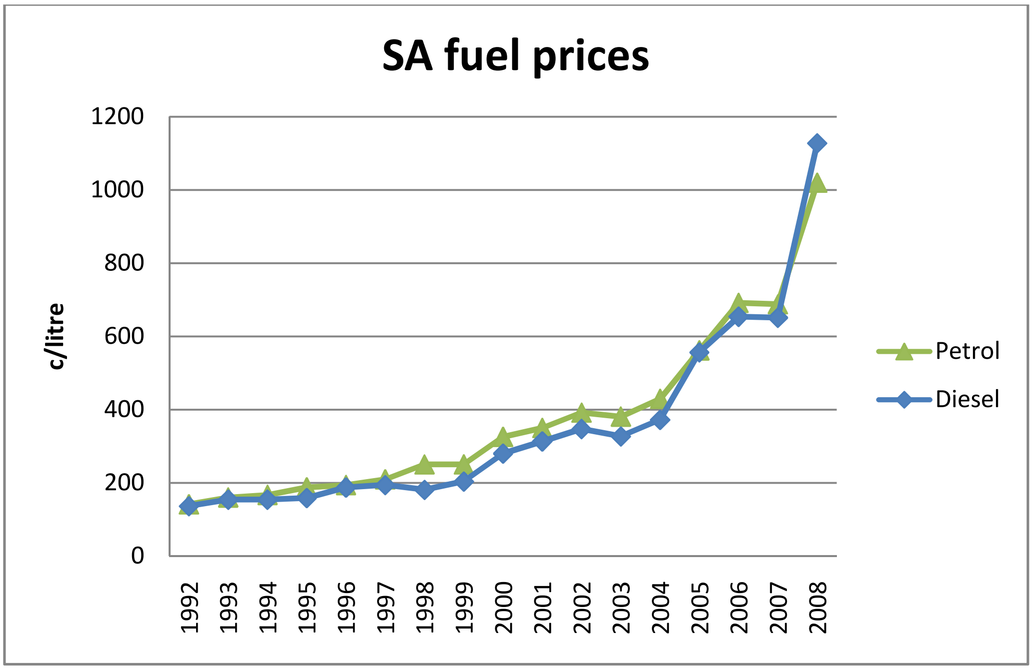

Figure 1.2 - South African Fuel prices (Created from Sasol (2008))

Botha (2008) from SAGraan, predicted what the input cost of farmers for the 2008/2009 season would be. In the prediction (Figure 1.3 and Appendix A) it can be seen that the fuel cost is one of the highest input cost for farmers. This sharp increase in fuel prices will increase this value even further in the future. In the article it is mentioned that a maize crop yield of under 3 tons/hectare would not be enough to make a profit from, due to the high input costs. If the cost of the fuel could be decreased, it can drastically increase their profit margins.

The company Ethanol Fuel Technologies (EFT) identified the need for small scale ethanol production on farms. The ethanol can then be used as fuel in internal combustion engines to drive the machinery on the farms and cut the cost of producing their crops dramatically.

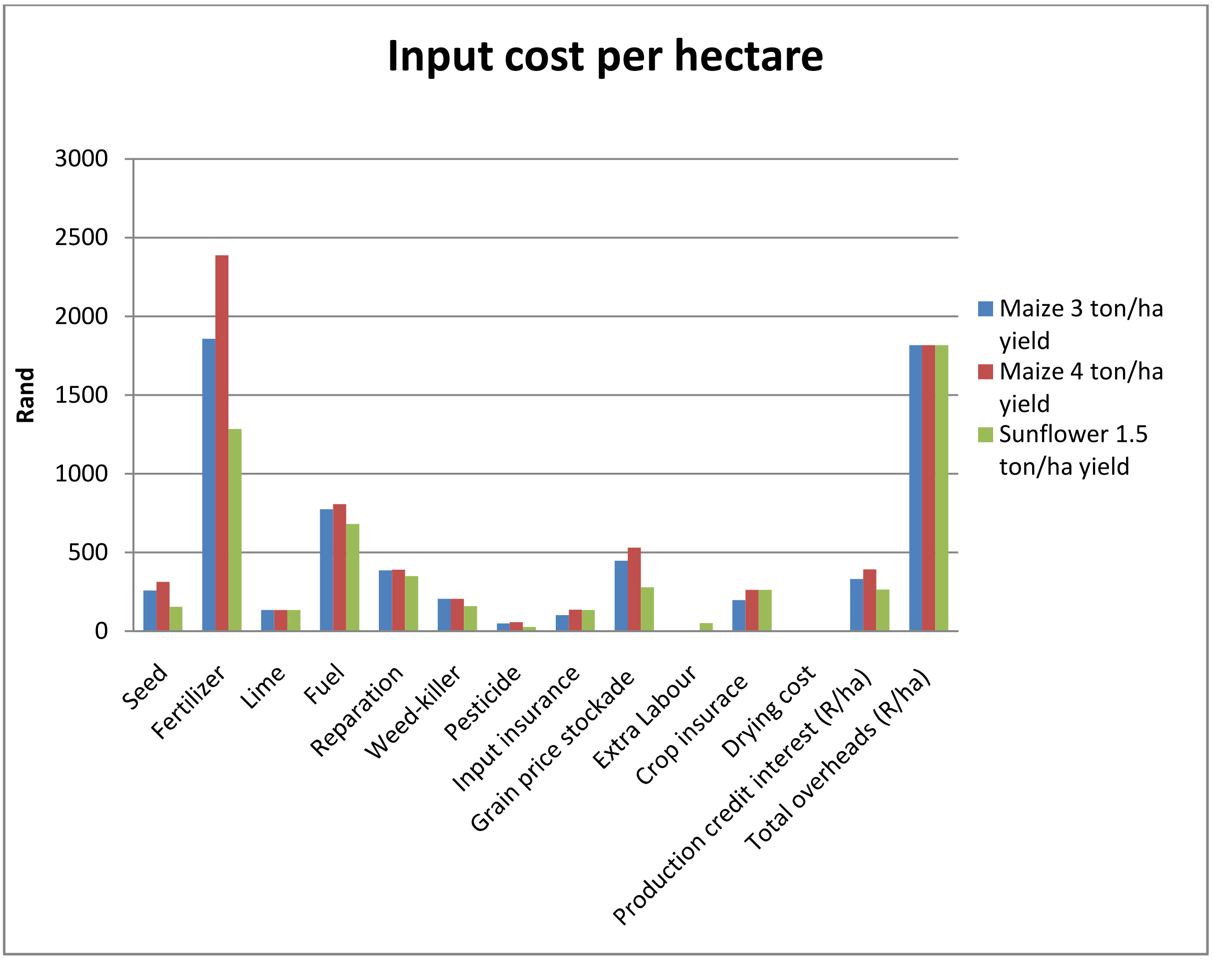

Figure 1.3 - Input cost for South African farmer for the 2008/2009 season (Created from Appendix A)

Bio-Ethanol and by-products like *dried distillers grain with solubles* (DDGS), which is an animal feed, can serve as additional products for the farmers to sell. Production of ethanol on farms in *small scale ethanol plants* can lead to increased job creation in rural parts of South Africa. Rural areas in South Africa can then be put in the position of providing a substantial contribution to the economy.

Identification of suitable crops and agricultural method also plays a big role in the production of bio-fuels from plant material. When a utilization of different varieties and suitable crops are implemented, it can lead to high ethanol production with lower expenses, without using crops that are mainly used for food.

This can also have the possibility of transformation on small farms, which could previously not be used effectively as agricultural land, because of their low crop yields. These farms can then primarily be used as *ethanol production farms*. High volumes of ethanol can be produced from small farms, if the right crops as raw material are selected and energy efficient production methods are used.

1.3 Application and market research

To justify the production of ethanol, a market demand has to exist for the product. Ethanol is widely used in the industry, in beverages and in the fuel industry. According to Figure 1.4 (Tait, 2006), it is shown that the worldwide ethanol demand for *industrial* use and *beverages* has stayed relatively constant from 1975 and will continue till 2010. Since 2000 however the demand for ethanol as *fuel* has increased dramatically. This trend seems likely to extend into the future.

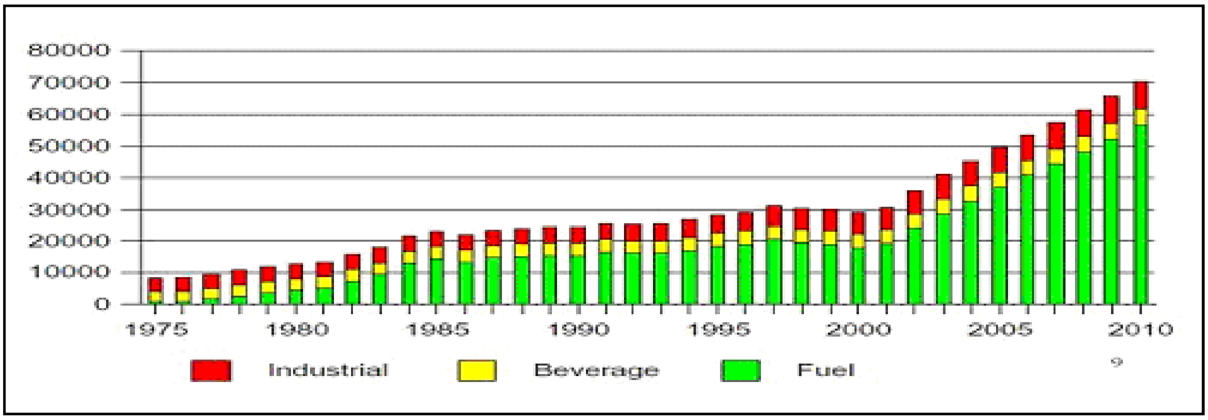

Figure 1.4 - World ethanol production (millions of litres)

Despite the remarkable growth of the ethanol market since 2000, it is still expected that worldwide ethanol demand will more than double in the next decade (Demirbas & Balat, 2006). More than 70% of the ethanol that is produced in the world is used as fuel, and due to increased demand its share is likely to increase further.

The production of bio-ethanol as fuel is driven mainly by environmental concerns over greenhouse gas emissions, high crude oil prices and our ever depleting fossil fuel deposits. The three main products from the ethanol production process are:

- Ethanol vehicle fuel
- Ethanol gel fuel
- DDGS

1.3.1 Ethanol vehicle fuel

Ethanol can be used either directly as fuel, mixture or as an additive to fuel. When used as an additive it is used to increase the octane value of the fuel. It then also serves as an oxygenate to the fuel. The increased oxygen allows the fuel to burn more completely and in turn, pollutes less.

Ethanol has the ability to reduce greenhouse gas emissions. This is mainly because it is a renewable energy source and is partly replacing gasoline in the fuel market. Ethanol is a viable and sensible way to reduce greenhouse gas emissions, reduce the consumption of fossil fuels and create a more diverse market for farmers.

Most modern cars can use ethanol blends of up to 10% ethanol without any engine adjustments. Flexible fuel vehicles (FFV) are also being produced by car manufacturers that can run on any ethanol blended gasoline. They have onboard control systems, like those produced by Magneti Marelli (2008).

In Brazil the company Magneti Marelli produces a system that makes it possible to use any blend of ethanol and petrol, pure petrol or pure hydrated ethanol. The system automatically adjusts to the mixture of fuel that is used. On-board sensors monitor the fuel mixture and the on-board computer adjusts spark timing and fuel flow to optimize performance. At present Brazil is the only country that uses ethanol as a 100% substitute for petroleum (Berg, 2004).

The advantages and disadvantages of ethanol fuel are listed in table 1.2 (Kim & Dale, 2005).

Table 1.1 - Advantages and disadvantages of ethanol fuel

Advantages	Disadvantages
External source of additive octane.	Increase Reid Vapour Pressure in gasoline.
Reduction of benzene and sulphur in gasoline.	Production of bio ethanol is embroiled in politics and relies on government support.
Reduction of greenhouse gas emissions up to 19% and CO emissions up to 30%.	Lower accumulation rate of soil organic carbon.
Increase in engine efficiency and cleaner combustions systems for car manufacturers.	Less energy per litre that implies higher fuel consumption.

1.3.2 Ethanol gel fuel

Ethanol gel fuel has great potential as it is a clean renewable and low-cost cooking fuel. This could be a product for African countries and even South African rural communities where wood, paraffin and charcoal are largely used. Environmental problems such as deforestation of vast areas and respiratory diseases due to indoor paraffin and charcoal use can be addressed. The large-scale replacement of paraffin and charcoal by ethanol gel fuel offers the opportunity to alleviate major health, social and environmental problems currently afflicting our continent. Ethanol gel fuel provides a safe, spill-proof, non-toxic, smoke free and efficient alternative energy source for the urban poor, who are the main consumers of paraffin in the country.

The production of gel fuel is a very simple technical process. Denatured ethanol is mixed with a thickening agent (methyl hydroxyl propyl cellulose) and water to form a combustible gel (Utria, 2004). Ethanol gel fuel as a renewable energy source can be produced locally by farming communities in South Africa.

1.3.3 DDGS

DDGS is the by-product of the ethanol production process. It is obtained from the slurry that is left from a fermented raw material, after the removal of ethanol in the distillation process. Most of the water is removed from the slurry and the remaining mixture is dried.

DDGS is a mid-level protein feed, with a slight deficiency in amino acids. DDGS can be mixed up to a concentration of 15% into the diets of all major livestock feeds without having any negative side effects (Noll, 2003). Farmers can supply DDGS to the feed industry of the South African market, or be used locally on their own farms.

1.4 Energy efficient ethanol production with heat pumps

Ethanol can be produced from the fermentation of bio-mass. As mentioned in paragraph 1.1, bio-mass (plants) converts solar energy and carbon dioxide in the atmosphere to organic compounds, via the process of photosynthesis. The captured energy can then be converted into usable form with the fermentation process. A variety of different raw material can be used to produce ethanol, but belong to the following main categories:

- Sugars, which contain carbohydrates in sugar form;
- Starches, which contain carbohydrates in starch form; and
- Cellulose, in which the carbohydrate molecular form is more complex.

Ethanol production is discussed in detail in Chapter 2. In short it is produced by two main processes: *wet milling* and *dry milling*. The *dry milling* process is done by the following processes:

- Raw material preparation
- Liquefaction
- Saccharification
- Fermentation
- Distillation

These processes are very energy intensive. Large amounts of heating and cooling is needed throughout the process. This will be discussed in detail in Chapter 3. Conventional systems have boilers to provide steam at high temperatures for the heating requirements. Cooling towers are used for the cooling requirements. An immense quantity of energy is discharged to the atmosphere from the condensers of the cooling towers. This makes these systems very energy inefficient.

To increase the energy efficiency of an ethanol plant, the energy needed to produce ethanol should be as low as possible. Simultaneous heating and cooling demand gives the opportunity of recycling heat energy throughout the process. This will be discussed in detail in paragraph 8.2.

According to IEA (2006), the following facts should be considered when designing any kind of heat supply system:

- Direct combustion to generate heat is never the most efficient use of fuel;
- Heat pumps are more efficient because they use renewable energy in the form of low-temperature heat;
- If the fuel used by conventional boilers were redirected to supply power for electric heat pumps, about 35-50% less fuel would be needed, resulting in 35-50% less emissions;
- Around 50% savings are made when electric heat pumps are driven by CHP (combined heat and power or cogeneration) systems;
- Whether fossil fuels, nuclear energy, or renewable energy is used to generate electricity, electric heat pumps make far better use of these resources than do resistance heaters;
- The fuel consumption, and consequently the emissions rate, of an absorption or gas-engine heat pump is about 35-50% less than that of a conventional boiler.

Heat pumps have the capability of making better use of the energy needed in the ethanol production process, thus being more efficient. This can reduce the energy consumption of the ethanol plant and in turn lead to reduced greenhouse gas emissions, because less energy is needed from a primary fossil fuel energy source.

The applications and different types of ***heat pump technology*** are discussed in detail in paragraph 4.4 and 4.5.

1.5 Purpose of study

The company Ethanol Fuel Technology (EFT) envisaged the possibility of producing ethanol on small farms in rural South Africa. The ethanol has to be produced in a small scale ethanol plant that requires only 120 kW of heating. The plant has to produce at least 350 litres of ethanol per day from a 3000kg batch process. This could give farmers the possibility of reducing the cost of farming by using the ethanol as fuel. Ethanol and its by-products can even be sold to the South African Market. The energy consumption of the ethanol plant should be low, to make the production of the renewable energy with high energy efficiency possible.

The purpose of the study is to determine if *heat pump technology* can be viably integrated into the design of a *small scale ethanol plant*. The emphasis will be on the simulation of a viable high temperature heat pump that can produce sufficient high temperature for the processes in an ethanol plant. The high working temperatures can be a severe limitation to conventional heat pump working fluids, thus an alternative has to be found.

A second objective is that a small ethanol plant must be simulated, in order to obtain the parameters to which the heat pump must adhere. The mass and energy balance of a small plant must be determined, to evaluate the heating and cooling requirements. The critical temperatures and heat transfer must be calculated and then a study can be done on a suitable heat pump technology.

In the analysis the following issues will be addressed:

- An in depth understanding of the energy requirements in an ethanol plant is required.
- A theoretical simulation of the *heat pump* must be done, to meet the heating and cooling requirements in a ethanol plant.
- An economic analysis will be done to determine the viability of using a hybrid heat pump instead of the traditional components in ethanol plants.

1.6 Structure of work

The structure of the work will explain the procedure performed during the study:

- Chapter 2, provides background of the ***ethanol production process*** will be given, to understand the fundamentals of ethanol production.
- Chapter 3, a ***material and energy balance*** on the proposed ethanol plant is done in order to obtain the heating and cooling requirement of the heat pump in the ethanol plant
- Chapter 4, ***background of heat pump technology*** is discussed, to understand the different types of heat pumps and the working fluids.
- Chapter 5, a ***literature survey on hybrid heat pumps*** is provided, to investigate its potential as a high temperature heat pump.
- Chapter 6, the *theoretical model* of the ***hybrid heat pump model*** is discussed. The model is simulated according to the basic thermodynamic requirements and information gathered from the mass and energy balance of the ethanol production process.
- Chapter 7, the ***results*** of the heat pump simulations and a ***summary*** of the findings ars discussed.
- Chapter 8, ***economic comparison*** between the heat pump system and a conventional heating system with boilers and cooling tower is done in order to evaluate the implementation of hybrid heat pumps in the small scale ethanol plant.
- Chapter 9, ***conclusion*** of the study is formulated and ***recommendations*** for further research will be identified.

Chapter 2 - Ethanol production process

2.1 Introduction

Bio-ethanol is an alternative fuel produced by the fermentation of bio-mass. The key step in the growth of bio-mass is the capture of solar energy as fixed carbon via photosynthesis, during which carbon dioxide is converted to organic compounds. Ethanol can be produced from three main types of raw material:

- Sugar bearing materials, which contain carbohydrates in sugar form;
- Starches, which contain carbohydrates in starch form; and
- Cellulose, in which the carbohydrate molecular form is more complex.

In this chapter a literature survey was conducted on the process that the company EFT propose to use in their small ethanol plant. The different steps for the production of ethanol discussed are the raw feed preparation, liquefaction, saccharification, fermentation and then the proposed separation system that will deliver the two products: ethanol and DDGS.

2.2 Process choice

EFT wants the plant to utilize different raw materials from which to produce ethanol. Ethanol production from starches like maize is more energy intensive than production from sugar crops. Maize is widely used in ethanol plants in the USA and because it is one of the crops that will be used in the plant, it is best to describe the process for production of ethanol from maize.

Maize-to-ethanol can be accomplished by two processes: wet milling or dry milling. Dry milling process was chosen for the design, because it is less complex than *wet milling* and ideal for using in smaller plants. Buchhiet (2002) stated that the *dry milling* process is the most widely accepted ethanol conversion process, due to lower capital costs associated with building and operating these plants. *Dry milling* produces ethanol as well as carbon dioxide and a mid level protein feed commonly known as dried distillers grain with solubles (DDGS), as by-products.

The decision was also based on the following information from literature:

- The dry milling process is the most commonly used method for the production of fuel ethanol and accounted for 79% of the production capacity in the USA for 2005 (RFA, 2006).
- Wet milling facilities have immense production capacities, but the operating and capital costs are higher due to more complex and expensive equipment than dry milling facilities; (Butzen & Hobbs, 2002).
- Wet milling yields numerous by-products that require a target market; however DDGS produced by the dry-grinding process is preferred by meat producers when used as feed.
- Another advantage of a smaller dry milling facility is that it does not necessarily require a water refinery, resulting in capital costs reduction (Shapouri et al., 1998).
- The dry milling process yields 420 litres ethanol per ton maize (Kwiatkowski et al., 2005) compared to 375 litres per ton for wet milling (Butzen & Hobbs, 2002).
- Dry milling is a more versatile process and can make use of a wide variety of feedstock's like maize, wheat and sorghum (Kwaitkowski et al., 2005). The dry milling process would thus require the least amount of modifications if other raw materials are to be used as feedstock.

From this data it is evident that the dry milling process is the best process choice.

2.3 Dry milling process

The production of ethanol through fermentation is probably one of the oldest chemical processes known to man. The ancient Egyptians and the Mesopotamians brewed beer from as early as 3 000 BC (Buchhiet, 2002).

As mentioned in paragraph 2.2 the dry milling process will be implemented for the production of bio-ethanol from maize. More detail regarding the raw material feed and catalysts utilized during the process as well as the products and by-products formed by the process is given in this paragraph.

A simplified process flow diagram for the production of ethanol can be seen in Figure 2.1 (Fong, 1982).

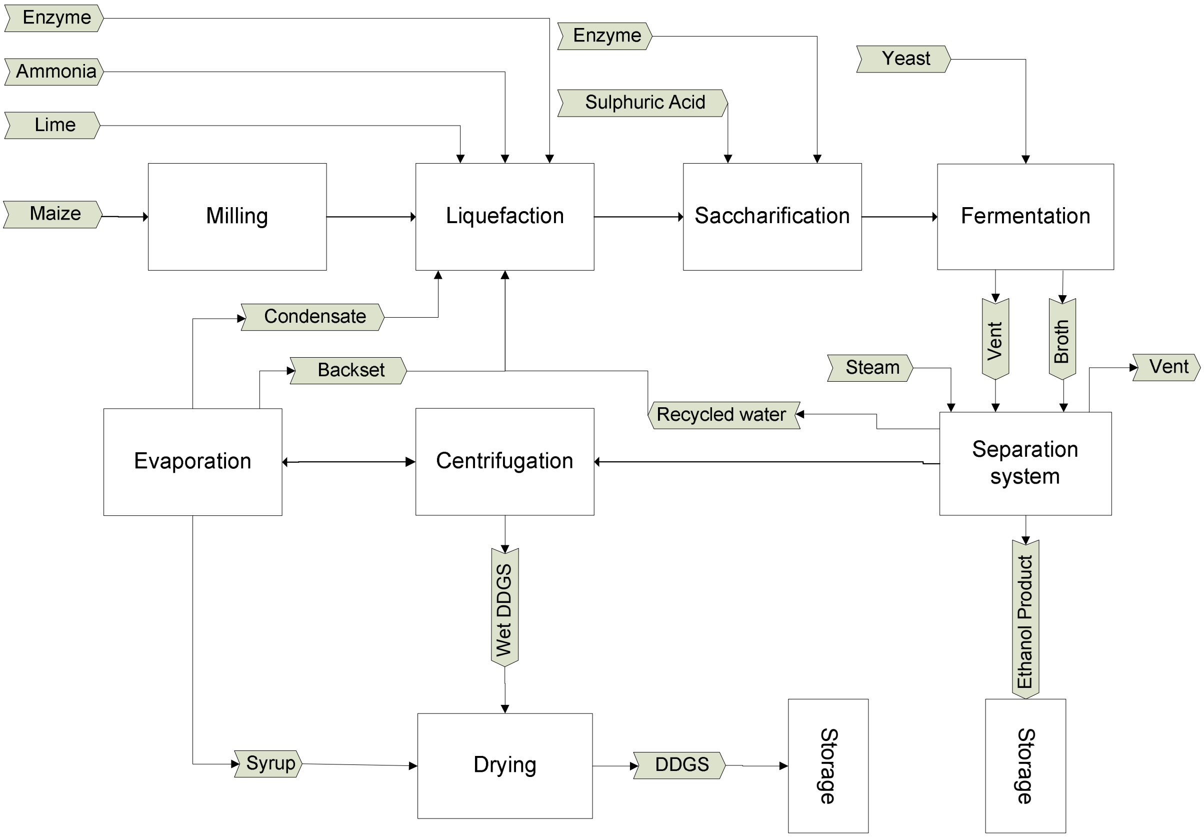

Figure 2.1 - Process flow diagram to convert maize to bio-ethanol. (Recreated from Fong 1982)

The dry milling process in figure 2.1 can be described by the following:

- Grain is delivered by truck or rail, weighed, checked for quality, unloaded into receiving hoppers, pre-cleaned and transferred by conveyor system to storage.
- The dry milling of maize involves the cleaning and breaking of the maize kernel into fine particles using a hammer mill, creating a coarse flour-like consistency.
- This is followed by ***liquefaction*** to dissolve and gelatinise the starch.
- The next process step is to convert the starch into fermentable sugars by making use of enzymes in the ***saccharification***. ***Liquefaction*** and ***saccharification*** can be skipped with sugar crops like sweet sorghum.
- Hereafter ***fermentation*** of the bio-mass takes place, producing ethanol.
- In the separation system ***distillation*** takes place, which removes the ethanol.
- The remaining mash residue is processed to produce the animal feed, DDGS. This is done first by removing 90% of the water and then drying the rest of the residue.

Each of these process steps are discussed in this paragraph. The relevant reaction information and reaction condition regarding each step is discussed.

2.3.1 Raw material preparation

In the preparation process the maize from the storage silos are cleaned, tempered and degermed. Valuable maize oil is extracted from the germ and the cellulose is stored to be mixed with the DDGS later in the process. The physical breakdown of the endosperm containing the sugar, starch and protein is achieved using mechanical mills. The ground feedstock is moved via conveyor for mash preparation.

With sugar crops, the juice is extracted with rollers or a mechanical press and is taken directly to the fermentation tanks. When using a suitable sugar crop it is possible to decrease the cost of the ethanol production process considerably because the energy intensive liquefaction and saccharification steps are skipped.

2.3.2 Liquefaction

This step breaks the individual starch molecules out of the tight feedstock matrix. These starch molecules are partially hydrolyzed or slightly reduced in size to dextrins with the help of the catalyst alpha-amylase.

The feedstock from the feeding and preparation is mixed in an agitated mixing vessel, *the cook tank*, together with recycled water, alpha-amylase, ammonia and lime. Alpha-amylase is a glycoprotein with optimum conditions for enzymatic activity at a pH of 5.8 and a temperature of 95℃. The ammonia provides nitrogen which is an essential nutrient for the yeast during fermentation and the lime provides the necessary calcium for the alpha-amylase catalyst (Bohlmann, 2002).

The slurry is then heated to liquefy the starch. It is soaked at 60℃ for approximately 15 minutes and is then pre-heated to 95℃. The starch is liquefied to dextrose at atmospheric pressure and 95℃ after one hour in the agitated *cook tank*. This reaction can be represented as follows:

$$C_6H_{10}O_5 \xrightarrow{\alpha-\text{Amylase}} C_x(H_2O)_x \quad \text{(Dextrins)} \qquad (2.1)$$

The slurry is combined with the backset, a recycle stream taken from DDGS recovery, which provides critical nutrients for the yeast later in fermentation. These combined streams are cooked and held for 15 min at 105℃ in the *cook tank* to ensure the destruction of contaminated bacteria, which may produce unwanted by-products during fermentation (Kwiatkowski et al., 2006, Meyer & Strauss, 2005).

2.3.3 Saccharification

This step breaks the starch into fermentable sugars, with the help of the catalyst gluco-amylase. The mash from the *cook tank* is cooled to 60℃ and the secondary enzyme, gluco-amylase is added to facilitate the conversion of starch to glucose. Sulphuric acid is also added to the reactor to reduce the pH to 4.5.

Gluco-amylase is a liquid enzyme that is easily soluble in water. The optimum operating temperature is between 58-60℃ with an optimum pH of 4 to 5 (Van der Veen et al., 2006). The activity of gluco-amylase decreases with increasing glucose concentration (Kwiatkowski et al., 2006). The starch is converted to fermentable sugars during saccharification, according to the following reaction:

$$C_x(H_2O)_x \xrightarrow{\text{Gluco}-\text{Amylase}} C_6H_{12}O_6 \quad \text{(Glucose)} \tag{2.2}$$

The agitated saccharification vessel has a residence time of 5 hours and optimum operating conditions of 60℃ at atmospheric pressure. The optimum operating conditions ensure maximum product yield, which can be defined as:

$$Yield=\frac{Glu\cos eFormed}{StarchConsumed} \tag{2.3}$$

Theoretically 1.1 kg glucose is formed from 1 kg starch, but commonly only 97% of the theoretical yield is achieved during saccharification. The remaining 3% unconverted starch is assumed to pass unchanged through the process and forms part of the DDGS.

2.3.4 Fermentation:

Following the *saccharification* reaction the slurry is cooled to the fermentation temperature of 33℃. Fermentation takes place when the yeast, Saccharomyces cerevisae is added. As the highly exothermic reaction commences, the yeast will consume the fermentable sugars and yield mainly ethanol, carbon dioxide gas and heat by anaerobic fermentation. Temperature and pH control is critical during the fermentation process, to ensure optimal yeast activity.

The fermentation reaction is:

$$C_6H_{12}O_6 \xrightarrow{\text{Yeast}} 2C_2H_5OH + 2CO_2 + \text{heat} \qquad (2.4)$$

Theoretically 0.51 kg ethanol is formed from 1 kg glucose, but commonly only 95% of the theoretical yield is achieved due to various side reactions. The effective ethanol concentration in the fermentation is 10-15 wt%. The heat produced during fermentation is 100 kJ/mol or 556 kJ/kg glucose. (Albers, et al. 2002)

Great care should be taken to ensure that the *fermentation tanks* temperature does not exceed 37℃, and for this reason the reactors are directly cooled using cooling water (paragraph 3.7). The yeast has a high tolerance for low oxygen levels, but is very temperature susceptive and could die at a temperature above 37℃. The yeast is also very receptive to high ethanol concentrations; catalyst poisoning may take place if the ethanol concentration in the fermentation broth rises to more than 14% by volume (Piskur and Langkjaer, 2004).

In addition to fermenting sugars to ethanol, 5% of the sugar is converted to unwanted by-products, such as lactic acid and acetaldehyde, due to the presence of contaminating organism Lactobacillus bacteria (Bohlmann, 2002).

The cycle time of each side agitated *fermentation tank* can be estimated as the following (Fong, 1984):

Table 2.1- Cycle time for Fermentation Tank

Ethanol production	
Process	Hours
Fermentation	36
Charging	4
Discharging	4
Cleaning	6
Total cycle time	50

The gaseous and gas-liquid mixture fermented effluent streams are transferred to the separation system for ethanol and DDGS recovery.

2.4 Separation system

The desired objectives for the ethanol production process are first to obtain a high purity product and second to recover a high percentage of ethanol. After fermentation, the ethanol content of the mash ranges from 12–15% on a volume basis and is then transferred into a distillation unit where the alcohol is separated from the solids and water (Buchheit, 2002). The analysis of the separation system can be broken down into three separate parts, which will be discussed in this section:

- Vapour recovery system;
- Ethanol recovery system; and
- DDGS recovery

In Figure 2.2 a diagram of the separation system is shown. For this study the fermented main effluent leaving the Fermentation tank is a two-phase mixture containing approximately 13 wt% ethanol, minute quantities of lactic acid and acetaldehyde as well as a small amount of carbon dioxide gas. The lactic acid and acetaldehyde formed during fermentation is miscible in water, and leave the *fermentation tanks* in an aqueous form after it is dissolved into the liquid effluent. This two-phase fermented effluent passes through a phase splitter, a degasser, and the liquid is sent to the liquid recovery system whilst the vapour is sent to the vapour recovery system.

The secondary gaseous fermented effluent stream contains mainly carbon dioxide and small quantities of ethanol, which must be recovered by a vapour recovery system.

The vapour recovery system will be briefly discussed, because it will not be included into the mass and energy balance of the small scale ethanol plant. It is assumed that some of the ethanol vapour will be recovered in the vapour recovery system.

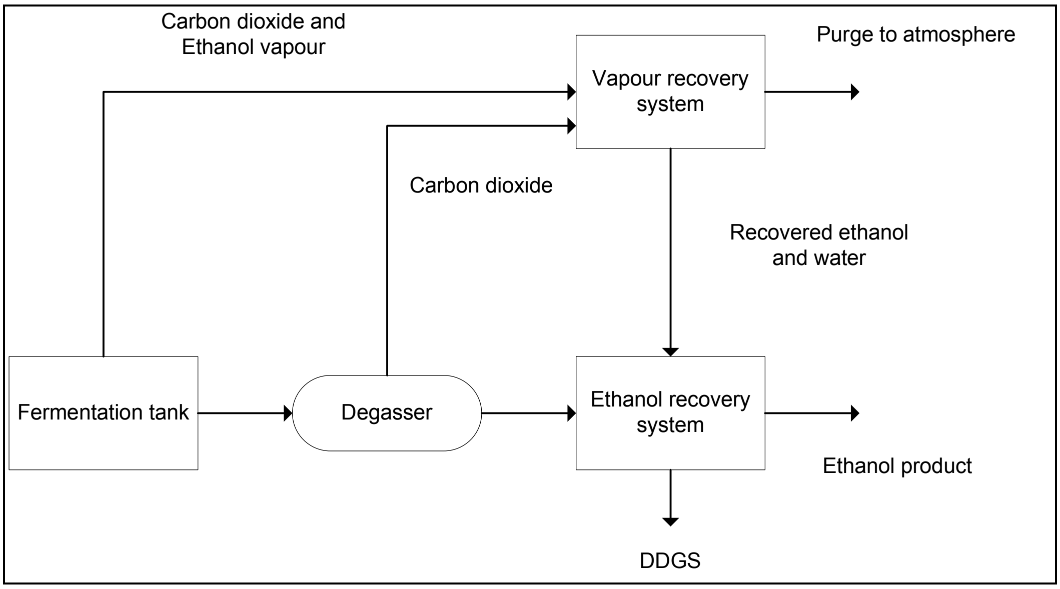

Figure 2.2 - Separation system

2.4.1 Vapour recovery system

The two-phase fermented effluent passes through a degasser where a phase split is achieved and the light ends, which means the CO_2, is flashed off. The degasser works on the principle of passing the fluid over a large surface area whilst blowing air against the flow. The resultant mass transfer of gas at the fluid interface removes the carbon dioxide gas.

The gaseous effluent stream from the *fermentation* process, degasser and vapour from the DDGS dryer, contains small quantities of ethanol, which must be recovered by a vapour recovery system. This is done with an absorption system (packed gas absorber), in which the reactor gases are quenched with a large spray of water. The product, ethanol, is infinitely miscible in water, which is used as the solvent liquid stream due to its relative cheap costs.

The outlet gas stream of carbon dioxide, lactic acid and acetaldehyde, can be cleansed before it is purged to the atmosphere. The liquid bottom, which contains the recovered ethanol and a volume of water, is transferred to the liquid separation section.

2.4.2 Ethanol recovery system

The stream that enters the liquid recovery system contains around 14 wt% ethanol, 80 wt% water and 6 wt% solids. Therefore, a liquid recovery system must be designed to firstly remove all the solids particles from the product stream and then secondly to purify the ethanol product stream. It is combined with the recovered ethanol from the vapour recovery system. This combined stream is fed to the *beer boiler*. The beer boiler is the bottom part of the *distillation column* which is the tank that receives the effluent and is directly heated with a heat transfer fluid.

The *beer boiler* is then heated to the boiling point of the mixture. The beer boiler is operated at 101.5℃ and 1.1 bar. The beer boiler is positively agitated, to prevent solids from burning to the heat exchanger surface. If the temperature at the bottom of the column reaches more than a few degrees above the boiling point of water, the shut-off controls will be activated, to ensure the desired product purity. This happens if either the column pressure gets too high or the Beer Boiler runs nearly dry. A illustration of the beer boiler in the Distillation column is displayed in figure 2.3.

Louvers are placed at the top of the *beer boiler* to ensure that no solids pass through the top with the vapour. The vapour ethanol-water mixture enters the *distillation column*. The difference in the boiling temperature of ethanol and water makes it possible to separate these two components by distillation. The temperature of the valve tray distillation column varies from 100℃ to 78.5℃. The desired ethanol purity leaves the top of the column, whilst the residual mash at the bottom is removed and processed (Meyer and Strauss, 2005).

The highest concentration of ethanol that can be obtained by distillation is 95.57% by weight, due to the azeotrope in the liquid equilibria of ethanol-water mixtures (Fong, 1982). Ethanol purity over 90wt% is desired for the use as direct hydrated ethanol fuel or for the other applications like ethanol gel fuel. An overall ethanol recovery of approximately 98% is achieved. The distillate stream is cooled to 25℃ and transferred to a storage vessel. The bottom slurry is also cooled to 25℃ and transferred for DDGS recovery.

The operating pressures of the separation units were chosen in such a way to facilitate the transportation of the gaseous stream. The *beer boiler* is operated at 1.1 bar, through which the stream then flows freely towards the atmospheric distillation column. The following figure gives a schematic representation of the liquid recovery system.

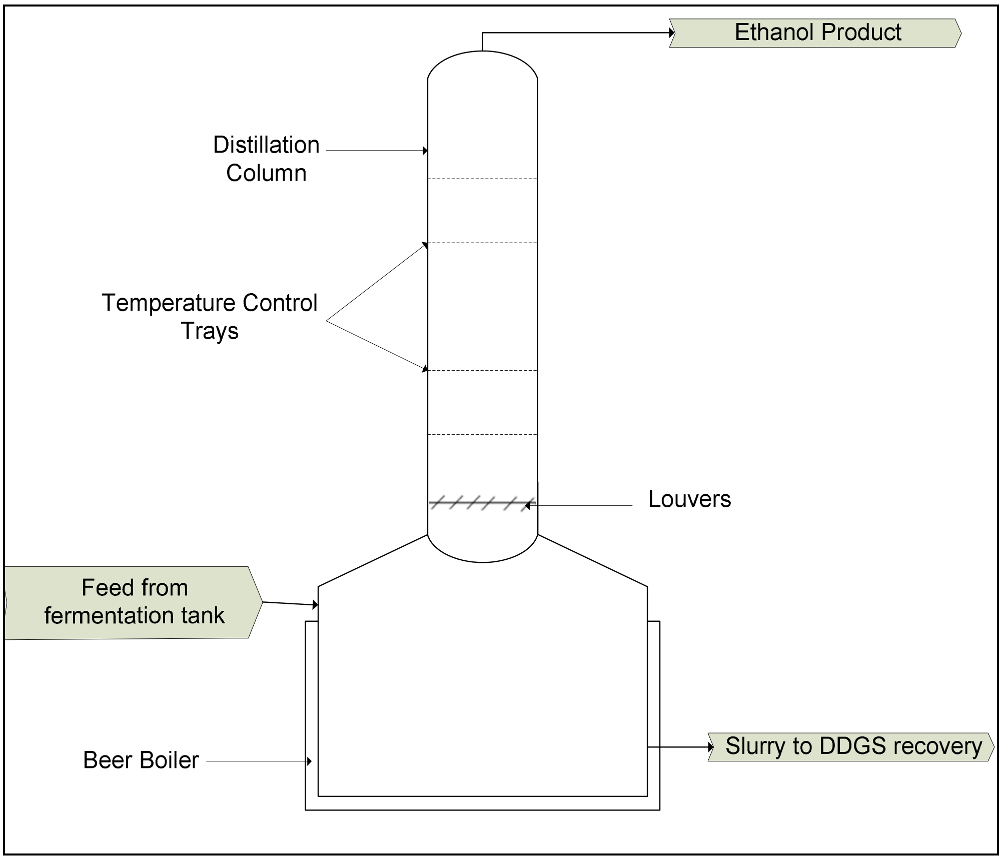

Figure 2.3 - Distillation column with beer boiler

2.4.3 DDGS recovery

The resulting almost alcohol-free mash is dewatered in a centrifuge and sent to the dryer as distiller's grains. Next, the liquid from the centrifuge is concentrated in evaporators, and the resulting syrup is blended with the dried distiller's grains creating DDGS (Buchheit, 2002).

The bottom slurry of the beer boiler is split into two streams. A stream is sent to an intermediate storage tank and will be recycled to the process as a backset. Stream passes through an evaporator removing 96% of the water from the slurry. The effluent vapour of the evaporator is condensed and transferred to waste water treatment, to be recycled to the process. The concentrated slurry from the evaporator is mixed with the cellulose and fat residue from the raw material preparation. The mixer is a horizontal continuous flow unit, designed to homogenously combine the two streams. The single-shaft enclosed plowshare mixer will be constructed of abrasion resistant steel. The plows will be lined with wear resistant material to prevent erosion and are capable of being replaced without replacing the entire shaft (Berk, 2005).

The wet DDGS has an approximated shelf life of only one week and if not sold to feed lots in that week the product will decay and become worthless. It is thus recommended to install driers and evaporators to dry the DDGS and indefinitely prolong its shelf life.

The stream from mixer is dried to a moisture content of 10% resulting in the product, DDGS. The outlet gas stream from the DDGS dryer is passed through the vapour recovery system before it is purged to the atmosphere.

2.5 Summary

The production of ethanol is a simple process and can easily be implemented into a small scale ethanol plant. In this chapter the literature on the production process of ethanol was done. The dry milling process is considered because of its relative simplicity. The process was discussed from the inputs to the outputs and the knowledge gained from this survey can now be implemented in doing further work on the subject.

The processes during liquefaction, saccharification, fermentation, distillation and drying will be discussed in the material and energy balance. This is because they are the main processes in the ethanol production process. The material and energy balance over the vapour recovery system, the evaporator and mixer will not be included, due to the fact that these components are not vital to the ethanol production process and will increase the cost of the small ethanol plant.

From the literature and the proposed ethanol plant requirements it is now possible to do a material and energy balance for the whole system. This will be done in chapter 3.

Chapter 3 - Material and energy balance

3.1 Introduction

The material and energy balances of the ethanol plant will provide the basis of the process design. A material balance taken over the complete process will determine the quantities of raw materials required and the amount of products produced. This will help determine the compositions during each of the processes described in Chapter 2. The material balance will make it possible to do a complete energy balance of the overall system as well as in the individual processes.

In this section the relevant material and energy balances were carried out for the major equipment during the most energy intensive processes. This will help determine how the heat pump can be implemented and integrated in the ethanol plant to make it more energy efficient than a conventional plant. The modelling of the ethanol plant was done in Excel.

3.2 Method

To calculate the material balance of the ethanol plant the following method was used. One of the system constraints set by the company EFT was that the batch size of the *cook tank* was limited to a maximum size of 3000 kg each. This is to reduce the cost of the ethanol plant. This also helped to simplify the calculations.

The plant proposed by Ethanol Fuel Technologies must be able to work with various kinds of raw material. As mentioned previously, starches like maize are a lot more energy intensive to produce ethanol from, than sugars crops. That is why a raw material similar to maize was chosen to be the raw material in the plant. If the ethanol plant uses a sugar crop, the *liquefaction* and *saccharification* steps are skipped, and decreases the overall energy requirement immensely.

Maize is an organic substance that consists of diverse biochemical components. The primary dry basis composition of South African yellow maize, as analyzed by S.A. Grain for the 2005/2006 harvesting season, is presented in Table 3.1. The moisture content varies between 10 -15% by weight.

Table 3.1 - Dry basis composition of yellow maize

Component	Weight %
Starch	81.3
Protein	8.9
Fibre	1.1
Fat	5.6
Ash	1.1
Sugar	2

The material balance of the plant was simulated as a batch process of 3000 kg throughout the system. A maximum ethanol yield of 12.5 wt% was selected for a batch, which is within the limits discussed in the paragraph 2.3.4. Then the process was calculated in reverse, and the inputs were adjusted accordingly.

After the material balance of the system is calculated it is possible to do the energy balance. To calculate the energy requirements for the processes, the change in energy from one temperature or state to the other was calculated. Due to the various solids and biochemical components the following equations were used to determine the change in enthalpy for each of the components.

The changes in enthalpy for organic compounds were calculated with the following equation obtained from the Aspen database using the NRTL base method.

$$\Delta H = \int A + BT + CT^2 + DT^3 + ET^4 dt \tag{3.1}$$

Where, T is the average temperature, in Kelvin, of the stream and ΔH is the change in enthalpy or energy of the compound given in cal/mol.K. The coefficients of the various organic compounds are given in Table 3.2.

Table 3.2 - Variables for organic compounds

Organic Compounds	Sugar	Protein	Starch	Lactic acid	Acetaldehyde
Molar mass [g/mol]	**342.30**	**132.12**	**180.16**	**90.08**	**90.08**
A	-8.51E+00	-3.02E+01	-3.26E+00	2.88E+01	7.72E+00
B	5.55E-01	2.37E-01	2.72E-01	8.42E-02	1.82E-01
C	-1.62E-03	0.00E+00	-7.16E-04	0.00E+00	-1.01E-04
D	4.46E-06	0.00E+00	2.03E-06	0.00E+00	2.38E-08
E	-3.79E-09	0.00E+00	-1.99E-09	0.00E+00	0.00E+00

The changes in enthalpy for inorganic compounds and chemicals were calculated with the following equation obtained from Felder and Rousseau (2000).

$$\Delta H = \int a + bT + cT^2 + dT^3 dt \qquad (3.2)$$

Where, *T* is the average temperature, in degrees Celsius, of the stream and and *ΔH* is the change in enthalpy or energy of the compound given in kJ/mol.C. The coefficient of the various inorganic compounds and chemicals are given in Table 3.3.

Table 3.3 - Variables for inorganic compounds

Inorganic compounds	Water (l)	Water (g)	Ethanol (l)	Ethanol (g)
Molar mass	**18.015**	**18.015**	**46.069**	**46.069**
a	7.54E-02	3.35E-02	1.03E-01	1.59E-01
b	0.00E+00	6.88E-06	0.00E+00	0.00E+00
c	0.00E+00	7.60E-09	0.00E+00	0.00E+00
d	0.00E+00	-3.59E-12	0.00E+00	0.00E+00
Inorganic compounds	**Ammonia**	**Lime**	**Sulphuric acid**	**Carbon dioxide**
Molar mass	**17.031**	**56.08**	**98.09**	**44.01**
a	3.52E-02	4.18E-02	1.39E-01	3.61E-02
b	2.95E-05	2.03E-05	1.56E-04	4.23E-05
c	4.42E-09	-4.52E-02	0.00E+00	-2.89E-08
d	-6.69E-12	0.00E+00	0.00E+00	7.46E-12

To obtain the desired temperature of each vessel, hot or cold heat transfer fluid will be passed through it. The optimal operating temperature is maintained by controlling the heat transfer fluid flow rate.

The temperature and amount of heat required from the stream of heat transfer fluid is calculated from the material and energy balance over each vessel. The heating will be indicated with a positive number.

The cooling of the vessels will be done in the same manner, but by passing cool heat transfer fluid through the vessels. The cooling demand will be indicated with a negative number.

3.3 The overall system

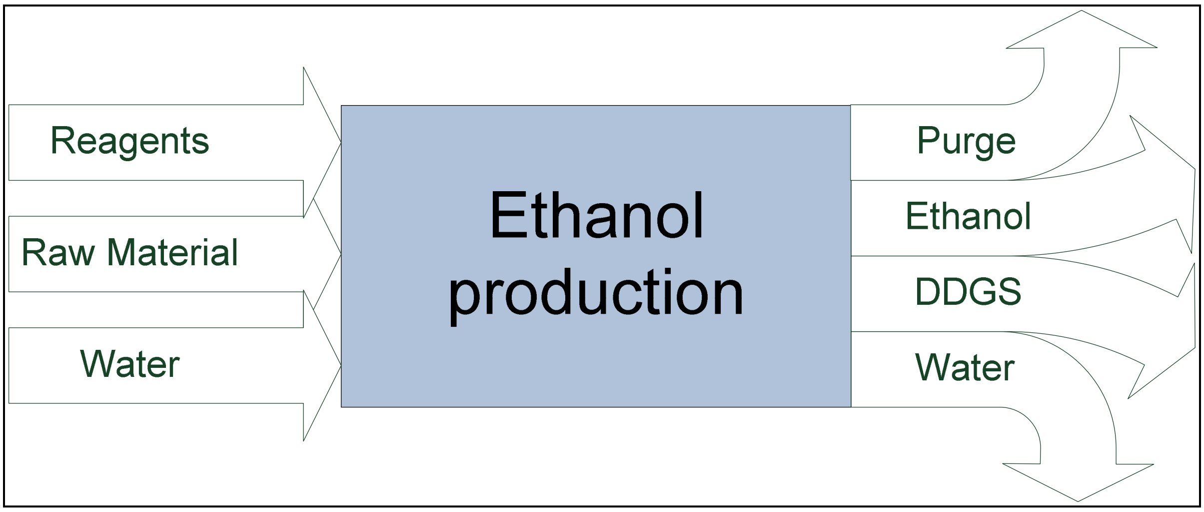

Figure 3.1 - Schematic of the overall system material balance

A schematic of the overall material balance for the inputs and outputs of the system is given in Figure 3.1. The reagents are all the chemicals and catalysts that are needed during the process. They include the ammonia, lime, sulphuric acid, alpha-amylase and gluco amylase. The raw material is the type of material that is used in the process to produce ethanol from. In this analysis it is maize. Water is also added to the process.

The products of the process are ethanol and DDGS. CO_2 and water vapour are purged to the atmosphere. Most of the water is also recycled during the process.

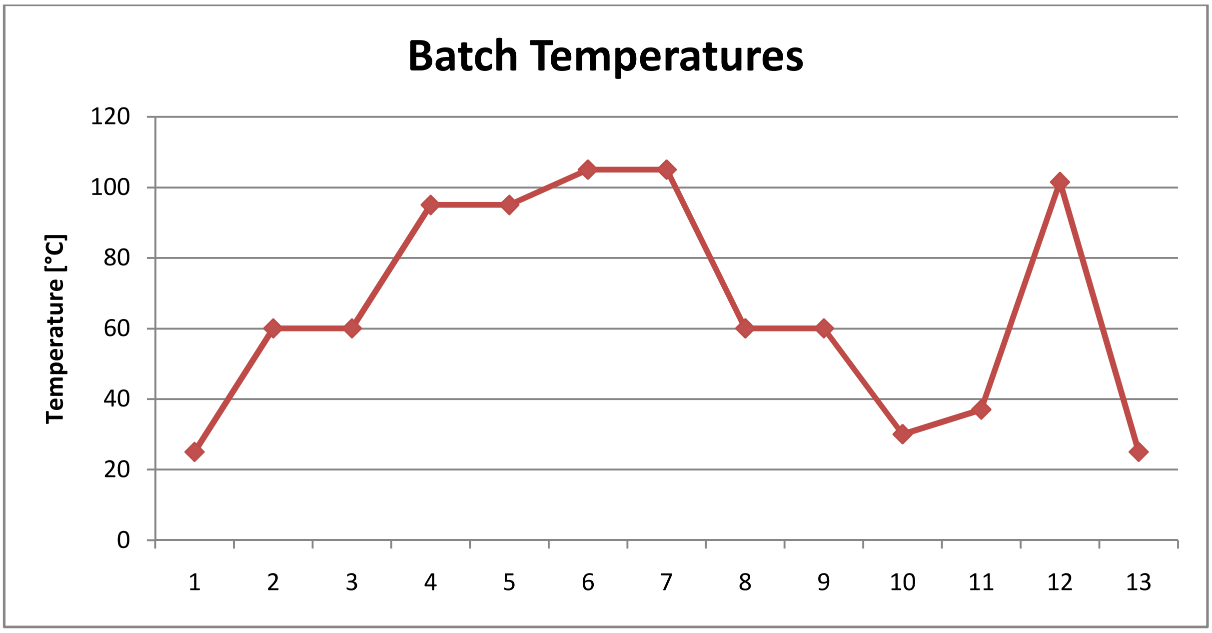

Figure 3.2 - Batch temperature profile of the Ethanol production process

A temperature profile can be created from the processes in the ethanol plant described in paragraph 2.3 and 2.4. The different temperatures of the batches throughout the ethanol production process are illustrated in figure 3.2. The processes from point 1 to 10 are completed in the cook tank. The heating and cooling processes in the cook tank can be summarized by the following steps:

- Step 1 – Mixing and soaking of the input compounds
- Step 2 – Liquefaction
- Step 3 – Cooking
- Step 4 - Saccharification
- Step 5 – Cooling for fermentation

Fermentation of the effluent takes place from point 10 to 11. The effluent then enters the distillation column where the ethanol mixture is heated to boil the ethanol , from point 11 to 12. The vapour effluent and remaining slurry is then cooled in the final step, from point 12 to 13, and sent either to ethanol storage or DDGS recovery and drying.

All the tanks are positively agitated during the reactions in them. The mass of the catalysts are very low (0.01% of the mixture) and are added to the water to simplify the material and energy balance.

3.4 Mixing

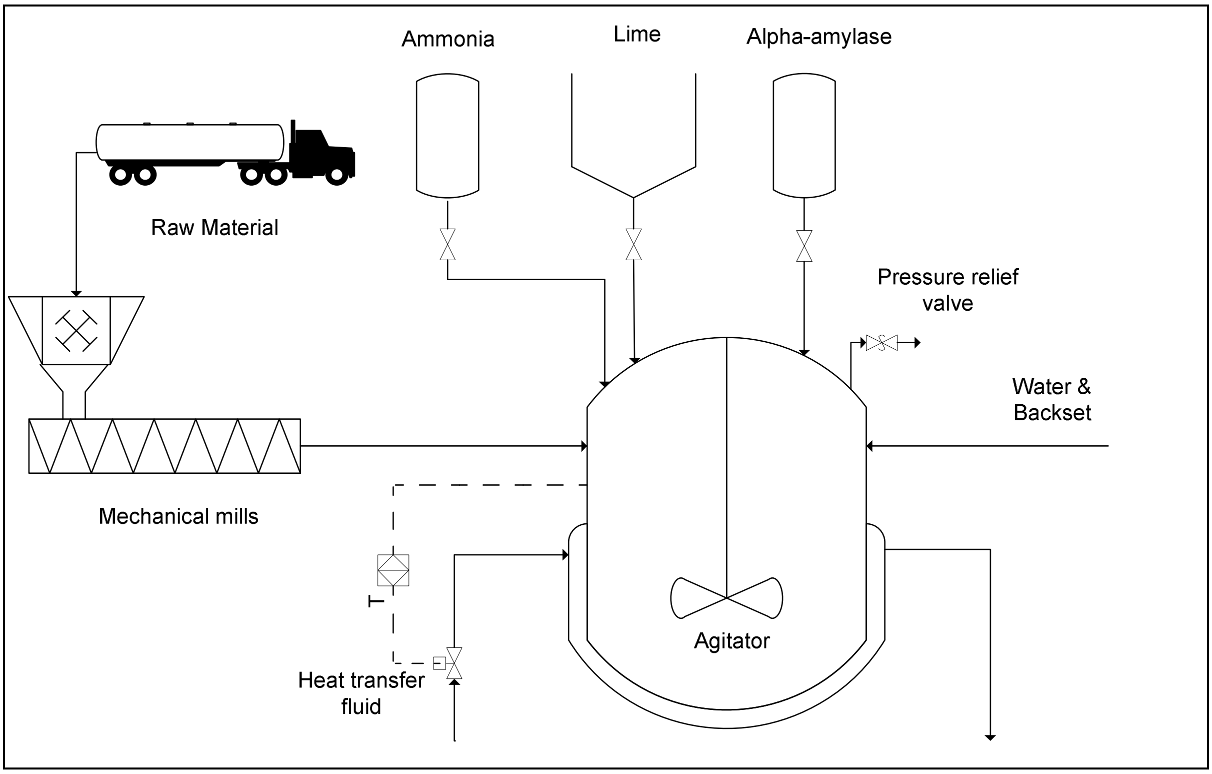

Figure 3.3 - Schematic diagram of the cook tank during mixing

The mixing is the first step in the cook tank. After the preparation of the raw material, it is broken down by mechanical mills. The ground raw material is mixed with recycled water, lime, ammonia and alpha-amylase. The water added can be new, recycled or mixed with the backset to provide essential nutrients to the yeast in the fermentation process. A schematic of the processes in the cook tank is illustrated in figure 3.3. The temperature of the inlet streams are approximately 25℃ and the vessel is operated at 60℃. Therefore, heat must be added to the vessel to achieve the desired operating temperature. The mixture is soaked for 15 minutes at 60℃. The material and energy balance are shown in Table 3.4.

Table 3.4 - Material and energy balance over the cook tank during mixing

Step 1	Start			End			ΔH	Q
Component	(kg)	wt%	[°C]	(kg)	wt%	[°C]	[kJ/kg]	[kJ]
Ammonia	1.5	0.05%	25	1.5	0.05%	60	74.8	112.2
Lime	1.2	0.04%	25	1.2	0.04%	60	30.1	36.1
Water	2112.9	70.48%	25	2112.9	70.48%	60	146.5	309523.2
Starch	714.4	23.83%	25	714.4	23.83%	60	45.1	32193.1
Sugar	18.0	0.60%	25	18.0	0.60%	60	46.3	834.2
Protein	150.0	5.00%	25	150.0	5.00%	60	49.6	7438.8
TOTAL	**2998.1**	**100.00%**	**25**	**2998.1**	**100.00%**	**60**		**350137.7**

3.5 Liquefaction and cooking

Step 2 is that after soaking the mixture, the cook tank is heated to 95℃. The starch is liquefied to dextrose, at atmospheric pressure and 95℃, after one hour in the cook tank.

The material and energy balance of the liquefaction is shown in table 3.5. Note that the starch is not transformed to sugar yet. The energy requirement for heating the contents of the tank to 95℃ is also shown.

Table 3.5 - Material balance over the cook tank during liquefaction

Step 2	Start			End			ΔH	Q
Component	(kg)	wt%	[°C]	(kg)	wt%	[°C]	[kJ/kg]	[kJ]
Ammonia	1.5	0.05%	60	1.5	0.05%	95	77.0	115.5
Lime	1.2	0.04%	60	1.2	0.04%	95	30.6	36.7
Water (l)	2112.9	70.48%	60	2112.9	70.48%	95	146.5	309523.2
Water (v)	0.0	0.00%	60	0.0	0.00%	95	0.0	0.0
Starch	714.4	23.83%	60	714.4	23.83%	95	50.1	35767.8
Sugar	18.0	0.60%	60	18.0	0.60%	95	52.4	942.4
Protein	150.0	5.00%	60	150.0	5.00%	95	58.8	8820.1
TOTAL	2998.1	100.00%	60	2998.1	100.00%	95		355205.70

After liquefaction, at 95℃, the effluent is cooked at 105℃ for 15 min to destroy bacterial contaminants, in step 3. It was assumed that about 10% of the water evaporates in the tanks during cooking, but is condensed when it is cooled.

The cook tank will be equipped with pressure relief and pop-off valves for safety reasons. This can be seen in the schematic diagram of the proposed cook retention tank control structure shown in Figure 3.3.

Table 3.6 - Material and energy balance over the cook tank during cooking.

Step 3	Start			End			ΔH	Q
Component	(kg)	wt%	[°C]	(kg)	wt%	[°C]	[kJ/kg]	[kJ]
Ammonia	1.5	0.05%	95	1.5	0.05%	105	22.4	33.6
Lime	1.2	0.04%	95	1.2	0.04%	105	8.8	10.6
Water (l)	2112.9	70.48%	95	1901.6	63.43%	105	41.9	79591.7
Water (v)	0.0	0.00%	95	211.3	7.05%	105	2287.4	483323.0
Starch	714.4	23.83%	95	714.4	23.83%	105	15.2	10868.0
Sugar	18.0	0.60%	95	18.0	0.60%	105	16.1	289.9
Protein	150.0	5.00%	95	150.0	5.00%	105	18.5	2773.7
TOTAL	2998.1	100.00%	95	2998.1	100.00%	105		576890.5

3.6 Cooling and saccharification

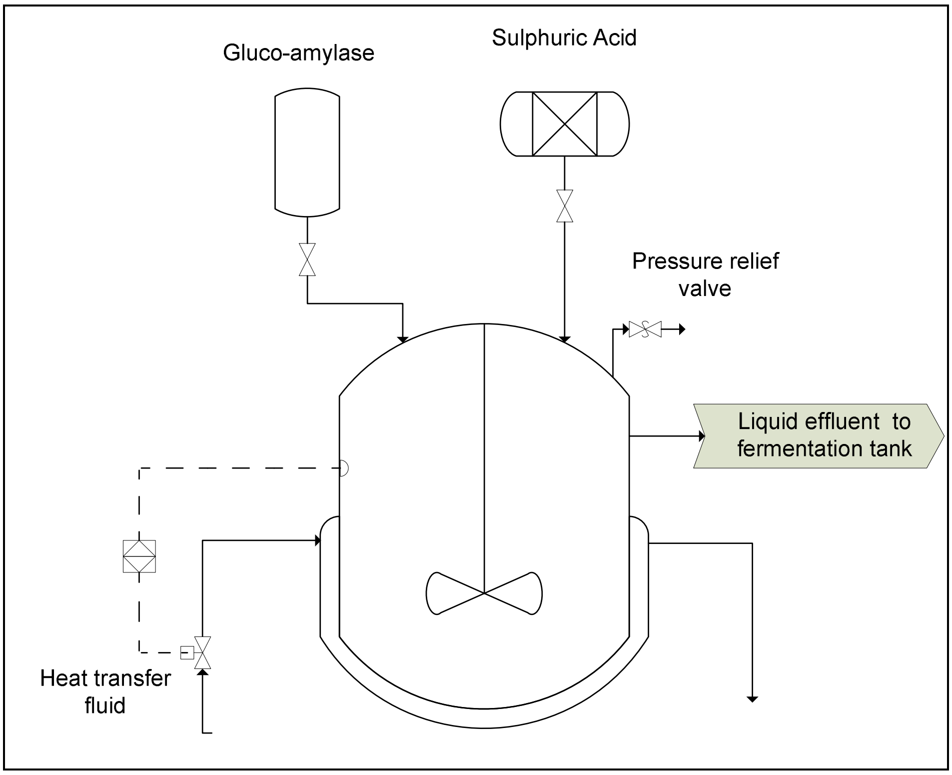

Figure 3.4 - Schematic diagram of cook tank during saccharification

The contents of the cook tank is cooked, it is cooled to 60℃ before saccharification starts, in step 4. Sulphuric acid is added to the reactor to reduce the pH to 4.5 and the gluco-amylase catalyst is added to facilitate the conversion of starch to glucose. The residence time in the saccharification reactors is 5 hours. Optimum pH control is very important for maximum starch conversion. A schematic diagram of the proposed saccharification reactor control structure is shown in Figure 3.4.

From the literature in paragraph 2.3.3. the reaction during saccharification is characterized by the following:

- Theoretically 1.1 kg glucose is formed from 1 kg starch,
- Yield of only 97% of the theoretical yield was assumed during saccharification.
- The remaining 3% starch remains unconverted.

The material balance over the saccharification reactors can be seen in Table 3.7. Note that almost all the starch has now been converted to sugar. The energy requirements for cooling the contents of the tank to 60℃ in given in Table 3.8. and cooling the tank further to 33℃ in given in Table 3.9.

Table 3.7 - Material balance over the cook tank during saccharification

Saccharification	Start		End	
Component	(kg)	wt%	(kg)	wt%
Ammonia	1.5	0.05%	1.5	0.05%
Lime	1.2	0.04%	1.2	0.04%
Sulfuric acid	1.5	0.05%	1.5	0.05%
Water (l)	2113.4	70.45%	2044.1	68.14%
Starch	714.4	23.81%	21.4	0.71%
Sugar	18.0	0.60%	780.3	26.01%
Protein/other	150.0	5.00%	150.0	5.00%
TOTAL	3000.0	100.00%	3000.0	100.00%

Table 3.8 - Energy balance over the cook tank cooling step 4

Step 4	Start			End			ΔH	Q
Component	(kg)	wt%	[°C]	(kg)	wt%	[°C]	[kJ/kg]	[kJ]
Ammonia	1.5	0.05%	105	1.5	0.05%	60	-99.4	-149.1
Lime	1.2	0.04%	105	1.2	0.04%	60	-39.4	-47.2
Water (l)	1901.6	63.43%	105	2112.9	70.48%	60	-188.3	-358162.5
Water (v)	211.3	7.05%	105	0.0	0.00%	60	-2433.9	-514275.4
Starch	714.4	23.83%	105	714.4	23.83%	60	-65.3	-46635.8
Sugar	18.0	0.60%	105	18.0	0.60%	60	-68.5	-1232.3
Protein	150.0	5.00%	105	150.0	5.00%	60	-77.3	-11593.8
TOTAL	2998.1	100.00%	105	2998.1	100.00%	60		-932096.2

Table 3.9 - Energy balance over the cook tank cooling step 5

Step 5	Start			End			ΔH	Q
Component	(kg)	wt%	[°C]	(kg)	wt%	[°C]	[kJ/kg]	[kJ]
Ammonia	1.5	0.05%	60	1.5	0.05%	33	-57.9	-86.9
Lime	1.2	0.04%	60	1.2	0.04%	33	-23.3	-27.9
Water (l)	1.5	0.05%	60	1.5	0.05%	33	-40.3	-60.4
Water (v)	2044.1	68.14%	60	2044.1	68.14%	33	-118.4	-242097.0
Starch	21.4	0.71%	60	21.4	0.71%	33	-35.2	-754.5
Sugar	780.3	26.01%	60	780.3	26.01%	33	-36.3	-28297.3
Protein	150.0	5.00%	60	150.0	5.00%	33	-39.1	-5860.3
TOTAL	3000.0	100.00%	60	3000.0	100.00%	33		-277184.4

3.7 Fermentation

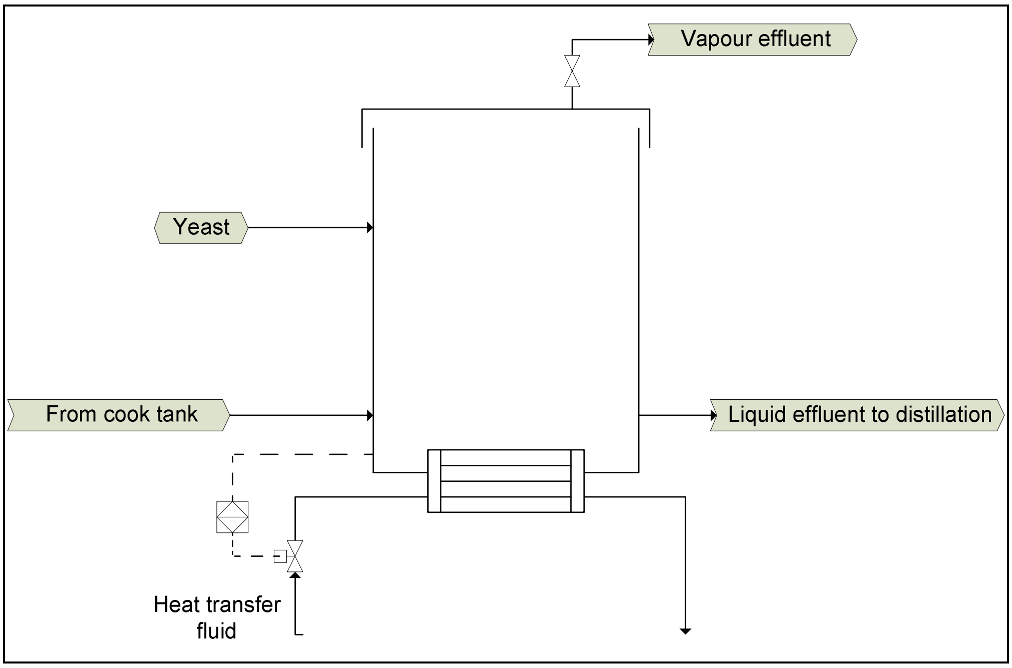

Figure 3.5 - Schematic diagram of fermentation tanks

After the contents of the cook tank is cooled to 33℃, which is the operating temperature of the fermentation, it is sent to the fermentation tanks. A schematic diagram of the fermentation tank is shown in Figure 3.5. By adding yeast to the fermentation tanks, the fermentable sugars are converted to mainly ethanol and carbon dioxide gas by anaerobic fermentation. From the discussion in paragraph 2.3.4 the reaction and assumptions for the material and energy balance over the Fermentation tanks are:

- Theoretically 0.511 kg ethanol and 0.489 kg CO_2 is formed from 1 kg glucose
- A yield of 95% was achieved, due to bacterial contaminants
- The remaining 5% glucose is converted to the unwanted by products acetaldehyde and lactic acid, 0.5 kg lactic acid and 0.245 kg acetaldehyde is formed from 1 kg glucose
- The acetaldehyde gas and lactic acid which is formed during the fermentation process dissolves in the water and leaves the fermentation tank in an aqueous form.
- The heat of the exothermic reaction is 555.6 kJ/kg glucose
- During fermentation 100% of the CO_2 exits the reactor as a gas stream and 3% of the water and 3% of the ethanol evaporates and leaves the reactor with the CO_2 gas stream

As mentioned previously, the fermentation tank has to be directly cooled, to prevent the temperature exceeding 37°C, which would cause the yeast to die. The CO_2 produced in the reaction causes pressure to build up in the reactor. This is controlled with a vapour effluent valve to the vapour recovery system.

If the optimum temperature and pressure is maintained throughout the 36 hours of residence time the desired ethanol composition in the effluent stream will be obtained and no further quality control is necessary. The material and energy balance, is shown in Table 3.10. The negative value presents the required amount of energy that has to be removed, by direct cooling, in order to operate the reactor at isothermal conditions. Also note that all of the sugar has been transformed into mostly ethanol and some lactic acid and acetaldehyde.

Table 3.10 - Material and energy balance over the fermentation tanks

Fermentation	**Start**			**End**			**ΔH**	**Q**
Component	**(kg)**	**wt%**	**[°C]**	**(kg)**	**wt%**	**[°C]**	**[kJ/kg]**	**[kJ]**
Ammonia	1.5	0.05%	33	1.5	0.05%	37	8.5	12.7
Lime	1.2	0.04%	33	1.2	0.04%	37	3.4	4.1
Water (l)	2044.1	68.14%	33	1992.7	66.42%	37	16.7	33360.9
Water (v)	0.0	0.00%	33	61.3	2.04%	37	2273.7	139430.9
H_2SO_4	1.5	0.05%	33	1.5	0.05%	37	5.9	8.8
Starch	21.4	0.71%	33	21.4	0.71%	37	5.0	107.7
Sugar	780.3	26.01%	33	0.0	0.00%	37	**-555.6**	-433503.5
CO_2 (g)	0.0	0.00%	33	362.4	12.08%	37	4.3	1545.5
Ethanol (l)	0.0	0.00%	33	367.5	12.25%	37	9.0	3289.9
Ethanol (v)	0.0	0.00%	33	11.4	0.38%	37	846.4	9620.4
Lactic acid	0.0	0.00%	33	19.5	0.65%	37	10.2	198.6
Acetaldehyde	0.0	0.00%	33	9.6	0.32%	37	10.2	97.8
Protein	150.0	5.00%	33	150.0	5.00%	37	5.4	816.3
TOTAL	**3000.0**	**100.00%**	**33**	**3000.0**	**100.00%**	**37**		**-245009.8**

3.8 Distillation

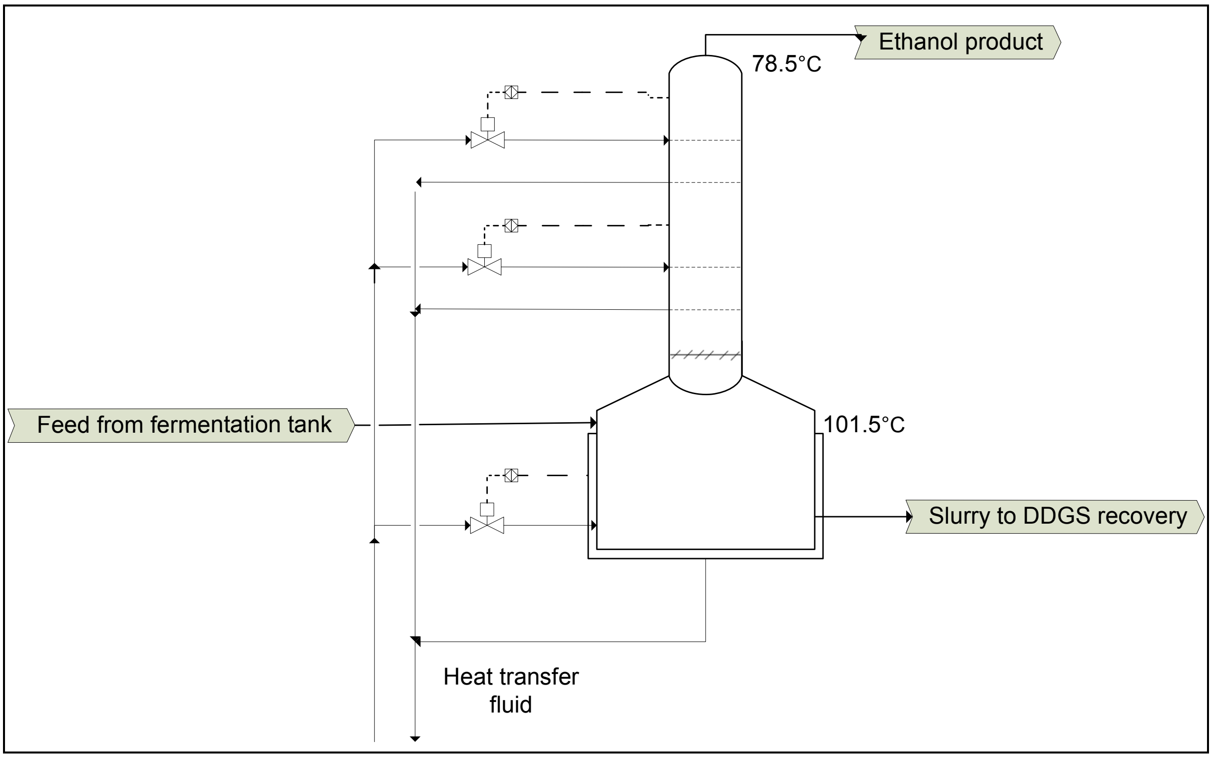

Figure 3.6 - Distillation column

The bottom liquid stream from the fermentation tanks is combined with the liquid effluent from the vapour recovery system and fed to the beer boiler, the bottom part of the distillation column. A schematic of the distillation column is given in figure 3.6.

The objective of the beer boiler is to remove all of the solids from the stream and evaporate the ethanol in the effluent stream. The boiler is operated at a pressure slightly higher than the distillation column (1.1bar) and is heated to 101.5℃. Temperature and pressure control is extremely important in the beer boiler to achieve the desired separation. The required heat is added by passing hot heat transfer fluid through the beer boiler.

Almost all of the ethanol and some water evaporate and exit the boiler at the top and then enter the distillation column. The objectives of the distillation column are to achieve an ethanol purity of over 90 wt% in the distillate stream and a product recovery of 98%. The water vapour is condensed due to the decreasing temperature higher up in the column, and the ethanol vapour exits with the required composition at 78.5℃. The distillate is then cooled to ambient temperature (25℃) and sent to a storage vessel. To achieve these objectives the column pressure, temperature and the composition of the outlet streams need to be controlled.

Due to the fact that it is impractical to control the composition of the product stream directly, the correct distillate composition will be achieved by controlling the other variables, in particular the column temperature. This will be done with heat exchanger trays placed in the distillation column.

After most of the ethanol has evaporated out of the boiler, the liquid effluent (slurry) is cooled and sent to DDGS recovery. A material and energy balance over the distillation column can be seen in table 3.11. Note the high concentration of the distillate from the top of the column.

Table 3.11 - Material balance over the beer boiler and distillation column

Distillation$_{heat}$	Start - 37°C		Top$_{out}$ - 78.5°C		Bottom$_{out}$ - 101.5°C		ΔH	Q
Component	**(kg)**	**wt%**	**(kg)**	**wt%**	**(kg)**	**wt%**	**[kJ/kg]**	**[kJ]**
Ammonia	1.5	0.06%	1.5	0.37%	0.0	0.00%	89.8	134.8
Lime	1.2	0.05%	0.0	0.00%	1.2	0.05%	55.7	66.8
Water (l)	2054.0	77.87%	0.0	0.00%	2030.3	90.98%	270.0	548100.7
Water (v)	0.0	0.00%	23.7	5.84%	0.0	0.00%	2430.7	57607.9
H_2SO_4	1.5	0.06%	0.0	0.00%	1.5	0.07%	98.6	147.8
Starch	21.4	0.81%	0.0	0.00%	21.4	0.96%	89.3	1914.4
Ethanol (l)	**378.9**	14.36%	0.0	0.00%	7.6	0.34%	144.3	1093.8
Ethanol (v)	0.0	0.00%	371.3	91.44%	0.0	0.00%	930.3	345427.0
Lactic acid	19.5	0.74%	0.0	0.00%	19.5	0.87%	171.4	3343.1
Acetaldehyde	9.6	0.36%	9.6	2.35%	0.0	0.00%	390.3	3730.3
Protein	150.0	5.69%	0.0	0.00%	150.0	6.72%	103.4	15514.8
TOTAL	**2637.6**	**100.00%**	**406.1**	**100.00%**	**2231.5**	**100.00%**		**977081.5**

A material and energy balance during the cooling of the distillate and liquid slurry can be seen in Table 3.12. Note that the overall balance remained the same even though they are separated.

Table 3.12 - Cooling Energy balance over the beer boiler and distillation column

Distillation$_{cool}$	Top$_{in}$ - 78.5°C		Bottom$_{in}$ - 101.5°C		Out - 25°C		ΔH	Q
Component	**(kg)**	**wt%**	**(kg)**	**wt%**	**(kg)**	**wt%**	**[kJ/kg]**	**[kJ]**
Ammonia	1.5	0.37%	0.0	0.00%	1.5	0.06%	-115.3	-172.9
Lime	0.0	0.00%	1.2	0.05%	1.2	0.05%	-66.0	-79.1
Water (l)	0.0	0.00%	2030.3	90.98%	2030.3	76.98%	-320.2	-650073.0
Water (v)	23.7	5.84%	0.0	0.00%	23.7	0.90%	-2430.7	-57607.9
H_2SO_4	0.0	0.00%	1.5	0.07%	1.5	0.06%	-116.2	-174.3
Starch	0.0	0.00%	21.4	0.96%	21.4	0.81%	-104.2	-2233.4
Ethanol (l)	0.0	0.00%	7.6	0.34%	7.6	0.29%	-171.2	-1297.3
Ethanol (v)	371.3	91.44%	0.0	0.00%	371.3	14.08%	-930.3	-345427.0
Lactic acid	0.0	0.00%	19.5	0.87%	19.5	0.74%	-201.7	-3935.2
Acetaldehyde	9.6	2.35%	0.0	0.00%	9.6	0.36%	-420.7	-4020.9
Protein	0.0	0.00%	150.0	6.72%	150.0	5.69%	-119.4	-17909.6
TOTAL	**406.1**	**100.00%**	**2231.5**	**100.00%**	**2637.6**	**100.00%**		**-1082930.6**

3.9 Dryer

The slurry from the bottom of the beer boiler is sent through a centrifuge where 90% of the water is removed. The material balance over the centrifuge is given in Table 3.13. The concentrated slurry is mixed with residue from the raw feed preparation. The stream is then dried to a moisture content of 10% resulting in the product, DDGS. The material and energy balance of the DDGS is given in Table 3.14.

Table 3.13 - Material balance over the centrifuge

Centrifuge	Start		End – Wet DDGS		End - liquids	
Component	**(kg)**	**wt%**	**(kg)**	**wt%**	**(kg)**	**wt%**
Water (l)	2030.3	90.98%	203.0	50.22%	1827.3	100.00%
Other	201.2	9.02%	201.2	49.78%	0.0	0.00%
TOTAL	**2231.5**	**100.00%**	**404.2**	**100.00%**	**1827.3**	**100.00%**

Table 3.14 - Material balance over the DDGS dryer

Dryer	**Start - 25°C**		**Top$_{out}$ - vapour**		**Bottom$_{out}$ - DDGS**		**ΔH**	**Q**
Component	**(kg)**	**wt%**	**(kg)**	**wt%**	**(kg)**	**wt%**	**[kJ/kg]**	**[kJ]**
Lime	1.2	0.05%	0.0	0.00%	1.2	0.05%	65.1	78.1
Water (l)	203.0	7.70%	0.0	0.00%	21.5	0.96%	313.9	6753.9
Water (v)	0.0	0.00%	181.5	44.70%	0.0	0.00%	2570.9	466661.8
H_2SO_4	1.5	0.06%	0.0	0.00%	1.5	0.07%	113.8	170.7
Starch	21.4	0.81%	0.0	0.00%	21.4	0.96%	102.7	2200.8
Ethanol (l)	7.6	0.29%	0.0	0.00%	0.0	0.00%	0.0	0.0
Ethanol (v)	0.0	0.00%	7.6	1.87%	0.0	0.00%	957.2	7253.0
Lactic acid	19.5	0.74%	0.0	0.00%	19.5	0.87%	198.9	3880.5
Protein	150.0	5.69%	0.0	0.00%	150.0	6.72%	117.5	17631.7
TOTAL	**404.2**	**15.33%**	**189.1**	**46.57%**	**215.2**	**9.64%**		**504630.5**

3.10 Summary and result

In this chapter the material and energy balances of the proposed small scale ethanol plant were calculated. The energy balance of each of the different processes in the plant was required to determine the amount of energy that has to be supplied by the heating and cooling system.

With conventional systems, steam from boilers is used for heating and water/glycol mixtures in the evaporative cooling towers for cooling. Simultaneous heating and cooling is needed in the plant. From the calculations it is illustrated that there is a large possibility for heat integration in the plant. A high temperature heat pump, that could reach the high temperatures needed in the plant, can be a valuable asset in reducing the amount of energy in the plant. Energy can be recycled and reused, instead of discharging it to the atmosphere like in conventional systems. The use of a single heat transfer fluid between the heating and cooling system and the ethanol plant can make it possible to simplify the control and transfer of heat.

The maximum yield for the batch process of 3000 kg was determined, as 379 kg (Table 3.11). From this the overall material balance the raw material input could be calculated. In Table 3.15 it can be seen that a batch process of 3000 kg, with a content of 882.43 kg raw material, can produce 406 kg of 91.44% proof hydrated ethanol primary product, 226.21 kg of DDGS and 362.41 kg CO_2. The overall mass balance also correlates with the theory in paragraph 2.2 which stated that dry milling has an ethanol yield of 0.42 kg/kg maize.

Table 3.15 - Overall mass balance

Overall Mass Balance	**IN**	**OUT - Product**
Component	**(kg)**	**(kg)**
Raw material	882	0
Reagents	5	0
Water	2113	1827
CO2	0	362
Ethanol	0	406
DDGS	0	215
Water loss	0	189
Total	3000	3000

In chapters 4 and 5 literature will be surveyed to find a heat pump technology that will be suitable in the ethanol plant that could make it possible of producing ethanol in a more cost effective way.

In chapter 6 a model of the heat pump will be developed for the energy requirements in the plant. The comparison between conventional heating and cooling systems and the heat pump system proposed in this study will be done in chapter 7.

Chapter 4 – Background on heat pumps

4.1 Introduction

Industries all over the world have become more energy conscious. By applying better management and energy saving initiatives in the industry, heat pumps are starting to play a significant role in increasing energy efficiency in heating and cooling applications due to their lower energy consumption.

Heat pumps offer the most energy-efficient way to provide heating and cooling in many applications. Heat pumps work on the principle of upgrading energy from low temperature heat sources, like waste heat. With application of a little more energy, it can transform low temperature energy to such a level that it can be utilized at higher temperatures. Heat pumps also provide simultaneous cooling during heating. This feature of heat pumps can drastically improve energy efficiency and environmental value to any heating system that is driven by primary energy sources such as fuel or electrical power (IEA, 2006).

In this chapter a literature survey on heat pumps in general is done. An overview of *heat pump technology*, performance, applications, types of heat pumps and refrigerants is given below. This is done to understand the principles of heat pumping and to make it possible to select the right kind of heat pump technology that will be utilized as a high temperature heat pump in the ethanol plant.

4.2 Heat pump technology

Heat flows naturally from a higher to a lower temperature. A heat engine is by definition a device that operates in a thermodynamic cycle and does a certain amount of positive work through the transfer of heat from a high temperature to a low temperature (Sonntag et al. 2003). Thus a heat engine takes high-grade heat, converts it into work and rejects the energy balance at a lower temperature than the source heat.

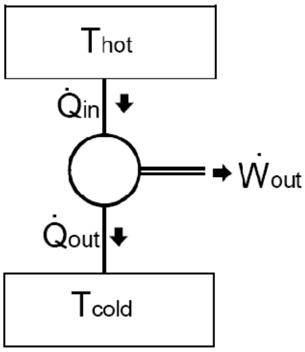

Figure 4.1 - Heat Engine

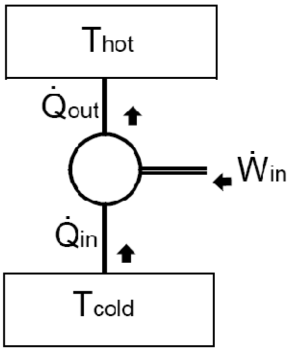

Figure 4.2 - Heat Pump

The definition of a heat pump is a device that transfers heat from a low temperature at the heat source, to a high temperature at a heat sink. The second law of thermodynamics states that heat cannot flow from a body of a low temperature to a body of high temperature, unless work is being done to supply energy to the system. This work may be performed mechanically or thermally. Thus a heat pump works as a reversed heat engine. A heat pump takes waste heat, applies work to the operating fluid and provides heat at a higher temperature than the waste heat source. (Sonntag et al. 2003)

The first law of thermodynamics states that all of the energy that goes into the heat pump should be rejected to the heat sink. The heat delivered by a heat pump is theoretically the sum of the heat extracted from the heat source and the energy needed to drive the cycle. (White et al. 2001)

The two operating modes for heat pumps are cooling and heating. Heat pumps can transfer heat from natural heat sources in the surroundings, such as the air, ground or water, or from man-made heat sources such as industrial or domestic waste, to a building or an industrial application. Heat pumps can also be used for cooling. Heat is then transferred in the opposite direction, from the application that is cooled, to surroundings at a higher temperature. Sometimes the excess heat from cooling is used to meet a simultaneous heat demand.

4.3 Heat pump performance

The Carnot cycle is an idealized example of an energy conversion cycle (Figure 4.3). For a vapour compression heat pump (VCHP) features isentropic compression and expansion as well as isothermal condensation and evaporation. This is a reversible process, but due to irreversibilities the performance of a real heat pump will be more like that of a Rankine cycle, as shown in Figure 4.4. This is because of entropy production during the compression, condensation, expansion and evaporation in the cycle. Thus, the theoretical performance ratio of a real cycle will be much lower. (Herold et al. 1996)

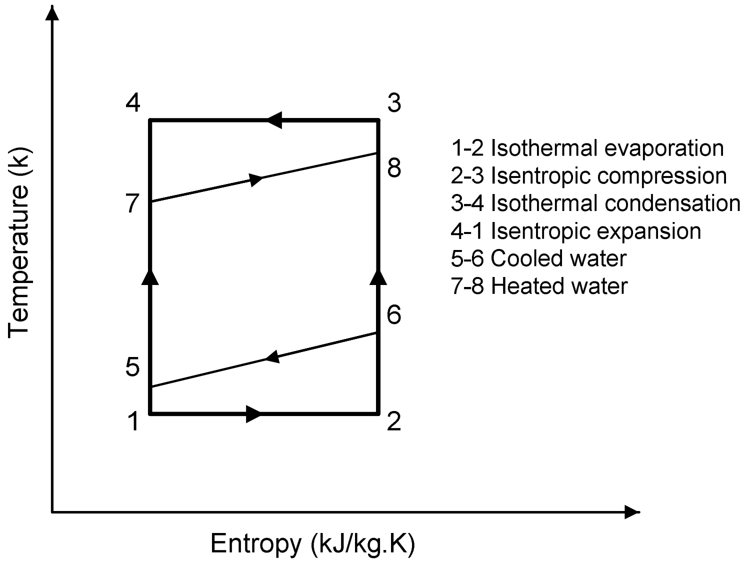

Figure 4.3 - Carnot cycle - ideal for pure refrigerant (Recreated from Radermacher et al. 2005)

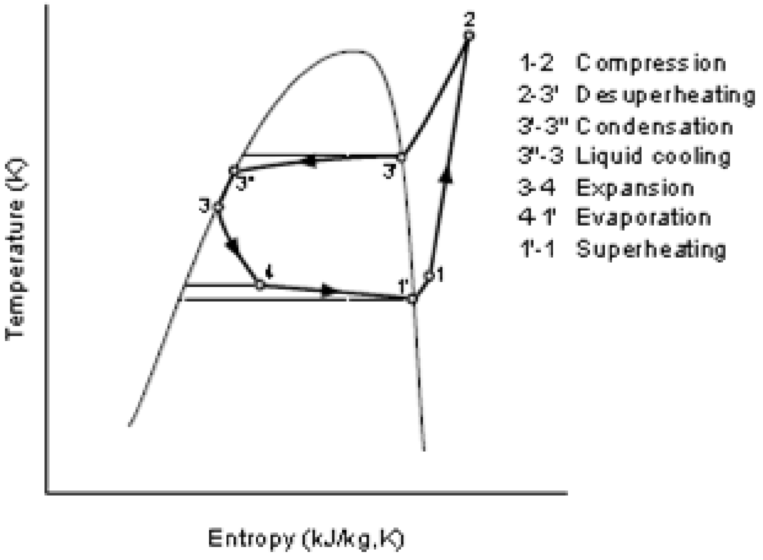

Figure 4.4 - Rankine cycle - real operating cycle (Genchap, 2006)

The Carnot cycle is based on constant temperature condensing and evaporation. The temperature in most external transfer fluids increase as heating transfers energy to the stream and decreases as cooling transfers energy from the stream. In Figure 4.3 it can be seen that there is a large temperature difference between the points 2-6 and 4-7. For an infinitely large heat exchanger, the difference in temperature will remain the same for those points. This causes entropy generation.

The Lorenz cycle is shown in figure 4.5. The Lorenz cycle is the idealized cycle for fluids or zeotropic mixtures with non constant temperature evaporation and condensation. The change in temperature of the working fluid can be matched to the external working medium. If the temperature profile for the heat exchange is parallel, the entropy would strive to be zero for an infinitely large heat exchanger. (Radermacher et al. 2005)

For the same heat exchange area, a Lorenz cycle can match the source and sink temperatures change better than a Carnot cycle. A cycle with characteristics of the Lorenz cycle will provide the highest possible efficiency for the heat exchange in that cycle.

The overall efficiencies for ideal Lorenz and Carnot cycles are however the same, according to the second law of thermodynamics. (Radermacher et al. 2005)

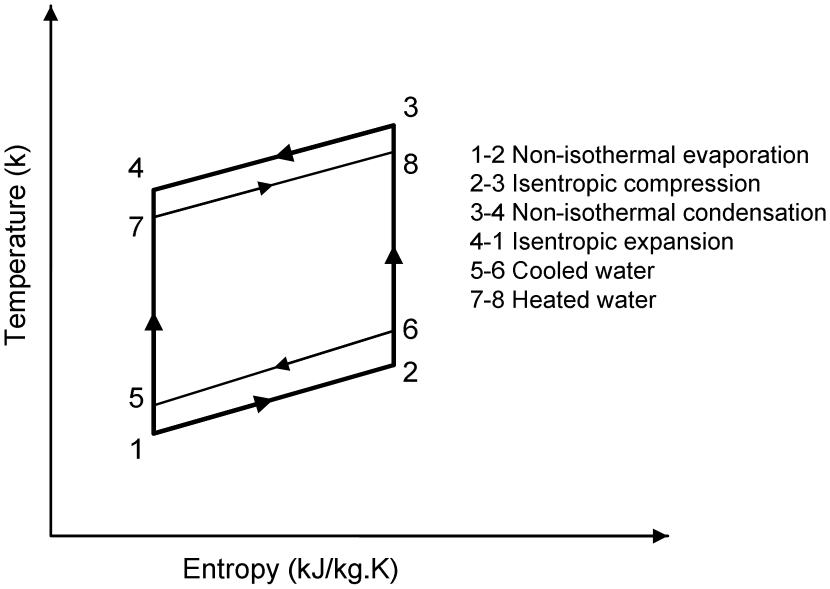

Figure 4.5 - Lorenz cycle - ideal for zeotropic mixtures (Recreated from Radermacher et al. 2005)

The coefficient of performance (COP) of heat pumps is described as the efficiency or the ratio of benefit obtained in a cycle. It can also be decribed as the heat transferred per unit of energy input. For heating, the COP_h is the amount of heat available at high temperature, divided by the expenditure of work requirement. (Herold et al. 1996)

$$COP_h = \frac{Q_h}{W_c} \tag{4.1}$$

The cooling COP can be defined as the ratio of cooling capacity over the work input.

$$COP_c = \frac{Q_c}{W_c} \tag{4.2}$$

When there are no losses in the cycle the following relationship for the coefficient of performance can also be derived as:

$$COP_h = COP_c + 1 \tag{4.3}$$

The COP of most established VCHP lie between 2 and 4. This means that if the COP is equal to 4, that for each unit of useful energy input, there is an output of 4 units of useful energy and a reuse of a renewable or waste heat source of 3 units. This is also called the multiplier effect of input energy of a heat pump. (Genchap, 2006)

4.4 Heat pump applications

Heating and cooling are some the most dominant requirements in the industrial environment. It is also very important in commercial and residential buildings. Heat can be recovered from waste energy streams or from low grade heat sources such as the environment. This can be done with direct heat exchangers in process streams. When the heat is required at higher temperature levels, heat pumps can be incorporated to increase and upgrade the quality of heat in industrial processes. Heat pumps represent a method of improving energy efficiency, while also reducing primary energy consumption. (Soroka, 2007)

Industrial heat pumps can lead to increased energy efficiency and reduction in combustion related emissions. If less energy is required in a plant it can lead to cost saving and it is also beneficial to the environment due to lower greenhouse gas emissions. Industrial heat pumps have been identified as suitable and mainly used for:

- space heating and cooling;
- refrigeration;
- heating and cooling of process streams;
- water heating for washing, sanitation and cleaning;
- steam production;
- drying/dehumidification;
- evaporation;
- distillation;
- concentration.

Due to the context of this project, more detail is only given to the following points (IEA, 2006) (Soroka, 2007):

- **Evaporation and distillation processes**
  Conventional evaporation and distillation is done by supplying energy to the process in the form of steam or an electric element. This energy is needed to supply the process with the necessary latent energy needed for vaporization of the volatile component in the mixture. In distillation processes the volatile component (distillate) is the product, and with evaporation processes the residue is the product.

  Heat pumps can reduce the requirements of these processes. This can be done by using the energy from the condensing volatile component (distillate). The volatile component is condensed in the evaporator of the heat pump. The heat is then absorbed by the evaporating refrigerant at low pressure in the evaporator of a heat pump cycle. This heat is then upgraded with a compressor, when the refrigerant at relatively high pressures and temperatures condense in the condenser of the heat pump. This condensation can then supply the energy requirements of the evaporation and distillation, and replace the steam heating of a reboiler. Because these processes are needed in chemical and food industries, and is very energy-intensive, heat pumps could be installed on most of the systems.

- **Combined Heating and Refrigeration**
  Heat from condensers that is usually released into the atmosphere in refrigeration systems can be utilized for water and space heating. Warm water is needed in the temperature range from 40-90ºC. This hot water is needed for washing, sanitation and cleaning purposes. Heat pump systems can be integrated to provide cooling and heating demand. Sometimes the temperature output or energy required from a refrigeration condenser may not be high enough for the end use. Extra thermal energy can be added or by running a two-stage heat pump to increase the temperature. A refrigerant with a high condensing and/or gliding temperature can also be used. The most dominant heat pumps found in this applications are electric closed-cycle compression heat pumps, absorption heat pumps and heat transformers.

- **Steam production**
  Vast amount of steam is needed in the industry, where it is used either directly in processes or for heat distribution. Steam is needed at low-, medium- and high-pressure steam in the temperature range from 100-200ºC. A few absorption heat transformers and vapour compression heat pumps, using cascade configurations, are in use for these high temperatures. According to the Heat Pump Centre, high temperature heat pumps are available that can provide steam of up to 150ºC and that a heat pump prototype has even achieved 300ºC.

- **Drying process**
  Vapour compression heat pumps are found in industrial drying and dehumidification at temperatures not exceeding 100℃. A difference in application is that not all the vapour is released with air, but is condensed using the evaporator of a heat pump. The latent heat from the condensation on the evaporators are recovered, upgraded and reused to heat the incoming air that is used in the drying process. The easy control and energy efficiency of such drying system provides an advantage over fuel-fired drying. Making use of a combustion engine to drive the compressor, can improve the performance of such a dryer even more. High temperature cooling water from the engine can be used for additional heating of the inlet air stream. By applying heat exchange between the incoming and outgoing air, you can increase the efficiency even further.

  A variety of drying processes are employed in petrochemical plants and in the timber and paper industry. Heat pump dryers in the timber industry have high performance and energy savings in the region of 40%, if they are compared with conventional kiln drying. This setup could be ideal for the drying of DDGS in the ethanol plant.

4.5 Types of heat pumps

Theoretically, heat pumping can be achieved by a wide range of cycles. For the context of this dissertation the vapour compression heat pump, absorption heat pump and hybrid heat pumps will be discussed. The discussion will start with the vapour compression heat pump cycle, because the principles of the absorption and hybrid cycles build on the fundamentals of the VCHP cycle.

4.5.1 Vapour compression heat pump (VCHP)

The vapour compression cycle is the thermodynamic process that is most widely used in heat pumps. Most of the energy that enters the vapour compression cycle is due to evaporation of a refrigerant in the evaporator. The energy leaving the cycle in the condenser is due to the condensing of the refrigerant in the condenser. This energy that leaves the cycle is a combination of the heat from the evaporation and the energy used to drive the cycle. This then satisfies the principles of the second law of thermodynamics (Incropera, 2002). Vapour compression cycle exploit the fact that the dew and boiling point temperatures of a refrigerant are tied to its pressure. This means that when the pressure is increased the boiling and dew point of a refrigerant are raised, and vice-versa.

The main components in such a heat pump system are:

- Compressor,
- Expansion valve
- Evaporator
- Condenser

The components are connected to form a closed circuit, as shown in Figure 4.6. A volatile liquid, known as the working fluid or refrigerant, circulates through the four components. This refrigerant transports energy throughout the cycle. The refrigerants will be discussed in paragraph 4.8.

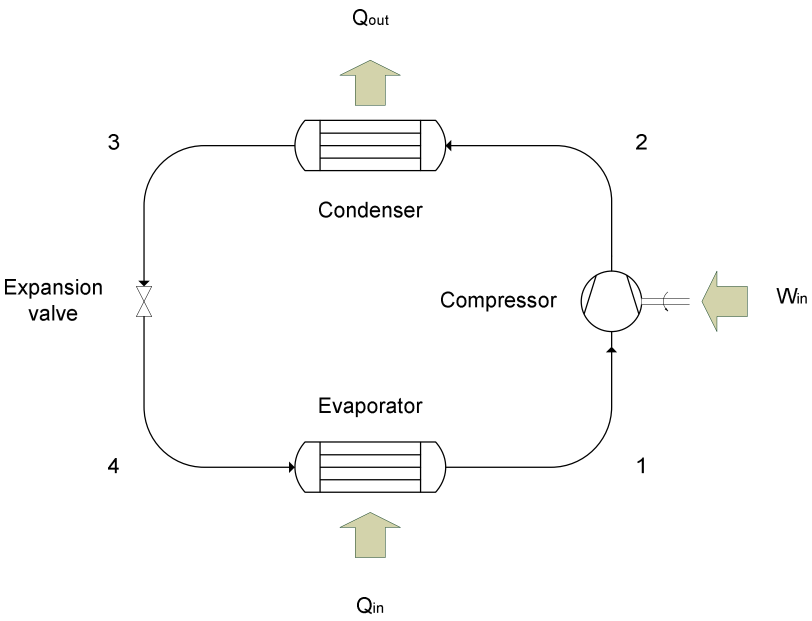

Figure 4.6 - Vapour compression heat pumps (VCHP)

A step by step explanation based of Figure 4.6 is given, to better understand the principle of vapour compression heat pumps.

- The cycle starts at point 1. The refrigerant at the inlet of the compressor is a low pressure gas.
- The vapour is compressed to a high pressure gas at point 2, adding mechanical energy to the refrigerant. This compression to a higher pressure causes the refrigerant to increase in temperature. The rate of work input is pointed out as W_{in}.
- The high pressure gas is condensed in the condenser by transferring heat to the external sink. The high pressure gas is totally condensed to a high pressure liquid at point 3. During the condensing of the refrigerant, the latent heat of the reaction is released to the heat sink at a rate Q_{out}. The pressure in the condenser is controlled, so that the temperature in the condenser is higher than the temperature of the heat sink.
- The cooled high pressure liquid at point 3 is flashed through the expansion valve or capillary tube to point 4. The pressure of point 4 is much lower than that of point 3 and the refrigerant starts to evaporate. This forms a two-phase mixture at point 4.
- The temperature of the refrigerant is kept below the temperature of the heat source, and causes heat to flow into the evaporator at a rate Q_{in}. This causes the refrigerant to totally evaporate to point 4. The refrigerant is now at its original state and the cycle repeats itself.

In most cases the compressor in the vapour compression cycle gets mechanical energy from an electric motor or internal combustion engine. A reciprocating steam engine or turbine can also be used. Electric motors can drive a compressor with very low losses. If an internal combustion engine is used, heat from the cooling water and exhaust gas is used in addition to the condenser heat. The overall energy efficiency of the heat pump strongly depends on the efficiency by which the electricity is generated. (IEA, 2006)

The temperature of evaporation and condensation needs to be matched to the temperature of the heat source and heat sink. A temperature differential should be allowed for efficient heat exchange, from a high to a low temperature. The liquid flow rate and liquid quantities should be controlled. This is needed to ensure that the liquid quantity in the evaporator and condenser stays within the limits and keeps a balance.

Vapour compression heat pumps in the industry rarely have output temperatures exceeding 80℃. The output temperatures are closely related to the refrigerant used. Typical maximum *temperature lifts* are 40℃ to 45℃, although with multi-stage units, lifts of up to 60℃ are possible. (Genchap, 2006)

4.6 Absorption heat pumps (AHP)

There exist a lot of similarities between the absorption heat pump and a vapour compression heat pump. The first difference between the cycles is the working fluid in the absorption heat pump. The working fluid in an absorption heat pump is a binary fluid consisting of a volatile component (refrigerant) and a non-volatile component (absorbent). When the components are mixed, the boiling point of the refrigerant increases. This phenomenon is known as boiling point elevation (Genchap, 2006). The boiling point elevation can be used in industrial processes, where temperatures of waste heat sources needs to be elevated.

The second difference is between the components of the absorption heat pump. The condenser, expansion valve and evaporator are identical as those found in VCHP, but the mechanical compressor is replaced by a thermal compressor. The thermal compressor consists of the combination of the following: generator, solution heat exchanger, absorber and liquid pump. The work done to satisfy the second law of thermodynamics is done by the thermal compressor.

The main components of an absorption heat pump system are listed below:

- Expansion valve
- Evaporator
- Condenser
- Generator/Desorber
- Liquid heat exchanger
- Absorber
- Pump

There exist two types of cycles derived from of the absorption principle. The first is the **absorption heat pump** (AHP) cycle. It can provide cooling at a low temperature level as well as heating at medium temperature heat (below 100 ºC). The main feature of AHP is that it increases the amount of medium temperature useful energy. The combined energy released from the condenser and absorber, has a greater energy content than the high or low temperature streams. (Crever, 2006)

The heat from the condenser and the absorber can be combined into a useful medium-temperature stream with a greater energy content (approximately 200% to 250%) than either the high-grade or low-grade streams.

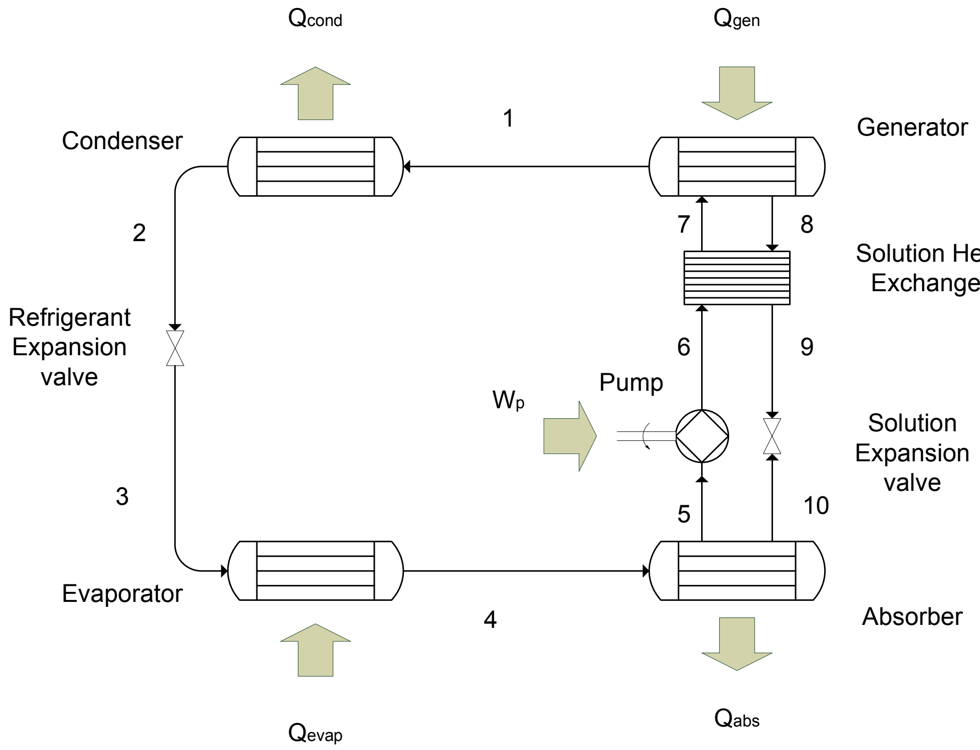

Figure 4.7 - Absorption heat pump (AHP)

A step by step explanation is given based of Figure 4.7, to better understand the principle of absorption heat pumping (Punwani, 2005)

- Refrigerant from the generator enters the condenser at point 1. The steam is condensed to liquid water at point 2 with the heat being rejected to the heat sink at a rate Q_{cond}.
- The liquid refrigerant is dropped in pressure through the expansion valve or orifice between points 2 and 3.
- At low pressure, the refrigerant boils in the evaporator absorbing heat from the chilled heat source.
- The low-pressure steam now travels to the absorber at point 4 where it is reabsorbed by the weak solution.
- This is where the **thermal compression** starts. The weak solution enters the absorber at 10. In the absorber, the weak solution is mixed with the refrigerant vapour. This mixing is an exothermic reaction. The mixture is then cooled by a heat rejection sink at a rate Q_{abs}. The mixture leaves the absorber as a liquid, rich in refrigerant.
- Rich solution that leaves the Absorber and is pumped to a higher pressure to the generator by the **solution pump**, between 5 and 6.
- The rich solution is pre-heated before entering the generator by the **solution heat exchanger** between points 6 and 7. Heat is exchanged with the high temperature weak solution leaving the generator, between points 8 and 9.
- In the high pressure **generator**, there is a heat input at a rate Q_{gen} from a high temperature source (e.g. by fuel combustion or waste heat). This boils the rich solution, releasing refrigerant to point 1 and decreasing the solution concentration. The solution, weak in refrigerant, leaves the Generator at point 8.
- The weak solution is cooled in the solution heat exchanger from point 8 to point 9, by giving of heat to the rich solution between points 6 and 7.
- The cooled weak solution at point 9 passes through an expansion valve or orifice, reducing in pressure. It is now at the low-pressure side of the system at point 10.
- The weak solution returns to the **absorber** at point 10 and is re-concentrated by the refrigerant.

In the vapour compression cycle, the increase in pressure in the cycle is done with a compressor that directly compresses the vapour. During the compression of the vapour, the refrigerant changes density and stores energy internally. This requires considerable amount of mechanical work input. In the absorption cycle the refrigerant is compressed with only a fraction of the mechanical work input. This is because the liquid working fluid is effectively incompressible. This pressure change is achieved with considerable less energy, if compared to the increase in pressure in a vapour compression process. Thermal energy is still needed in the generator, and heat is rejected in the absorber, decreasing the overall energy efficiency of the compression. (Punwani, 2005)

Due to boiling point elevation, the temperature of energy input and output from the *evaporator* and *condenser* is always lower than that of the *absorber* and *generator/desorber*.

There exists a system where no mechanical compression is needed in the compression process. The entire cycle can be gravity operated, except for a bubble pump that is incorporated into the system. The cycle uses ammonia, hydrogen, and water as the working fluids. Hydrogen is used to promote the evaporation of ammonia. (Jenkins, 2007)

The second cycle is called **absorption heat transformer** (AHT) cycle. This cycle elevates the temperature of a part of a waste stream, but does not have the multiplier effect of a AHP system. Heat is supplied at a medium temperature level in the Evaporator and Desorber and then about half of the energy is transformed to a high temperature level and the other half is transformed to low temperature level. The high temperature component is found at the absorber, where it can be used in high temperature industrial applications. The low temperature heat in the condenser can be rejected to the atmosphere. (Crever, 2006)

A step by step explanation based of Figure 4.8. is given to better understand the absorption heat transformer (Genchap, 2006).

- The working solution in the generator is heated with a waste heat stream at medium temperatures heat source.
- The refrigerant desorbs and causes a cooling effect in the generator while absorbing heat from the heat source at a rate Q_{gen}. The refrigerant vapour exits the Generator at point 4.
- The vapour refrigerant is condensed to a liquid at point 3 in the condenser, rejecting low temperature heat Q_{cond}.
- The liquid refrigerant is then pumped to the evaporator, increasing the pressure from point 3 to 2.
- The liquid refrigerant evaporates in the evaporator, absorbing more heat from the medium temperatures heat source, and leaves as a vapour at point 1.
- The pressure of the weak solution is increased by a liquid pump from point 5 to 6.

- The temperature of the weak solution is increased in the solution heat exchanger from point 6 to 7, by exchanging heat with the hot rich solution leaving the Absorber from point 8 to 9.
- The refrigerant vapour from point 1 and the weak solution from point 7, both at medium temperatures, are mixed. This causes an exothermic reaction until all of the refrigerant is absorbed, increasing the temperature of the mixture. This heat is then rejected as useful heat to the heat sink. The high temperature mixture exits the absorber at point 8.
- The high temperature mixture from point 8 is cooled in the solution heat exchanger from point 8 to 9.
- It then passes an expansion valve from point 9 to 10, decreasing the pressure to that of the low pressure side. This causes the mixture to flash and enter the generator as a two-phase mixture at point 10.

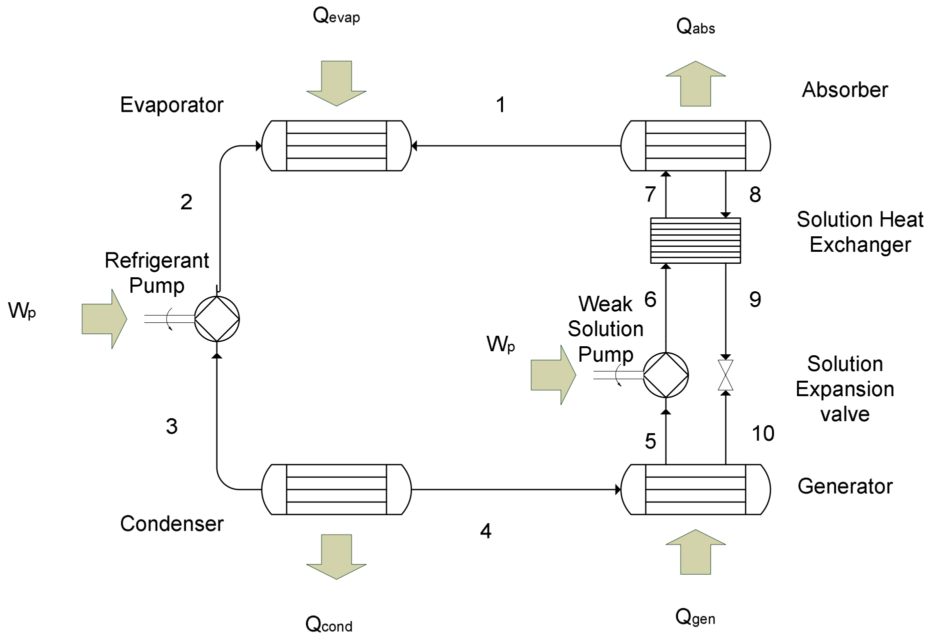

Figure 4.8 - Absorption heat transformer (AHT)

There are a number of different configurations for both the AHP and AHT cycle. Multistage cycles and different working fluid mixtures can be used to increase COP and temperatures of the cycles.

AHP systems with water/lithium bromide as working pair achieve an output temperature of 100ºC and a temperature lift of 65ºC. The COP typically ranges from 1.2 to 1.4. AHT can achieve a delivery temperature of up to 150ºC, typically with a lift of 50ºC. COPs under these conditions range from 0.45 to 0.48. (IEA, 2006)

4.7 Hybrid heat pumps (HHP)

Hybrid heat pump (HHP), also called compression/absorption or compression/resorption heat pump, is a closed loop thermodynamic system using a binary working fluid with a zeotropic nature (paragraph 5.8). It combines substantial parts of both absorption and compression machines. It utilizes a mixture of absorbent and refrigerant as in ***absorption heat pumps*** and a compressor as in ***vapour compression heat pumps***. Desorption in the hybrid cycle occurs under low temperatures and pressures. Absorption occurs under high temperatures and pressures.

A hybrid heat pump consists of a solution circuit that is incorporated in a vapour compression heat pump. The evaporation and desorption of the working fluid in the desorber is incomplete. A solution pump is incorporated to re-circulate the liquid that doesn't evaporate. This is called incomplete evaporation in the desorber (evaporator). If all of the solution is recirculated via a solution pump, the cycle is called the "Osenbrück cycle". When all of the solution is sent through the compressor, thus eliminating the need for a solution pump, the cycle is referred to as ***total wet compression cycle***. A variation between the two can be used when a part of the solution is sent through the compressor and the rest is still recirculated with a solution pump. (Itard, 1998)

The HHP consists of a vapour compression heat pump with a solution circuit incorporated into it. The main components in the HHP cycle are:

- Compressor
- Absorber
- Desorber
- Solution heat exchanger/Economizers
- Expansion valve
- Pump

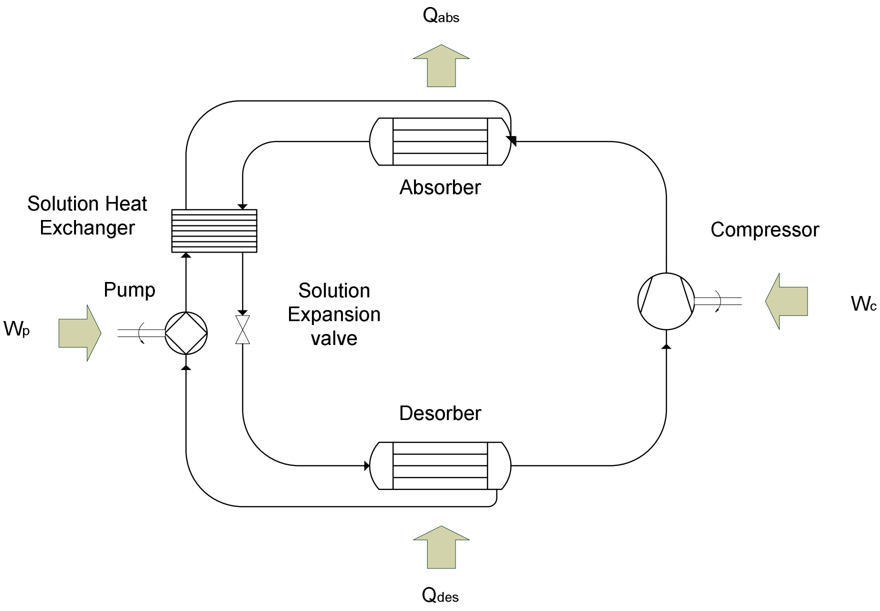

Figure 4.9 - Hybrid heat pump (HHP)

The operating principle based on Figure 4.9, according to Brunin (1997) is the following:

- It is a hybrid machine in the sense that it has a compression stage and an absorption stage. It uses two fluids: an absorbent and a refrigerant, with the refrigerant (ammonia) being more volatile than the absorbent (water).
- Desorption and evaporation of most the refrigerant and some of the absorbent takes place due to low pressures in the desorber. The low pressures are caused by the suction side of the compressor. The desorption and evaporation are endothermic reactions, which lead to a cooling effect in the desorber. Heat is transferred from the heat source which helps the desorption process even further.
- The liquid solution, weak in refrigerant, is recirculated to the absorber via a solution pump. The pressure is increased and passed through a solution heat exchanger to increase the temperature of the solution closer to its saturation temperature. The solution can also pass through the oil exchanger/cooler; this completes the preheating of this solution.
- Vapour from the desorber, rich in refrigerant, is compressed by the compressor. The compression raises them to a high pressure and temperature. The energy required for this is supplied by an electric motor.
- In the absorber the compressor delivers the compressed vapour to the absorber, where they enter into contact with the weak solution. The latter then absorbs the vapours which are rich in refrigerant fluid. The absorption and condensation of the

refrigerant into the mixture, causes an exothermic reaction that generates heat. The heat generated by this phenomenon is released to the heat sink.

- After absorption is completed, the solution rich in refrigerant fluid is collected, at the absorber outlet. The rich solution then passes through the solution heat exchanger, where it preheats the weak solution. It then passes through an expansion valve and is fed into the desorber.
- Due to the lower pressures in the desorber the solution is expanded into a two phase mixture. The vapour phase is directed towards the compressor inlet, and the liquid phase towards the desorber liquid outlet and the cycle then repeats itself.

The compressor is incorporated to boost the absorption and desorption process in the cycle. The compressor firstly decreases the pressure inside the desorber, promoting the desorption process of the more volatile component from the working fluid. This also makes it possible for the desorber to work at lower temperatures. The compressor then increases the temperature and pressure through the compression process. At the Absorber the increased pressure promotes the absorption of the refrigerant into the working fluid. This will lead to higher temperatures of heat produced by the absorber.

The higher temperature of the heat delivery, like that of AHT, is of great advantage to the HHP cycle. Using an ammonia/water mixture (NH_3-H_2O), the hybrid cycle has the potential for a superior COP to a high temperature mechanical heat pump using a HCFC. This will be discussed in detail in paragraph 5.3.

4.8 Refrigerants

As discussed in the previous paragraphs**,** all closed-cycle heat pumps require a working fluid. The working fluid is the medium that transports energy throughout the cycle. The working fluid needs to meet some of the following thermodynamic and property requirements even though no single fluid is capable of satisfying all of them. A few of these characteristics are (Jenkins, 2007):

Chemical Health, safety and environmental

- High chemical stability (hence the prior preference for the chlorofluorocarbons);
- Inert;
- Non-toxic;
- Non-flammable;

- Benign environmental impacts;
- Irritability for safer handling;
- Low water solubility to reduce corrosion.

Thermophysical Properties

- Critical and boiling temperature appropriate for the application;
- Low vapour heat capacity;
- Low viscosity;
- High thermal conductivity;
- High heat transfer characteristics;
- High latent heat of vaporization to reduce the necessary mass flow rate for the total heating or cooling effect;
- Evaporating pressure greater than 1 atm to prevent air intrusion into the fluid side of the heat pump ;
- Condenser pressure moderately low so that low pressure tubing may be used;
- Critical-point and triple-point temperatures must span the range of operating temperatures.

Miscellaneous

- Soluble in lubricating oil;
- High vapour dielectric strength;
- Low freezing point;
- Compatible with common materials;
- Easy leak detection;
- Low cost.

An important design consideration for a heat pump is the pressure-boiling point temperature relationship for the refrigerant. Many refrigerants are compatible and can be mixed to provide different thermal characteristics in the condenser and evaporator units. An important design consideration is the temperature range over which condensation and evaporation occurs. (Genchap, 2006)

4.9 Types of refrigerants

Traditionally Chlorofluorocarbons (CFCs) and Hydrochlorofluorocarbons (HCFCs) have been the main refrigerants in heat pump. The most common of these have been (IEA, 2006)

- CFC-12 Low- and medium temperature (max. 80℃);
- CFC-114 High temperature (max. 120℃);
- R-500 Medium temperature (max. 80℃);
- R-502 Low-medium temperature (max. 55℃);
- HCFC-22 Virtually all reversible and low-temperature heat pumps (max. 55℃).

These refrigerants have found to be harmful to the environment, because of their high stability and chlorine content. They have both a high ozone depletion potential (ODP) and a global warming potential (GWP). The Montreal Protocol called for an international phase out of CFCs in 1996 and for HCFC by 2020.

A few refrigerants have been identified as long term alternatives and environmentally satisfactory (IEA, 2006) (UNEP, 2002):

- **Hydrofluorocarbons** (HFCs) are either methane- or ethane-based, with fluorine replacing some of the hydrogen. They are chlorine free refrigerant and do not contribute to ozone depletion. They still have Global Warming Potentials (GWP) and relate to the greenhouse effect. In Sweden, HFC-134a has been used in a heat pump that produces hot water at 80℃. Very high condensing pressures were required for this pressure. They also have limited capabilities as refrigerants for high temperature heat pumps at temperatures exceeding 100℃.

- **Hydrocarbons** (HCs) are flammable working fluids, but have favourable thermodynamic properties and material compatibility as refrigerants. They are already widely used in the industry, but due to the high flammability a lot of safety precautions has to be taken when using Hydrocarbons. In Japan a promising high temperature heat pump prototype has been developed producing hot water at 150℃.

- **Carbon dioxide** (R-744) is a refrigerant that has attracted a lot of attention worldwide, even though it is still in development. It is non-toxic, non-flammable and is compatible to normal lubricants and common construction materials. It has low COP when compared to conventional heat pump cycles. A study done in New Zeeland mentioned a model with compressor discharge pressures of 130-150 bar producing hot water at 90°C (White et al. 2001).The high pressures will then increases the cost of such a cycle tremendously, while the heat pump will still not be capable of exceeding 100°C.

- **Ammonia** (NH_3/R-717); is one of the earliest refrigerants found in heat pumps. The first patent of a heat pump using ammonia as refrigerant was in 1860 for an ammonia/water system. In many countries it is the leading refrigerant in medium- and large refrigeration and cold storage plants. It is an excellent refrigerant with a high latent heat and excellent heat transfer characteristics. It is also low in cost and is a thermodynamic substitute to many prohibited working fluids. Condensing temperatures of 78°C have been achieved in heat pump systems. Ammonia is not yet used in high-temperature industrial heat pumps because there are currently no suitable high-pressure compressors available (40 bar maximum). If efficient high-pressure compressors are developed, ammonia will be an excellent high-temperature working fluid.

  Disadvantages are the toxicity, flammability and corrosive nature to copper. The corrosive nature to copper means that different materials should be used in heat exchanger and plant design. Codes, regulations and legislation have been developed mainly to deal with the toxic and to some extent, the flammable characteristics of ammonia". Although ammonia is certainly toxic in sufficiently high concentrations, its pungent smell is a very effective warning of its presence, and thus it is in many ways safer to use ammonia than many odourless refrigerants (Punwani et al. 2005).

- **Water** (H_2O/R-718) is another working fluid that is attractive for high-temperature industrial heat pumps. It has excellent thermodynamic properties and it is non-toxic and non-flammable. A test plant has been constructed in Japan with condensing temperatures of 300°C and COP of 2.4. Even higher COP can be expected from large scale plants.

  A disadvantage of the water is the low volumetric heat capacity. This requires large and expensive compressors, especially with low temperatures, that needs low pressures, in evaporators. Another disadvantage is the freeze point of water. This means that evaporators can not be exposed to temperatures below 0°C.

- **Mixtures** of refrigerants give another possibility for efficient refrigerants. A mixture consists of two or more pure working fluids. The mixture can have different properties than those of the original pure refrigerants. They can be azeotropic or zeotropic. Azeotropic mixtures have constant temperatures when it evaporates and condenses, and the mixture composition stays the same. Zeotropic mixtures evaporate and condense at a temperature glide, because the composition of the mixture in the vapour and liquid phases changes. This change the boiling point as evaporation or condensation commences. This temperature glide can be used to increase the performance of heat pumps due to heat exchange between streams that can be matched. Studies have shown a COP improvement of more than 25% for zeotropic mixtures, compared with a pure refrigerant (paragraph 5.2)

  Absorption heat pumps make use of a zeotropic mixture, where the one component has a high volatility (refrigerant) and the other component has a significantly lower volatility (absorbent). The absorbent should also have a high affinity for mixing with the refrigerant. This is due to a strong molecular attraction between the refrigerant and absorbent. (Herold et al. 1996)

  The affinity leads to heat release when the refrigerant and absorbent is mixed. This leads to the fact that more energy exchanged with absorption and desorption of the zeotropic mixture, than that of a pure refrigerant that evaporates and condenses. The most common absorption cycle working mixtures are aqueous lithium bromide/water ($LiBr/H_2O$), water is the refrigerant, and ammonia/water (NH_3/H_2O), ammonia is the refrigerant.

  Since these affinity forces cause the fluids to deviate from ideal fluid behaviour, the transport and thermodynamic properties of the refrigerant and solution have to be determined experimentally. Consequently, it is difficult to find fluids that have better characteristics than what is currently being used. The study also has shown that water and ammonia are the best choices regarding the latent enthalpy. Literature on zeotropic mixtures will be discussed further in paragraph 5.2.

4.10 Summary

From the literature it can be concluded that heat pumps could be an energy efficient way of cooling and heating throughout the ethanol production process. Heat pumps can be extensively used in energy intensive processes like the liquefaction, saccharification, distillation and drying throughout the ethanol production process.

Heat can be recycled throughout the ethanol production process. Throughout the process, there is a continuous demand for heating and cooling, where the tank temperatures have to be changed and the effluent stream has to be evaporated and then condensed. Heat pumps can be a valuable asset due to their simultaneous heating and cooling capabilities. The most common waste heat streams in the thermal plant are cooling water, effluent, condensate, moisture, and heat from cooling water from fermentation tanks. If the heating and cooling is integrated it can lead to significant saving in energy, and subsequently CO_2 reduction.

This could eliminate the need for boilers and cooling towers for the heating and cooling demand in the ethanol production process. Because of the fluctuation in waste heat supply, it can be necessary to use large storage tanks for accumulation to ensure stable operation of the heat pump.

Hybrid heat pump is the most attractive heat pump technology for the application in ethanol plants. The benefits of VCHP and absorption systems are combined in this cycle. The refrigerant that looks the most promising for high temperatures is the mixture of ammonia and water. They are well known natural refrigerants, with negligible GWP and ODP. Other benefits include:

- High temperature of heat delivery
- High COP that can be achieved with HHP
- Use of zeotropic mixture (Ammonia and water) as working fluid

In the next section a more detailed discussion will be given over HHP.

Chapter 5 - Literature on the hybrid heat pump

5.1 Introduction

From the previous sections of the ethanol production process and heat pumps, it seems that hybrid heat pump technology is promising for utilization in an ethanol plant. The high temperature of heat delivery and simple design can make it possible to be integrated into the plant producing ethanol while using less energy.

In this chapter a literature survey on hybrid heat pumps (HHP) is done to better understand their capabilities and working principle. It must be noted that the focus of the survey was on HHP systems as a whole in the ethanol plant. Because no detail simulations of the different components in the HHP cycle will be done, the literature on the different components will provide information needed in the overall simulation and to help with component selection for appropriate economic evaluation of a HHP in the ethanol plant. The literature survey will cover the following:

- Previous work
- Overview of previous work
- Compressor
- Heat exchangers
- Zeotropic working fluid
- Other components

5.2 Previous work

The research of the hybrid heat pump is based on the Osenbrück cycle. The principle of the Osenbrück cycle has been known since 1895. The subject appeared again in the work of Altenkirch in 1950 and 1954 and was forgotten till the 1970’s. This might have been due to the lack of interest in reducing energy consumption of machines. (Itard 1998)

Since the 1980’s a lot of research has been done on hybrid heat pumps. Examples of research groups include the following:

- Test plants have been built and tested on the Osenbrück cycle principle. Satapathy et al. (2004) and Risberg et al. (2004) reported on dry compression systems. Experimental facilities are also listed in Åhlby and Hodgett (1990), Brunin (1997) and

Bergmann and Hivessy (1990). F. Chiriac, et al. (2006) designed and constructed a hybrid heat pump for district heating applications.

- Hultèn and Berntsson (1998, 2002), investigated the potential differences with changes in parameters and comparisons with VCHP.
- Itard (1995, 1998), investigated the potential of HHP working with wet compression, having the potential to significantly improve the performance of heat pump cycles based on the vapour compression principle. For high temperature industrial heat pumps, a gain of about 25% in comparison with 'conventional' vapor compressor heat pumps can be attained.
- Infante Ferreira, C. Zamfirescu, D. Zaytsev (2003, 2005, 2006) worked on the design of a twin screw compressor for hybrid heat pumps and have tested them in experimental plants. They used injection into the compressors to achieve wet compression.
- Multistage CAHP designs are discussed by, for example, Ziegler and Spindler (1993) and Mehendale and Radermacher (1996). In the second paper, the authors propose multistage designs, suitable for high temperature lifts where a single-stage cycle would require excessively high pressure ratios. The lowest temperature lift studied in that paper is 72℃.

5.3 Overview of previous work

The HHP can be operated over a wide range of temperatures, between -10 and 160℃, using ammonia-water as the working fluid and with pressures not exceeding 20 bar (Stokar and Trepp 1986). At higher pressures, temperatures up to 200℃ can be achieved. (Rane & Radermacher; 1991) According to Infante Ferreira et al. (2006), HPP have a 20% gain when compared to VCHP systems for high temperature application.

An **extra degree of freedom** is given to HHP design due to the fact that evaporation and condensation, at constant pressure, of a non-azeotropic mixture take place at non-constant temperature. A system working with a pure refrigerant has only one degree of freedom: the temperature is a function of the pressure only. A non-azeotropic mixture possesses two degrees of freedom: the temperature is a function of the pressure and of the liquid concentration. During the evaporation and condensation the liquid compositions changes that in turn change the temperatures during the evaporation and condensation (Itard; 1998). This will be discussed in more detail in paragraph 5.5.

This change in temperature is the **temperature glide** and affects performance and design of heat exchangers that operate under different conditions, compared to standard heat pumps. Theoretically, better efficiencies could be achieved, because it might be possible to get constant temperature difference between streams, along the length of heat exchangers. The mixing and separation of ammonia and water, can theoretically also lead to a better COP. When the components are mixed together heat is produced. Heat is also consumed when the mixture is separated. Thus the same amount of refrigerant in a mixture can deliver more heat energy then a pure one. (Jancic; 2007)

According to Jancic (2007), Hybrid heat pumps offer a great possibility for energy savings, especially for outlet temperatures higher than 80℃ and for high temperature lifts between heat source and heat sink. This may be useful mainly for the ethanol production process and could be implemented into other industrial purposes.

Minea & Chiriac (2006) found that the HHP cycle effectively proved to be a valuable alternative to cycles using artificial refrigerants. The HHP can achieve better performance than simple fluid cycles for high output temperatures. Under the same condition energy consumption to run the HHP was lower, which in turn increases the COP of the cycle. The higher working temperatures are also made possible since ammonia molecules are more stable. The critical point of an ammonia/water mixture is also higher than that of the conventional refrigerants. Moreover, ammonia and water has no ozone depletion potential. They still found that the design of the main heat exchangers in extended ranges of pressures and temperature seem to be a significant challenge.

Hultén (1998) compared HHP and VCHP under the same temperatures and heat exchanger area and found that the main advantages and disadvantages of the HHP can be summarized by the following:

The main advantages of the HHP are:

- The compressor has a small swept volume, because of higher temperatures at lower vapour pressures than VCHP.
- High heat transfer coefficients can be achieved in the heat exchanger, depending on the techniques used.
- Well-known and non-ozone-depleting working media.
- High COP can be achieved due to low pressure ratio's for compressors and high efficiencies in heat exchangers.

- The extra degree of freedom provided by a non-azeotropic mixture of variable composition. This makes a given heat pump installation more flexible so that it can easily be adapted to changes in temperature level and capacity.
- The high working temperatures that can be obtained (at least 150℃).
- The absorber glide can be fitted to match the gliding temperatures of the heat source and heat sink, if any, thus lowering the system irreversibility and leading to a higher COP.

The main disadvantages are:

- Leakage of ammonia or water will change the composition mixture. This can compromise the working temperatures and pressures in the system
- Ammonia is inflammable and toxic, but well known. High concentration of ammonia exists only during the vapour phase, before and after compression. This is actually a small part of the cycle.
- Little practical experience with zeotropic mixtures.

5.4 High temperature lift with HHP

Zhou and Radermacher (1996) experimented with high temperatures as well as high temperature lift on HHP systems. They found that single stage configurations are better for conventional applications with the added advantage of adjusting temperature glide and capacity control. This is not achievable with heat pumps working with pure working fluids. However, single stage systems are not good for high temperature lift application, due to large pressure ratios. High pressure ratio will in turn significantly increase the cost of compressors and other equipment in a single stage system. More advantages of working with a binary zeotropic mixture will be given in paragraph 5.8.

Radermacher (1991; 1996) conducted more research on *two stage hybrid heat pump* (TSHHP) systems. The two-stage system worked on the same principle as conventional cascade cycles, where a low temperature cycle provides the heating for the evaporator of the second high temperature cycle. The two stage hybrid heat pumps could achieve temperature lifts of 100℃. This could be ideally utilized in high temperature lift applications like those found in the proposed ethanol plant.

They found that when high temperature lifts are required, the high temperature cycle pressure should increase or the solution concentration should decrease, or both. In the absorber they found that as the pressure decreases the concentration also decreases. This made it difficult to decrease solution concentration and increase pressures for high temperature lifts simultaneously. They then fixed the maximum pressures by using a single compressor for both the high and low temperature cycle absorbers.

In the study they came to the conclusion that the solution concentration on the high temperature cycle and the low temperature cycle should be adjusted individually and independently. A low concentration in the absorber of the high temperature (HT) cycle is required, as well as a high concentration in the desorber of the low temperature (LT) cycle, to achieve high temperature lift. With the high temperature lift, small temperature glides were attained. The glide will be discussed in paragraph 5.8.2.

When compared the COP of the single stage system was the best for low temperature lift. Although the COP of two stage systems were lower, a very high temperature lift range was achieved.

Two stage HHP working at high temperature lifts, have very low pressure ratios and has relative simplicity in design and small number of components. This low pressure ratio as compared to conventional heat pumps can lead to significant energy savings due to a potentially more efficient compression process. They also found that the reduced pressure ratio of the cascade configuration, improved the volumetric and overall efficiency of the compressor.

A two stage HHP can be looked upon as a two single stage HHP's coupled together. Experimental results from the work of Radermacher (1991) for the TSHHP demonstrated that:

- High temperature lifts of up to 100℃ can be achieved, with pressure ratios less than half as large as for conventional heat pumps operating between the same source and sink temperatures. Pressure ratios as low as 7.1 were reported compared to pressure ratios of 20 for conventional single fluid systems.
- Hybrid heat pump can be operated under stable conditions using the control mechanisms incorporated in the experimental setup and strategies developed. (paragraph 5.9.3)
- Cooling COP of around 1.00 can be achieved, while pumping heat through a lift of 100℃. Thus a heating COP of over 2 is achievable for HHP in high temperature lifts.

5.5 Compressor

The compressor is one of the vital components in the cycle. The type of compressor strongly depends on what type of hybrid cycle configuration is going to be used. The desorption process that is incomplete in the Desorber makes this possible, because the liquid has to be circulated in the cycle. Dry compression, wet compression or a variation between the two can be used.

- With **dry compression** the saturated vapour is compressed by a compressor and all of the liquid is recirculated via a liquid solution pump. (Osenbrück cycle). With dry compression the working fluid is compressed by the compressor and is superheated. This is the same as conventional VCHP. The superheating causes a lot of irreversibility due to entropy generation. This is the norm for heat pump cycles working on the Rankine cycle.

- **Wet compression** eliminates the need for a pump, by using the compressor as a pump. The liquid solution is sent through the compressor, and helps with superheating of the vapour as well as irreversibility's due to leakages (Itard, 1995). Wet compression brings the Rankine cycle closer to the ideal Carnot cycle for pure refrigerants and closer to the Lorenz cycle for non-azeotropic refrigerants. This has large advantages, because they have the highest possible efficiencies and COP for heat pump cycles.

- The variation of **partial injection,** is that only a part of the solution is sprayed into the compressor for cooling (Hultén, 1997). If the correct amount of solution is injected, it will reduce superheating of the working fluid, which will reduce the irreversibility.

Itard (1995,1998) has done extensive research on different ways of implementing the compression of HHP cycles. She investigated the differences between wet compression types and dry compression types. According to the research they found that dry compression faces two major problems: (i) irreversibility losses due to vapour superheating degrade the overall performance of a cycle;(ii) dry compressors require oil lubrication that causes oil contamination of the liquid refrigerant, that also causes degradation of performance. The oil and liquid refrigerant have similar densities, and oil separation must be implemented that will increase the cost of the entire system. Itard (1995) also found that when simulations of wet compression and dry compression with zeotropic mixtures are compared, the wet compression has higher COP. This advantage could be overcome if total wet compression is not possible in the compressor or if the isentropic efficiency is too low.

Thus total wet compression cannot be considered above solution recirculation due to the fact that no practical evidence exists of wet compression superiority.

Zatsev (2003) did a comparison of different compressor types. Compressors that were compared for high temperature and pressures are:

- Reciprocating
- Twin screw
- Single screw
- Sliding vane
- Liquid ring
- Scroll

In the study they found that reciprocating and screw compressors are suitable for the high temperatures in the heat pumps. Literature on reciprocating and screw compressors in HHP is given below.

5.5.1 Reciprocating compressors

Minea and Chiriac (2006) used dry reciprocating compressors in their 4.5 MW Hybrid Heat Pump. They concluded that the use of dry ammonia compressors solved the well known problem of lubrication. The possibility exist of lubricating the compressor with the poor solution of ammonia and water. Another possibility is by using organic solvent for lubrication.

In the study of Hultén (1997) soluble oil for compressors was selected in the HHP simulation. This was done to prevent coating of heat exchangers and to cope better with water oil interaction. Insoluble oil was not considered due to the fact that it tends to be dragged through the cycle where it causes fouling of heat exchangers. The high temperatures encountered in a HHP will make it difficult to use soluble oil.

In the experimental plant of Zhou and Radermacher (1996), water cooling was internally used to prevent the compressor from overheating. This is necessary due to the high discharge temperatures of the ammonia. An oil separator was also installed after the compressor discharge line. This is to prevent oil circulation through the cycle, causing fouling of the heat exchangers. Oil had to be changed every two months to prevent water entering the compressors. They also found that the reduced pressure ratio of the cascade configuration, improved the volumetric and overall efficiency of the compressor.

Vorster and Meyer (1999) found that dry compression should be used when using a zeotropic mixture in heat pumps with reciprocating compressors. Even though only saturated vapour enters the compressors, liquid droplets find their way into the compressors and could damage the compressor. If liquid droplet is trapped in the head of the cylinder it could damage the valves or the cylinder head. Another problem is that of accelerating wear, because liquid droplets can wash away lubricating oil from the cylinder walls.

5.5.2 Twin screw compressor

The twin screw compressor is a positive displacement machine with two parallel helical rotors. The rotors mesh together. The one is called a male rotor and the other the female rotor.

Two types of screw compressors are available: oil injected and oil-free. Oil injected types have oil injected into the compression cavity to provide lubrication, sealing and cooling. No timing gear is necessary because the oil prevents contact of the two intermeshing rotors. The rotors are driven directly. In oil free types the two rotors are connected with a timing gear, that makes it possible for the rotors to mesh together when they are rotated without making physical contact. The gears, bearings and seals are still lubricated. The male rotor is usually driven by an external drive, which in turn drives the female rotor. (Zatsev, 2003)

The compression cavity is enclosed between the helical surface of the meshed rotors and the inside surface of the housing. When the rotors rotate, the volume of the compression cavity increases linearly, from almost zero to its maximum value. This is the suction phase of the compressor, which causes a low pressure. The working fluid flows into the suction port. The compression cavity then decreases from its maximum value back to its minimum value. This is called the compression process. After compression the compressed working fluid is discharged at the discharge port.

Most compressors on the market use oil for lubrication and cooling. The oil also helps with sealing in the compressor to prevent leakages of the compressed vapour. Oil free compressors are also available, but with lower efficiencies due to increased leakages. Improving efficiencies to levels of oil lubricated compressors is more expensive. Oil free screw compressors with high efficiencies and capability of handling temperatures of up to 225℃ are available, like those of Howden (2008). They are either air or water cooled.

In some applications liquid refrigerant or water is injected into the compression cavity instead of oil. Infante Ferreira et al. (2006) stated that oil-free compressors operating under wet conditions avoid superheating. The liquid refrigerant is used as lubricant. Lubrication of the bearing and additional components like gears is still done with oil, but is separated from the compression process with labyrinth seals.

The twin screw compressor is a lot simpler than other compressors. When Zatsev (2003) compared the different positive displacement compressors, the twin screw was chosen because the screw compressor has a small number of moving parts, no reciprocating or eccentrically rotating masses, no clearance volume and no valves. The major advantage of twin screw compressors is that it is tolerant to liquid carry over and is capable of providing high pressure ratios (2-15) and efficiencies. Thus, it is a good candidate for wet or partial wet compression in HHP systems.

In the prototype of Zatsev, inlet temperatures of up to 81℃ were used. Low isentropic efficiencies were a major problem. This was due to oversized clearances and evaporation of the liquid when injected at the suction port. The liquid flashed and greatly reduced the volume of displaced vapour. He also concluded that drawbacks of twin screw compressors are the fixed built-in volume ratio and internal gas leakage. The internal working fluid leakage is due to inevitable clearances between the meshing rotors and between the rotors and the housing.

Infante Ferreira et al. (2006) continued on the study of Zatsev to get answers for the problems he encountered. They did a redesign of the compressors taking thermal expansion into account. It also had decreased clearances. They found that the liquid injection into the suction port increases the pressure slightly and it reduces the flow rate into the compressor. They found that the ideal place to inject the liquid was at the start of compression, in the compressor directly into the compression cavity. Labyrinth seals were used to separate the oil lubricated bearing housing from the oil-free process. They encountered substantial leakages in that area which had a negative impact on the compressors performance. With the study they concluded that injection at the start of the compression increased the isentropic efficiency from 5 to 51%. If the labyrinth leakage was lowered the performance of the compressor would increase further.

In the study they also stated that the lack of information related to two-phase compression processes, and the use of liquid refrigerant itself as a lubricant, makes the development of a suitable ‘wet compressor’ difficult.

5.6 Heat exchangers

Radermacher (1991) used horizontal shell and tube heat exchangers in his high temperature lift, test plant. He used a cascade of two hybrid cycles. In the heat exchanger between the two cycles, absorber/desorber, absorption occurred on the shell side and desorption on the tube side. In the absorbers, the weak solution from the desorbers and the compressed vapour enter at the top and when totally condensed and absorbed, leaves the cycle at the bottom. In the desorbers the strong solution enters at the top and weak solution exits at the bottom while the vapour is also extracted. Counter current is maintained through the heat exchangers. Both cycles, high temperature and low temperature, were set up in the same way. An ethylene glycol-water mixture is used to transport the heat from the tubes of the absorber.

In 1997, Groll highlighted the fact that there is a lack of detailed heat exchanger analysis. Then Hulten and Berntsson (1997) did a detail design of the heat exchangers. They used falling-film tube-and-shell heat exchangers, to get good heat transfer with the mixture. The transport properties were calculated with a correlation from Reid et al. [19]. They made the assumption that the superheated vapour discharged by the compressor and liquid from Economizer is ideally mixed. They also integrated the oil cooling and superheated vapour to exchange heat with the sink. They found that the total area requirement will be approximately the same with oil cooling or not. The saturated liquid solution leaving the absorber does not need to be sub-cooled as it will not increase COP and is not necessary. A comparison of HHP and VCHP was also made with the same heat exchanger areas and temperatures. The result of their study concluded that HHP have either similar or greater efficiencies (12%) than VCHP under the constraints of the comparison.

Brunin (1997) stated that **pinch points** should be fixed at the heat exchangers. They found it to be one of the extremities of the heat exchangers and set it to a minimum value of 3℃. This is to ensure that there is a minimum temperature difference in the temperature profile of the heat exchangers is not passed. The temperature glide should not result in impossible heat transfers.

Minea and Chiriac (2006) also used horizontal shell and tube heat exchangers. In Figure 5.1 a schematic illustration of the **absorbers** in their plant is given. The tubes are wetted by spraying the recirculated weak liquid solution over the tubes on the shell side. The vapour rich in refrigerant from the compressor is now mixed with the weak solution and the ammonia gets absorbed. The heat generated by absorption is transferred through the film, the tube wall and finally, by forced convection, to the heat sink (water) flowing into the tubes.

During the constant pressure absorption process, the solution temperatures continually vary according to the different levels of the concentration, and the overall heat transfer coefficient has a direct impact on the system's performance. Values between 2000 and 3000 $Wm^{-2} K^{-1}$ was used in their calculations.

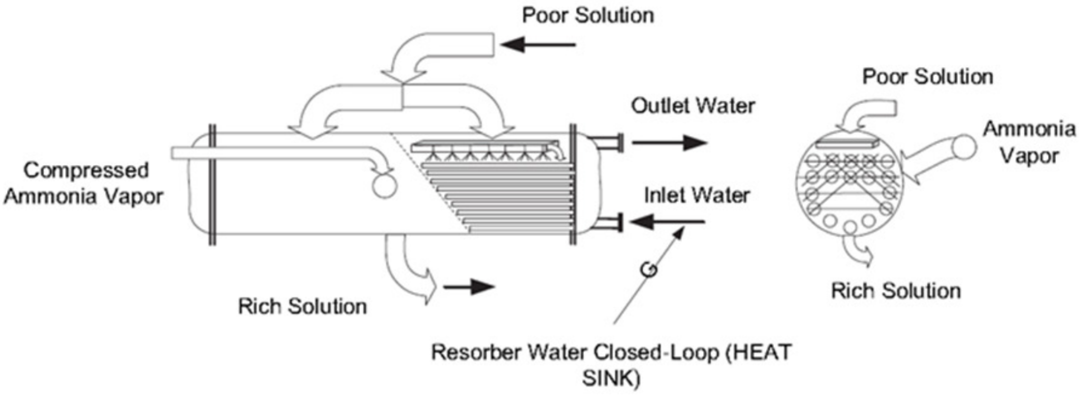

Figure 5.1 – Horizontal multi-tube Absorber with weak solution falling film (Minea and Chiriac, 2006)

The **desorber** of all the plants are similar. The desorption process takes place on the tube side with water or glycol-water mixture on the shell side. Hulten et al. (1997) used vertical counter current shell and tube heat exchangers, while Minea et al. and Radermacher used horizontal desorbers.

An **internal heat exchanger**, also called the *economizer* or *solution heat exchanger*, is also incorporated into the designs. This is liquid-to-liquid counter current heat exchanger. It is used to heat the weak solution from the Desorber with the hot rich solution from the absorber which is cooled in the process. Itard (1995) mentioned that it is necessary to bring the weak solution liquid closer to saturation temperature. This increases the cycle performance. Hulten et al. (1997) modelled the economizer as a black box heat exchanger. This means that only inlet and outlet conditions are considered when the heat exchanger is modelled. Actual temperature profiles, heat transfer coefficients and pressure drop is not considered. They also assumed an overall heat transfer coefficient of 2000 $Wm^{-2} K^{-1}$, which is attainable in tube-and-shell liquid-to-liquid heat exchangers.

5.7 Absolute level of pressure and glide

According to Åhlby (1990) the best performance of the HHP is always achieved when the pressure on the high-pressure side (absorber) is as high as possible, while being within the design parameters of the compressor and pressure vessel. Hulten et al. (1997) found that the higher the pressure in the absorber, the lower the water concentration gets. If there is a higher ammonia concentration present that evaporates in the desorber, the mass of solution that has to be recirculated decreases. This means that there is lower losses in the cycle, due to friction and the economizer efficiency that causes irreversibility. The liquid also has a low specific heat and makes heat transfer difficult. Reducing the liquid mass will decrease the size of the economizer. Thus all calculations should be carried out with the maximum allowed pressure for the components. Most modern compressors can supply 25 bar of pressure. The composition in the cycle will then vary with both the absorber temperature level and the absorber glide.

In 2002, Hulten and Berntsson, did further investigations on HHP. They found that the outer conditions of the heat exchangers play a big role in the composition change of the working fluid. It influences the temperature glide and heat transfer in the cycle. If more liquid is desorbed, it can inhibit the compressors ability to displace the higher mass of vapour.

Hulten (2002) opted that you can describe conditions in the absorber and desorber with the temperature glide, solutions pump flow rate or composition change. If the solution flow rate is increased, it will decrease the glide and composition change in the heat exchangers. They also found that the temperature glide in the Absorber is larger than in the Desorber by a factor of 1.4 – 1.6. This all depends on the concentration, pressure and temperature in the cycle. The economizer can also play a role in the glide. If the solution flow rate is high, with a larger economizer, the smaller the difference between the glide of the absorber and desorber.

5.8 Zeotropic working fluid

Hulte et al. (1998) stated that new heat pump working fluids must be found, because of heating and cooling demand that will definitely increase at mid-high temperature levels (80 - 120°C). As mentioned in paragraph 4.8., refrigerants like CFC-114 that worked earlier at these temperatures are either banned or to be banned. These high temperatures were also very close to the working fluid actual limits and thus there was no margin for improvement.

According to Brunin (1997), the banning of conventional CFC and HCFC working fluids, leaves only two alternatives for high temperature heat pumps:

- Hydrocarbon in Vapour Compression Heat Pump cycles.
- Ammonia/water (NH_3/H_2O) mixture in Hybrid Heat pump cycles.

In the study Brunin also concluded that the Ammonia/water mixture is the best option for heat pump systems with condensing temperatures 80 - 120℃. Despite ammonia toxicity and flammability it has long been used in the industry under proper safety conditions. When compared to hydrocarbon it also has a lower flammability and is easily detected due to its pungent smell. Minea and Chiriac (2006) also mentioned that the high concentrations of ammonia is only present in the vapour phase during compression in low quantities.

Itard et al. (1995) also identified the ammonia/water mixture as suitable future working fluids in the working range of up to 200℃. The ammonia/water mixture is possible to cover high temperature applications with a good level of system performance.

Ammonia and water is also natural refrigerants and has no ozone depletion potential (ODP) and global warming potential (GWP).

5.8.1 Composition change

The use of a mixture of two refrigerants lead to a supplementary degree of freedom in heat pump systems during evaporation and condensation. A pure refrigerant in the two-phase region, has only one degree of freedom: temperature as a function of the pressure only. A zeotropic mixture has two degrees of freedom: temperature as a function of both the pressure and the liquid concentration. (Vorster et al. 1999)

A difference in principle is the big difference in vapour pressure between the two components, so that virtually only one component (in this case ammonia) is evaporated in the Desorber (corresponding to the evaporator) and condensed in the Absorber (corresponding to the condenser). The water content in the vapour phase is normally considerably lower than that of the ammonia.

Evaporation and condensation of the pure refrigerants with azeotropic nature takes place at constant temperatures (Fig 5.2a). When a zeotropic mixture exchanges heat, it coincides with a drop or rise in temperature at a constant pressure, due to the change in liquid composition during desorption and absorption, as shown in Fig. 5.2(b). The temperature increases during evaporation from point 4 to 1 and decreases during condensation from point 2’ to 3. This temperature glide is common among mixtures of refrigerants due to the fact that the different parts of the mixtures exhibit different evaporating and condensing temperatures. (Vorster et al. 1999)

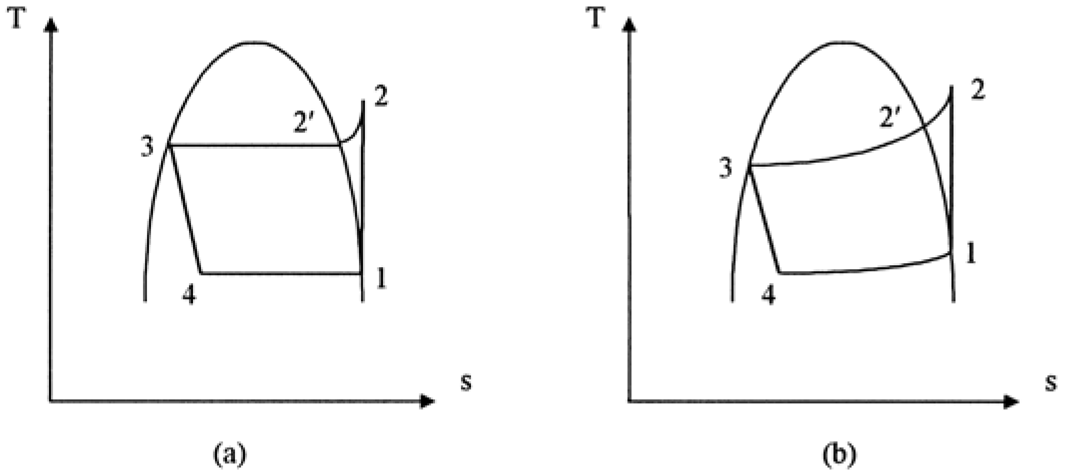

Figure 5.2 - Vapour compression cycle for (a) azeotropic and (b) zeotropic refrigerant (Vorster et al. 1999)

There exists a possibility of adjusting the concentration to fit a given working domain. The composition change has a substantial influence on the COP and, in fact, also influences the optimal design of the individual components and is, therefore, an important design parameter. The optimal concentration difference and, hence, the optimal absorber glide vary with the outer conditions (Hulten, 1998).

5.8.2 Temperature glide

With linear temperature glides, the pinch point (point of closest temperature approach between cold and hot streams), must be located at either sides of the heat exchanger. If the lines are parallel no pinch point exists. From the ideal Lorenz cycle (paragraph 4.3), it would achieve the maximum possible efficiency and lowest possible entropy production for the heat transfer.

However, the difference in volatility and change in concentration of a binary mixture of the two components (refrigerant and absorbent) causes a non-linear temperature glide during heat transfer. The refrigerant also has lower latent heat of evaporation, when compared to the absorbent. Thus in evaporation, if the refrigerant concentration is high in the vapour, temperature glide will be lower than when more of the high latent heat absorbent is evaporated.

The nonlinearity introduces challenges for the heat exchanger design. The existence of the pinch point limits the heat transfer rate. The location however could be controlled by selecting the same thermal capacity or heat transfer for both fluids. (Radermacher et al. 2005)

The larger the temperature difference between the heat transfer streams, the higher the irreversibility. Thus it is important to match the glides in heat exchanger to improve efficiency. Care should be taken when matching the gliding temperature of the zeotropic mixture and the external liquid. Unfeasible matching of temperature profiles could be the result. The pinch point must be set to the minimum value between the profiles and temperature difference or approach between the two streams must never become smaller than that specific value. (Itard, 1998)

In Figure 5.3(a) it can be seen that the heat transfer for a pure azeotropic mixture is at constant temperature. Figure 5.3(b) shows a non-linear heat transfer for a zeotropic mixture at non-constant temperature. The pinch point for the convex profile is found in the middle, at the minimum difference between the lines. If a concave profile should exist, the pinch point would be located at the end points of the heat transfer. Unfeasible heat transfer is also indicated, when the temperature profile passes the profile of the external medium.

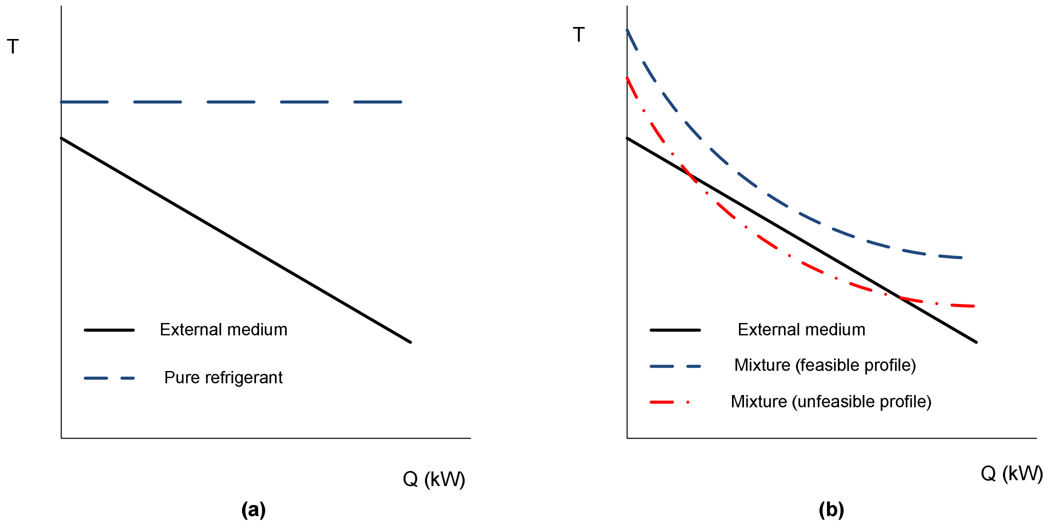

Figure 5.3 - Temperature profiles for heat transfer (a) pure refrigerant (b) zeotropic mixture (Recreated from Itard, 1998)

5.8.3 Temperature-concentration diagram

To better understand the composition change of the desorption and absorption in the HHP cycle, an example of the temperature-concentration diagram is illustrated.

A schematic for the temperature-concentration diagram (T-x diagram) for the mixture of ammonia and water is given in figure 5.4. The diagram was created in EES at constant atmospheric pressure of 1 bar, with the concentration of ammonia varying from 0 (only water present) to 1 (only ammonia present). Definitions for the specific lines and areas are given below:

- The boiling point line indicates the temperature at which the first bubble is formed for the specified pressure and concentration.
- The dew point line indicates the temperature at which the first liquid droplet is formed when a gas mixture of given concentration is cooled.
- The area below the boiling point line represents the subcooled liquid
- The area above the dew the dew point line represents superheated vapour.
- The area enclosed by the boiling and dew point lines is in the two-phase region.
- The boiling point for a mixture of concentration x is located at the intersection of the line at constant concentration with the boiling line.
- The boiling point of the pure components are found on the respective ordinates.

From literature in *Heat conversion systems* (Alefeld et al. 1994) the use of the T-x diagram is demonstrated. The example of an evaporation process of an ammonia/water mixture at constant pressure is discussed (points with a double prime indicate liquid phase: points with a single prime indicate vapour phase):

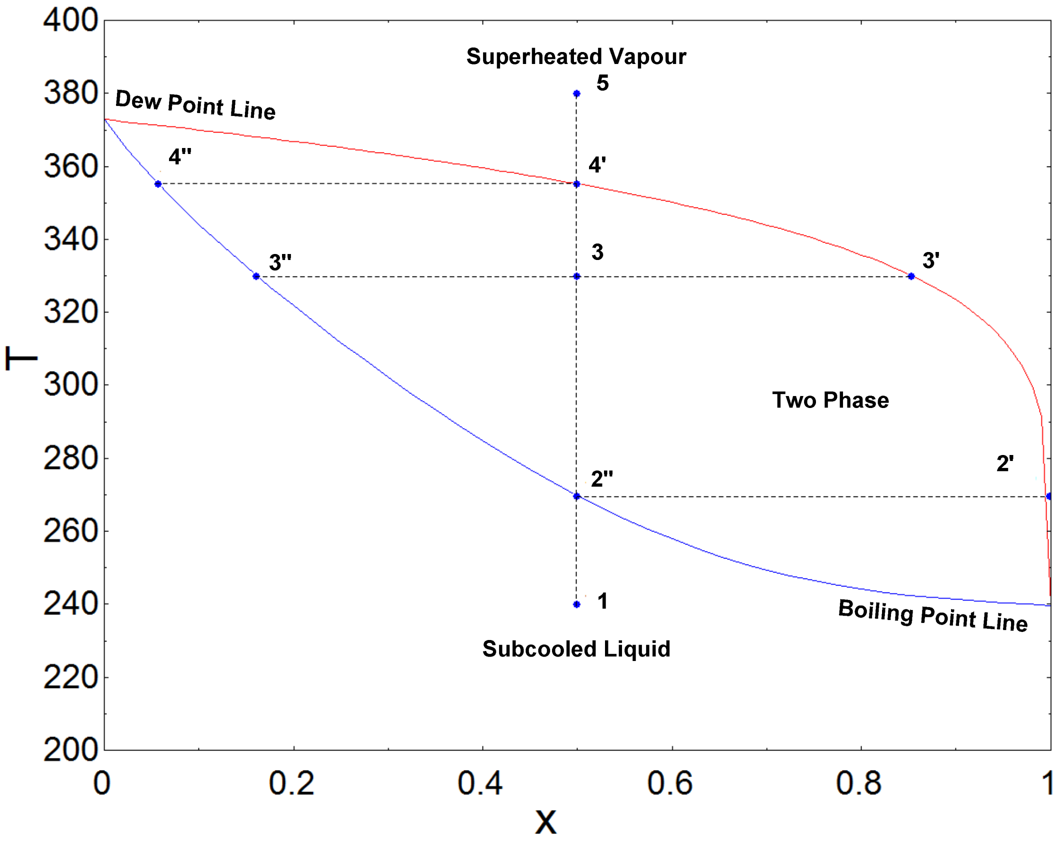

Figure 5.4 - T-x diagram for constant pressure

The refrigerant is the component with the higher vapour pressure of the two components. The other component is the absorbent. The temperature of a subcooled mixture at point 1 is increased to the boiling point line at 2”. Here the first bubble forms. The concentration of the vapour in the bubble which is in thermal equilibrium with the surrounding liquid is found at point 2’. This vapour has a large concentration of refrigerant. More heat is added to point 3 and more evaporation takes place. If all the vapour remains in contact with the remaining liquid, then the concentration of the vapour in equilibrium with the remaining liquid is represented by point 3’. The concentration of the remaining liquid is indicated by 3” after it has been depleted by the component at 3’. The vapour at 3’ also contains more of the evaporated absorbent than previously. The concentration of the liquid and vapour phases follow the boiling and dew point lines. More heat is added and point 4’ is reached where the evaporation process is completed. The vapour has the same concentration as the original subcooled liquid, and the concentration of the last evaporated droplet is indicated by 4”. If the mixture is heated further, a superheated vapour is produced at point 5’.

The values are given in the following table:

Table 5.1 - Concentration diagram values

Point	Temperature	Concentration	Quality
	T [K]	X [kg NH_3/kg mixture]	q
1	240	0.50	-0.001
2"	269.8	0.50	0
2'	269.8	0.99	1
3	330	0.50	0.49
3"	330	0.16	0
3'	330	0.85	1
4"	355.2	0.50	1
4'	355.2	0.06	0
5	380	0.50	1.001

The temperatures of the different point are given in Kelvin. The concentration is given as the mass of ammonia over the total mass at the point. The vapour quality is the mass of vapour over the total mass present at the point. The vapour quality is given as:

- -0.001 for subcooled liquid
- 0 for saturated liquid
- 1 for saturated vapour
- for superheated vapour.

During the constant pressure evaporation process, the saturation temperature changed from Point 2 to Point 4. The temperature difference is termed “temperature glide”. The temperature glide for this case is 85.4 K.

5.9 Other components

5.9.1 Pump

Minea and Chiriac (2006) found that cavitation exist in the pump when the desorption pressure is too low. This happens when the static pressure at the inlet of the liquid pump is close to the vapour pressure of ammonia in the mixture. This will cause bubbles to form in the impeller passages. These bubbles will collapse during compression in the pump and may damage the impeller.

This can be overcome by subcooling the liquid before the pump (Radermacher, 1991), increasing the pressures in the Desorber or providing the pump with a net positive suction head (NPSH) (Minea & Chiriac, 2006). The NPSH will cause a pressure in excess of the vapour pressure to prevent cavitation. The NPSH of each system will vary with the speed and capacity of the pump. Radermacher found that if subcooling was used to overcome the cavitation, that under stable conditions the subcooling in the solution line would be reduced to less than 0.5℃.

Hulten et al. (1998) mentioned that the solution pump can be modelled as isentropic. Big industrial pumps have isentropic efficiencies above 90% and thus the assumption of an isentropic pump could be reasonable.

5.9.2 Control

Radermacher (1991) used back-pressure regulating valves to regulate the pressure in the absorber very closely to a set value. This was done irrespective of the flow rates and eliminates continuously adjusting setting manually, especially during start-up operations.

Zhou and Radermacher (1996) also introduced a bypass across the compressor suction and discharge lines. This helped for start-up and capacity control. The cycle was bypassed completely during start-up. The bypass can then be gradually opened to the cycle, to achieve steady state conditions.

5.9.3 Expansion valve

In all the literature surveyed the expansion valve is assumed to be isenthalpic. This is the same as for vapour compression heat pumps.

5.10 Conclusion

In this chapter a survey was conducted on previous work done on the subject of hybrid heat pump (HHP) systems. From the literature it was found that HHP's are excellent for high temperature heat pump applications. High temperature lifts in the region of 100℃ with good COP can be achieved when coupling two cycles in a cascade. This is ideal for the high temperature gradients in the ethanol plant, where the temperatures in the processes vary between 25℃ and 105℃.

Various configurations of liquid recirculation are mentioned and will be investigated. Two stage HHP cycle with dry compression, wet compression and variation between the two will be investigated in paragraph 6.9. The work of Zatsev, Infante Ferreira and Zamfirescu could prove vital if the superheating of the working fluid is too high. The injection into the compressors will also be investigated in the simulation of the cycle.

The literature on the components also gives an idea of what components should be used to evaluate the economic analysis of the HHP in the ethanol plant. It can also help to give an indication of what components to use in an experimental prototype.

In several earlier studies the ammonia/water mixture has been identified as the most interesting working fluids. This non-azeotropic mixture has, therefore, been chosen for the present study.

Chapter 6 - Hybrid heat pump model

6.1 Introduction

In the chapter 3 of the *ethanol plant model*, it was found that high temperatures of up to 105°C was needed in the ethanol production process. There is also a large temperature difference between the tanks that vary from 25°C to 105°C.

The literature surveyed in the previous chapter stipulated that a two stage HHP, using ammonia and water as working fluid, would be ideal for application on the ethanol plant because of the high temperature lift and high temperatures that can be achieved.

In this chapter the *model* of the *hybrid heat pump* and the theory behind it will be discussed. The model was constructed within the constraints set by the company EFT. Making use of a heating source in the region of 120 kW could reduce the cost of the small ethanol plant. Thus the model of the heat pump should be modelled to satisfy this requirement.

6.2 Simulation strategy

The purpose of this simulation model is to predict the thermodynamic state of all the points in the cycle. This will make it possible to calculate the energy requirements of the compressor and the heat transfer in the heat exchangers. Even though the heating requirement of the plant is already known, the transfer of energy throughout the overall *two stage hybrid heat pump* (TSHHP) is needed to calculate the duration of heating and cooling in the plant.

The two cycles of the TSHHP can operate with different concentrations and pressures, due to the zeotropic nature of the ammonia/water mixture. According to Radermacher (paragraph 5.4) the pressures of the LT and HT cycles could be matched, with the HT cycle working with a low concentration of ammonia and the LT cycle working with a high concentration of ammonia. This procedure could simplify the calculations. Thus the maximum pressures of both cycles were fixed. This is feasible because back pressure expansion valves can be used to regulate the pressures. To create a base model the low pressure sides of the respective cycles were also fixed and matched.

The extra degree of freedom of the ammonia/water mixture, allows the temperature to be a function of the pressure and concentration of the mixture. If the pressures are fixed to certain values, the concentration can then be adjusted to achieve the required temperature and temperature lift for each cycle in the system.

The thermodynamic state of three points in the cycle is known. At the absorber outlet the ammonia/water mixture is a saturated liquid, with all of the ammonia absorbed in the mixture. At the desorber outlet, the desorption is incomplete and the working fluid leaves in two phases. A phase split is achieved, with a saturated vapour that leaves the desorber and flows to the compressor and a saturated liquid that leaves the desorber and flows to the pump.

A temperature gradient should be kept over the heat exchangers. Good practice is to set the temperatures in the absorber a few degrees higher than the inlet temperature of the external fluid. The same must be done on the desorption side, where the temperature in the desorber should be lower than the temperatures in of the external fluid.

Due to the high temperatures in the ethanol plant, the outlet temperature of the high temperature absorber is adjusted to approximately 105℃, the highest temperature. The outlet temperature of the desorber is fixed at 25℃, because it is the lowest temperature in the plant. From these precautions, heat transfer should easily take place, with the external streams now being heated or cooled. All of this is done to prevent unrealistic heat transfer, by supplying a minimum positive temperature gradient between the streams. The same is done at the absorber/desorber.

The mass flow of the system is also unknown. In order to obtain the mass flow, the heat duty at the desorber is fixed in the model. The heat duty of the desorber can then be adjusted to achieve the required heat duty at the absorber of around 120 kW.

In order to maintain the operating point of the mixtures in the cycle, it was decided not to change the temperatures and concentration for capacity control. The heat pump would work at the same operation conditions, but the external working fluid mass flow rate would be adjusted to keep the heat transfer from and to the hybrid heat pump constant.

Due to the cycle being a relative new technology, no detail component design was done for the individual components. In this study the model will only be used to evaluate the thermodynamic and economic feasibility of such a heat pump in the ethanol production process. In further research the model will be able to provide a basis from which to do detail design of the components.

As mentioned in paragraph 5.6, the successful experimental plant of Minea and Chiriac (2006) used a horizontal shell and tube heat exchanger with the recirculated weak solution forming a falling film over the tubes in the absorption process. To achieve this design, the TSHHP has to be modelled with the absorption taking place on the shell side of the absorber and the desorption on the tube side of the desorber. The same configuration used in the model of Radermacher (1991). Thus the configuration was chosen for the design of the absorber, absorber/desorber and desorber. The economizers are liquid to liquid shell-and-tube heat exchangers.

6.3 Ammonia/water properties

In order to calculate the thermodynamic state of all the points in the cycle, a simulation program has to be used for the modelling. Engineering Equation Solver (EES) V7.938-3D software (Klein, 2007) was used for the modelling, because it has a built in library for ammonia/water mixtures. With EES the thermodynamic properties of the ammonia/water mixture in the liquid and vapour phases are obtained. It can be used in the subcooled, saturated and superheated states.

The thermodynamic properties in EES are based on the correlations provided by Ibrahim and Klein (1993). They assumed ideal gas behaviour for the ammonia/water mixture in the vapour phase to obtain the properties. For the liquid phase, however, they used the Gibbs excess energy equation to account for the deviation from ideal gas behaviour. This helped to determine the properties of the mixtures, especially during liquid or two-phase regions.

The NH3H2O procedure in EES is used to return properties of the ammonia/water mixture. The Call statement is the procedures used to recall properties from EES (From EES Help file):

```
CALL NH3H2O(Code,In1,In2,In3: T, P, x, h, s, u, v, q)
```

The four parameters to the left of the colon are inputs to the procedure and the eight values to the right are outputs whose values are set by the NH3H2O procedure. The NH3H2O routine operates in SI units with:

- T = Temperature [K],
- P = Pressure [bar],
- x = Ammonia mass fraction [kg ammonia/kg mixture],
- h = Enthalpy [kJ/kg],
- s = Entropy [kJ/kg.K],
- u = Internal energy [kJ/kg],
- v = Specific volume [m^3/kg]
- q = Quality or vapour mass fraction [kg vapour/kg mixture].

For saturated states, $0 \leq q \leq 1$. Subcooled states are indicated with q = -0.01; superheated states have q = 1.01.

In order to obtain the property output, three of the eight properties of the mixture must be known in order to compute the others. The In1, In2, In3 refers to the known properties and Code to the position of the properties in the CALL procedure. For example, if the pressure, temperature and concentration are known, the Code should be 123.

Even if one of the outputs is known and only two inputs, the EES program will calculate the values iteratively. The transport properties of the mixtures were not calculated in this study. The viscosity, thermal conductivity, surface tension and diffusion coefficient of the liquid and vapour phases will however be needed to do detail design of the separate components in future work.

6.4 Thermodynamic cycle and model

The two stage hybrid heat pump (TSHHP) work on the same principle as a single stage HHP. The only difference is that a TSHHP comprises of two HHP cycles coupled together with a shared heat exchanger and has a greater temperature lift. According to Kotas (1995), the higher the temperature of energy, the higher the grade of the energy and ability to do work.

The low temperature (LT) cycle is used to transfer low grade energy to intermediate grade energy. This is where the high temperature (HT) cycle upgrades the intermediate energy to high grade energy. The cascade configuration gives the cycle the opportunity to upgrade low temperature heat to high temperature heat over a large temperature lift.

Components in the cycle are;

- Desorber;
- Absorber/desorber;
- Absorber;
- High temperature economizer;
- Low temperature economizer;
- Two expansion valves;
- Two compressors;
- Two liquid solution pumps.

The desorber has the lowest temperature in the TSHHP. This is where the TSHHP exchanges heat with the source. The shared heat exchanger, absorber/desorber, works at an intermediate temperature between the two cycles. It is actually the absorber of the low temperature cycle and the desorber of the high temperature cycle. The absorber works at the highest temperature in the TSHHP and is where heat is rejected to the sink.

In the following paragraph the operating principle and thermodynamic simulated model of the TSHHP cycle will be discussed. This will include the assumptions and the thermodynamic equations used in the model. Throughout the model only steady state conditions of the conservation equations were used. A schematic of a TSHHP is given in Figure 6.1. In the following paragraphs the points on the figure will be used as reference points.

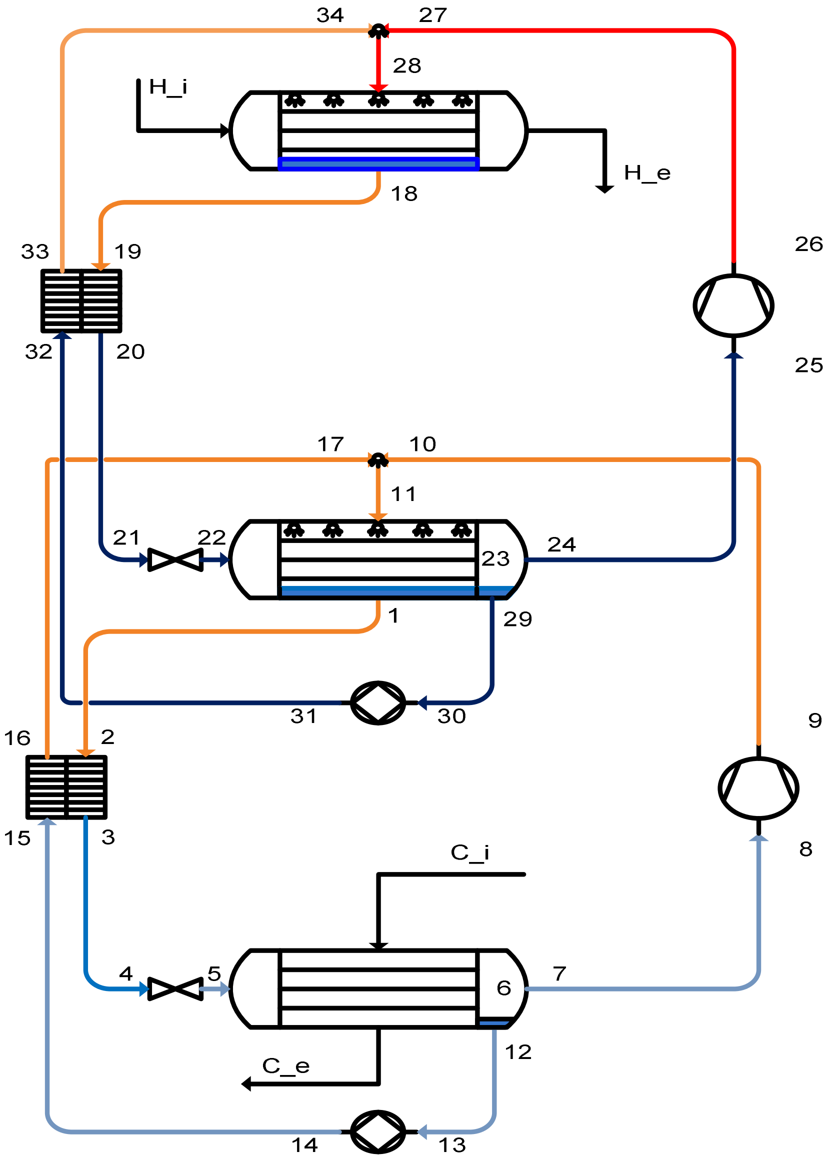

Figure 6.1 – Two stage Hybrid Heat Pump (TSHHP)

6.4.1 Operating point

The operating point (OP) is found at point 1, in the absorber/desorber, and at point 18, in the absorber. Saturated liquid ($q = 0$) leaves the shell side, after the absorption process took place. The point at the exit of the absorber is chosen as the operating point, because it is the only point in the respective cycles where the working fluid is in a single phase, total mass flow is not separated and the temperature could be fixed. The liquid solution at the OP also has a high concentration of ammonia, because all the ammonia is absorbed into it.

At the OP the concentration and high pressures of each cycle can be adjusted respectively. From the NH3H2O procedure (paragraph 6.3), the thermodynamic properties can be calculated:

$$T_{OP}; h_{OP}; s_{OP}; u_{OP}; v_{OP} = f\ (P_{OP}; x_{OP}; q_{OP})$$

With

$$P_{OP} = \text{Fixed value}$$

$$x_{OP} = \text{Fixed value}$$

$$q_{OP} = 0$$

6.4.2 Economizer

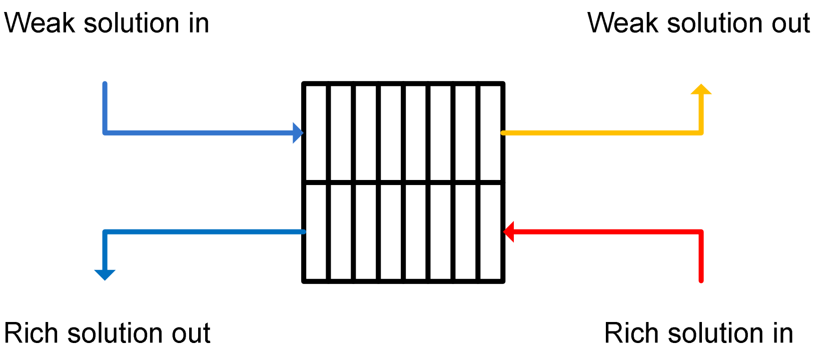

Figure 6.2 – Schematic of the economizer

The economizer is a counter current solution-to-solution heat exchanger. It is an important part of the cycle, because it increases the efficiency of the cycle by cooling and heating the liquid streams.

In the economizer the rich solution, liquid with a high concentration of ammonia, exchanges heat with the weak solution, liquid with low concentration of ammonia. The rich solution is at a high temperature and pressure and originates at the OP which is at the exit of the absorber side of the heat exchangers. The weak solution originates at the liquid outlet of the desorber, where it is pumped to the economizer.

On the rich solution side, temperature is decreased to lower the temperature of the liquid before passing through the expansion valve. This will lower the temperature at which the desorber operates, even more than if no liquid heat exchange is done, and increase the temperature lift of the cycle. The energy balance of the rich solution side, from LT cycle points 2–3 and HT cycle points 19-20, is given below:

$$Q_{economizer} = \dot{m}_{rich,i}h_{rich,i} - \dot{m}_{rich,e}h_{rich,e} \tag{6.1}$$

On the weak solution side, temperature is increased to bring the recirculated solution temperature closer to the saturation temperature of the mixture before entering the Absorber. The energy balance of the weak solution side, from LT cycle points 15-16 and HT cycle points 32-33, is determined by:

$$Q_{economizer} = \dot{m}_{weak,e}h_{weak,e} - \dot{m}_{weak,i}h_{weak,i} \tag{6.2}$$

The mass balance for the binary mixture and ammonia, over the economizer is determined by:

$$\dot{m}_{rich,i} + \dot{m}_{weak,i} = \dot{m}_{rich,e} + \dot{m}_{weak,e} \tag{6.3}$$

$$\dot{m}_{rich,i}x_{rich,i} + \dot{m}_{weak,i}\,x_{weak,i} = \dot{m}_{rich,e}x_{rich,e} + \dot{m}_{weak,e}\,x_{weak,e} \tag{6.4}$$

6.4.3 Expansion valve

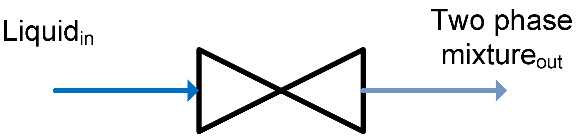

Figure 6.3 – Schematic of the expansion valve

After the liquid solution is cooled, it passes through an expansion valve from LT cycle points 4-5 and HT cycle points 21-22. The liquid is passed from a high pressure, on the absorber side, to the lower pressure, on the desorber side. The working fluid is expanded, causing it to flash into a cool two-phase mixture. The expansion valve is isenthalpic. Thus there is no heat transfer in the expansion process. The energy balance over the expansion valve is determined by:

$$\dot{m}_{liquid,i}h_{liquid,i} = \dot{m}_{mix,e}h_{mix,e} \tag{6.5}$$

The mass balance for the binary mixture and ammonia, over the expansion valve is determined by:

$$\dot{m}_{liquid,i} = \dot{m}_{mix,e} \tag{6.6}$$

$$\dot{m}_{liquid,i}x_{liquid,i} = \dot{m}_{mix,e}x_{mix,e} \tag{6.7}$$

With the properties calculated at the exit, with the inlet enthalpy:

$$h_{mix,e}\ ;q_{mix,e} = f\ (P_{mix,e};x_{mix,e};h_{mix,i}) \tag{6.8}$$

6.4.4 Desorber

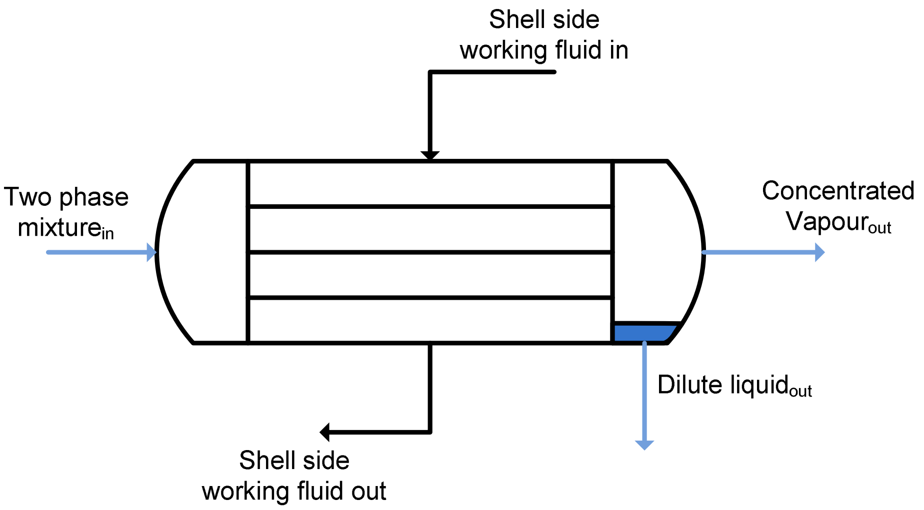

Figure 6.4 – Schematic of the desorber

The desorber is a shell-and-tube heat exchanger with the desorption process taking place on the tube side. The cool two-phase mixture from the expansion valve enters the desorber. The working fluid on the tube side absorbs heat from a hot external working fluid on the shell side of the desorber, from LT cycle points 5-6 and HT cycle points 22-23.

The transfer of heat from the heat source causes more evaporation/desorption of ammonia and a small amount of water from the working fluid. The nature of the zeotropic mixture of ammonia and water lets the evaporation/desorption temperature increase through the desorber. This means that the temperature at the outlet is higher than the inlet. This phenomenon is known as the temperature glide and is discussed in paragraph 5.8.2. The desorption process in the desorber is incomplete at the end of the heat transfer, and a phase splitter or separator is used to direct the vapour to the compressor and the liquid to the pump.

A temperature difference should be maintained throughout the length of the desorber. The temperature on the tube side should be kept lower than the temperature of the external working fluid, to maintain natural transfer of energy from a high temperature to a low temperature. The counter-current nature of the shell and tube heat exchanger, allows to fix the maximum temperature at the outlet of the desorber. This will be done at a temperature that will always be lower than the lowest temperature in the ethanol production process.

$$T_{desorber,e} = \text{Fixed value} \tag{6.9}$$

The heat transfer can be calculated according to the difference in enthalpy across the heat exchanger. This will give a measure of the change in energy between the inlet and outlet.

The overall heat transfer to the desorber can be calculated with the energy balance:

$$Q_{desorber} = \dot{m}_{desorber,e}h_{desorber,e}-\dot{m}_{desorber,i}h_{desorber,i} \tag{6.10}$$

The mass balance for the binary mixture, over the desorber is determined by:

$$\dot{m}_{desorber,i}= \dot{m}_{desorber,e} \tag{6.11}$$

Even though there is a concentration change of the liquid and vapour in the desorber, it only changes the boiling point of the stream. The overall concentration of the ammonia remains constant

$$\dot{m}_{desorber,i}x_{desorber,i} =\dot{m}_{desorber,e}\, x_{desorber,e} \tag{6.12}$$

6.4.5 Separator

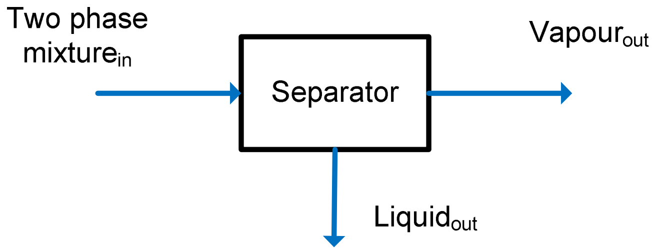

Figure 6.5 – Schematic of the separator

The separator is used as a phase splitter, to separate the vapour and liquid at the end of the desorber. In an actual heat exchanger, this would be done inside the desorber with a vapour outlet going to the compressor and a liquid outlet at the bottom, recirculating the undesorbed liquid with a pump.

It is modelled as an adiabatic separator with no heat transfer. The mixture enters as a two-phase mixture at points 6 and 23 for the respective cycles. The mixture is separated and leaves the desorber as a saturated liquid (q = 0) at points 12 and 29, from the bottom. A saturated vapour (q = 1), leaves from the top at points 7 and 24. This is done at constant pressure for both cycles. The vapour has a high concentration of ammonia, while the liquid has a low concentration of ammonia.

The energy balance over the separator is determined by:

$$\dot{m}_{mix,i}h_{mix,i} = \dot{m}_{vapour,e}h_{vapour,e}+\dot{m}_{liquid,e}h_{liquid,e} \tag{6.13}$$

The mass balance for the binary mixture and ammonia, over the economizer is determined by:

$$\dot{m}_{mix,i} = \dot{m}_{vapour,e}+\dot{m}_{liquid,e} \tag{6.14}$$

$$\dot{m}_{mix,i}\,x_{mix,i} = \dot{m}_{vapour,e}x_{vapour,e}+\dot{m}_{liquid,e}x_{liquid,e} \tag{6.15}$$

With the properties of the exit conditions calculated iteratively

$$h_{vapour,e} = f\ (P_{vapour,e};x_{vapour,e};q_{vapour,e})$$

$$q_{vapour,e} = 1$$

$$h_{liquid,e} = f\ (P_{liquid,e};x_{liquid,e};q_{liquid,e})$$

$$q_{liquid,e} = 0$$

6.4.6 Compressor

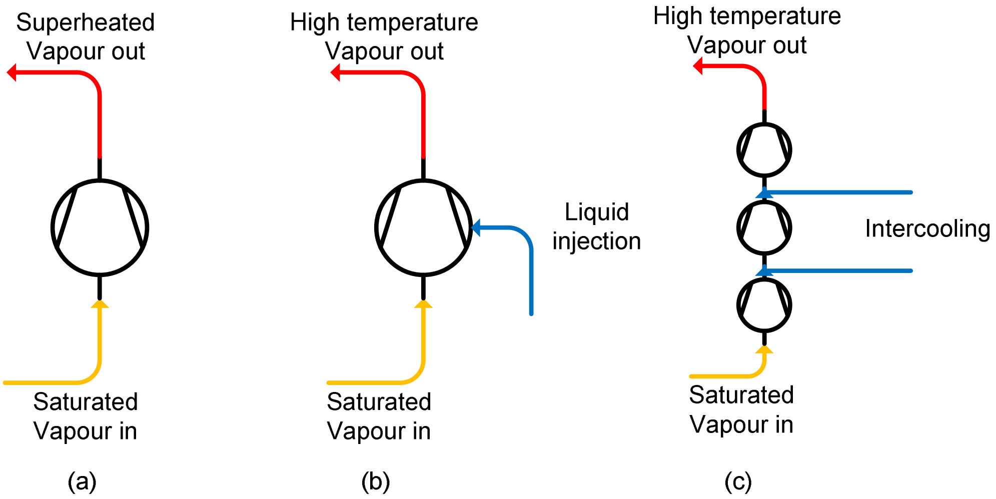

Figure 6.6 – Schematic of the three types of compressor models. (a) Dry compression (b) Liquid injection (c) Multistage compression with intercooling

The vapour from the desorber enters the compressor, where it is compressed, raising the pressure and temperature. The compression is done for LT cycle from points 8–9 and HT cycle from points 25-26.

From the literature surveyed in paragraph 5.5 it is found that the compression can be simulated in three different ways: wet compression, dry compression, and a variation between the two. Wet compression was found to be impractical, because it is a concept that is still in the development stages. Dry compression and partial injection of the liquid into the compressor was considered in the model. Twin Screw compressors are tolerant to liquid carryover, and will be used in the model.

With dry compression the following method was used in the calculation. The work done by the compressor is calculated as the difference in enthalpy over the compression:

$$W_{compressor} = \dot{m}_{compressor,e} h_{compressor,e} - \dot{m}_{compressor,i} h_{compressor,i} \tag{6.16}$$

To obtain the work over the compressor the following procedure was followed:

The mass balance for the binary mixture and ammonia, over the compressor remains constant. Only vapour enters the compressor.

$$\dot{m}_{compressor,i} = \dot{m}_{compressor,e} \tag{6.17}$$

$$\dot{m}_{compressor,i}x_{compressor,i} = \dot{m}_{compressor,e}x_{compressor,e} \tag{6.18}$$

The energy balance over the compressor is done first by determining the inlet enthalpy of the vapour. The inlet vapour is considered to be saturated vapour (q = 1).

$$h_{compressor,i} \ ;s_{compressor,i} = f\ (P_{compressor,i};x_{compressor,i};q_{compressor,i}) \tag{6.19}$$

The conservation of momentum is simplified as:

$$\Delta P_{compressor} = \left(P_{compressor,e} - P_{compressor,i}\ \right) \tag{6.20}$$

With the pressure ration given by:

$$PR = \frac{P_{compressor,e}}{P_{compressor,i}} \tag{6.21}$$

Isentropic compression is assumed. For ideal isentropic compression the entropy over the compressor remains constant.

$$s_{is} = s_{compressor,i} \tag{6.22}$$

Isentropic enthalpy can then be derived as

$$h_{is} = f(P_{compressor,e};x_{compressor,e};s_{is})$$

With the work for isentropic compression given by

$$W_{isentropic} = \dot{m}_{compressor,e}h_{is} - \dot{m}_{compressor,i}h_{compressor,i} \tag{6.23}$$

According to Hulten (1997) the isentropic efficiency of a screw compressor can be given by the following:

$$PR = 2 - 3.5 \qquad \eta_{is} = -0.143 + 0.55PR - 0.0867PR^2 \tag{6.24}$$

$$PR = 3.5 - 10 \qquad \eta_{is} = -0.766 + 0.0131PR \tag{6.25}$$

The isentropic efficiency can then be used to calculate the actual compressor work. The isentropic efficiency of the compressor is defined as

$$\eta_{is} = \frac{W_{isentropic}}{W_{compressor}} \tag{6.26}$$

If some of the liquid is injected into the compression chamber as in the work of Infante Ferreira et al. (2006), the amount of superheat and in turn the maximum temperature can be reduced. To simulate this an ideal adiabatic mixer was used before the compression model.

The two-phase mixture is then sent through the compressor. The outlet enthalpy is then assumed to be saturated vapour with $q_e = 1$.

$$h_e = f\ (P_e;x_e;q_e)$$

The same procedure is then followed to calculate the compressor work.

The volume displaced by the compressor was calculated by the following. The inlet specific volume was taken as a function of the inlet conditions and then multiplied with the mass flow.

$$v_{compressor,i} = f\ (P_{compressor,i};x_{compressor,i};q_{compressor,i})$$

$$\dot{V}_{compressor} = \dot{m}_{compressor,i} v_{compressor,i} \qquad (6.27)$$

Assumption was made that all the energy required by the compressor would be transferred to the stream, because the compressor cooling heat transfer fluid would also reject heat to the sink.

The different compression configuration, shown in figure 6, was also investigated in the model.

6.4.7 Pump

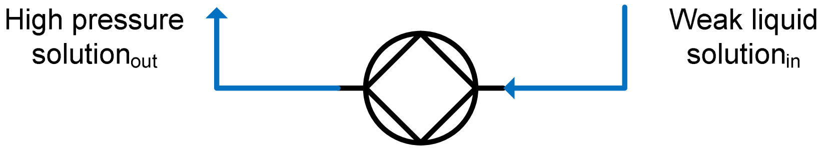

Figure 6.7 – Schematic of the liquid pump

The liquid from the desorber, with a low concentration of ammonia, is recirculated with a pump to the absorber after passing through the economizer. The pump increases the pressure of the weak solution for LT cycle from points 13–14 and HT cycle from points 30-31. The energy conservation over the pump can be described with:

$$W_{pump} = \dot{m}_{pump,e} h_{pump,e} - \dot{m}_{pump,i} h_{pump,i} \qquad (6.28)$$

The following procedure was used to calculate the pump work:

First the thermodynamic properties was calculated for the saturated liquid (q = 0) leaving the desorber. The inlet pressure and the concentration is the same as in the pressure and concentration of the liquid leaving the desorber after the separator.

$$h_{pump,i};v_{pump,i} = f\,(P_{pump,i};x_{pump,i};q_{pump,i})$$

The mass balance for the binary mixture and ammonia, over the pumps remain constant. Only liquid enters the pumps.

$$\dot{m}_{pump,i} = \dot{m}_{pump,e} \tag{6.29}$$

$$\dot{m}_{pump,i}x_{pump,i} = \dot{m}_{pump,e}x_{pump,e} \tag{6.30}$$

This was used to calculate the hydraulic head of the pump over the temperature gradient

$$\rho_{pump} = \frac{1}{v_{pump,i}} \tag{6.31}$$

$$\dot{V}_{pump} = \dot{m}_{pump,i}v_{pump,i} \tag{6.32}$$

$$H_{pump} = \frac{(P_e\text{-}P_i)}{\rho g} + (z_e\text{-}z_i) \tag{6.33}$$

Since it is a closed circuit the height difference is zero

$$(z_e\text{-}z_i)=0 \tag{6.34}$$

Solving equations 6.32 – 6.34 and substituting them into equation 6.35 will deliver the pump work.

$$W_{pump} = \frac{\rho_{pump} g \dot{V} H_{pump}}{\eta_{is,pump}} \tag{6.35}$$

6.4.8 Mixer

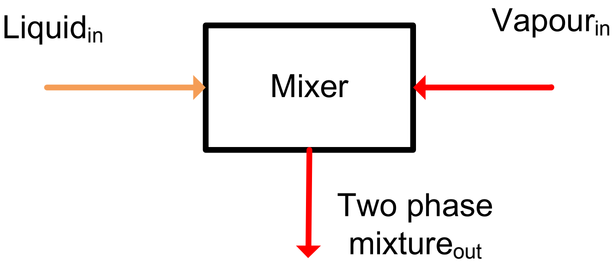

Figure 6.8 – Schematic of the Mixer

The mixer is used to combine the high temperature vapour leaving the compressor with the weak solution liquid that exits the economizer. For the LT cycle the streams from points 10 and 17 are combined and leaves at point 11 and for the HT cycle the streams from points 27 and 34 are combined and leaves at point 28.

In an actual heat exchanger, the mixing is only done in the vapour stream to desuperheat vapour from the compressor, while the rest is sprayed over the tubes in the absorber to promote the absorption process over the tubes on the shell side of the heat exchanger. For the model, the vapour from the compressor and liquid from the solution circuit is mixed ideally and enter the absorber as a two phase mixture. The mixer is adiabatic and the energy balance is given by:

$$\dot{m}_{vapour,i}h_{vapour,i} + \dot{m}_{liquid,i}h_{liquid,i} = \dot{m}_{mix,e}h_{mix,e} \tag{6.36}$$

The mass balance for the binary mixture and ammonia, over the mixer remain constant.

$$\dot{m}_{vapour,i} + \dot{m}_{liquid,i} = \dot{m}_{mix,e} \tag{6.37}$$

$$\dot{m}_{vapour,i}x_{vapour,i} + \dot{m}_{liquid,i}x_{liquid,i} = \dot{m}_{mix,e}x_{mix,e} \tag{6.38}$$

The properties of the mixture can then be calculated with the NH3H2O procedure.

$$T_{mix,e};s_{mix,e}\ ;u_{mix,e}\ ;s_{mix,e}\ ;_{mix,e} = f\ (P_{mix,e},;x_{mix,e};h_{mix,e})$$

6.4.9 Absorber

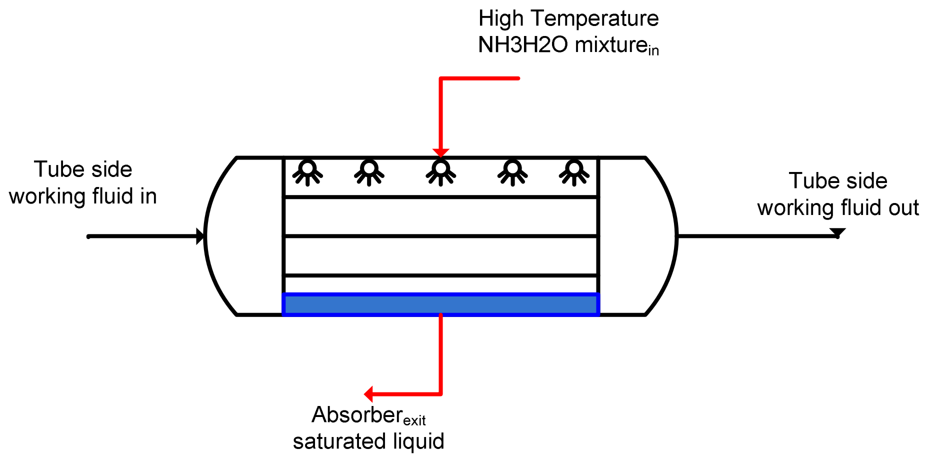

Figure 6.9 – Schematic of the Absorber

The absorption takes place on the shell side of the intermediate temperature absorber/desorber for the LT cycle from point 11-1. In the high temperature absorber, the absorption takes place from point 28-18. As mentioned in the mixer model, the ammonia is absorbed into the weak solution that forms a film over the outside of the tubes. The absorption of ammonia into water is an exothermic reaction that produces more heat.

A temperature difference should also be kept over the absorption on the shell side and the external fluid or desorption from the HT cycle on the tube side. Heat is then transferred to the tube side. The temperature in the absorber decreases as the concentration of ammonia increases. After all the heat is transferred to the tube side, the mixture leaves the absorber/desorber on the shell side as a saturated liquid (q = 0).

The overall heat transfer in the absorber can be calculated by the difference in energy of the streams over the inlet and outlet.

$$Q_{absorber} = \dot{m}_{mix,i}h_{mix,i} - \dot{m}_{absorber,e}h_{absorber,e} \tag{6.39}$$

The mass balance of the absorber remains constant

$$\dot{m}_{mix,i} = \dot{m}_{absorber,e} \tag{6.40}$$

Even though there is a concentration change of the liquid and vapour in the cycle, it only changes the boiling point of the stream. The overall concentration of the ammonia remains constant.

$$\dot{m}_{mix,i}x_{mix,i} = \dot{m}_{absorber,e}x_{absorber,e} \tag{6.41}$$

The vapour is absorbed into the solution, the remaining vapour condenses and leaves as a saturated liquid (q = 0). This is the same point as the OP in paragraph 6.4.1.

$$h_{absorber,e} = f\ (P_{absorber,e};x_{absorber,e};q_{absorber,e})$$

6.5 External heat transfer fluid

The external heat transfer fluid is used to serve as the heat source and a heat sink for the HHP model. A liquid with constant specific heat was chosen to simplify the model. Possible working fluids in the model are water or ethylene glycol/water mixture. At the high temperature side, the external fluid might change phase due to the high temperature. For water this can be countered by increasing the pressure of the external cycle or by using a high enough glycol/water mixture concentration to increase the boiling point of the mixture.

To simplify the external working fluid cycle and control in the ethanol plant it is proposed to adjust the mass flow of the external working fluid, to keep the heat transfer over the absorber and desorber constant. This will be easier than changing the concentrations or capacity of the compressors for control. It is expected that the efficiency of the desorber and absorber will also vary if the mass flow is adjusted.

On the heat sink side the heat transfer fluid receives the heat rejected by the absorber and its temperature increases:

$$Q_{absorber} = \dot{m}_{h,e}h_{h,e} - \dot{m}_{h,i}h_{h,i} \tag{6.42}$$

On the heat source side the heat transfer fluid rejects the heat to the desorber and its temperature decreases:

$$Q_{desorber} = \dot{m}_{c,i}h_{c,i} - \dot{m}_{c,e}h_{c,e} \tag{6.43}$$

The mass flow of the external stream also remains constant over the heat exchangers.

$$\dot{m}_i = \dot{m}_e \tag{6.44}$$

6.6 Friction and heat losses

Simple pressure losses were incorporated into the model for the heat exchangers and interconnecting piping.

$$\Delta P_{loss} = 0.5\alpha(P_e - P_i) \tag{6.45}$$

With $\alpha = 0.02$ for heat exchangers and $\alpha = 0.01$ for the piping as fractional losses. (Rousseau, 2007)

Even though all the equipment will be well insulated, a loss of heat over the piping was also introduced into the model for greater accuracy.

$$Q_{loss} = \dot{m}_e h_e - \dot{m}_i h_i \tag{6.46}$$

The mass flow through the piping network remains constant.

$$\dot{m}_i = \dot{m}_e \tag{6.47}$$

6.7 Heat exchange model

The economic analysis requires a realistic heat exchanger model in order to calculate the heat exchanger size and configuration. According to literature in Incropera and De Witt (2002:641-680) there are two main methods for determining heat transfer in heat exchangers:

- The log mean temperature difference (LMTD)
- Effectiveness-NTU

The LMTD method takes the variations of temperatures between the inlets and outlets. It is a simple method to use when the inlet and outlet conditions of the heat exchangers are known or easily determined. The LMTD method is given by:

$$Q = UA\Delta T_{LMTD} \tag{6.48}$$

$$\Delta T_{LMTD} = \frac{\left(T_{h,i} - T_{c,o}\right) - \left(T_{h,o} - T_{c,i}\right)}{\ln\left(\left(T_{h,i} - T_{c,o}\right)/\left(T_{h,o} - T_{c,i}\right)\right)} \tag{6.49}$$

Where U = Overall heat transfer coefficient [W/m^2.K]

A = Heat transfer area [m^2]

T = Temperature [K]

With subscripts

h = hot stream

c = cool stream

i = initial condition

e = exit condition

This method has limitations when the inlet or outlet temperatures need to be determined. The LMTD method will then require a iterative procedure. It is recommended that the effectiveness-NTU would be better suited to such cases, because it is based on the effectiveness of the heat exchanger to transfer a given amount of heat. Thus the effectiveness-NTU method would be better suited for modelling the heat exchange in the HHP.

The specific heat can be calculated during the ammonia/water mixture by applying the definition over a small increment, since the enthalpies and temperatures are easily available from the NH3H2O property function.

$$C_p = \frac{\Delta h}{\Delta T} \tag{6.50}$$

Where C_p = Specific heat [kJ/kg.K]

Δh = Change in enthalpy [kJ/kg]

ΔT = Change in temperature [K]

In order to define the effectiveness of the heat exchanger it is nessasary to determine the maximum possible heat transfer. The minimum of the product of the mass flow and specific heat are first calculated. This is needed because in an infinitely large heat exchanger, one of the fluid streams have the capability of achieving the maximum temperature difference between the hottest and coldest temperature:

$$\Delta T_{max} = \left(T_{h,i} - T_{c,i}\right) \tag{6.51}$$

$$C_{max/min} = \dot{m}C_p \tag{6.52}$$

$$C_{ratio} = \frac{Cmin}{Cmax} \tag{6.53}$$

$$Q_{max} = C_{min}\,\Delta T_{max} \tag{6.54}$$

Where ΔT_{max} = Maximum change in temperature [K]

Q_{max} = Maximum possible heat transfer [kW]

The *effectiveness* of the heat exchanger can now be defined by:

$$\varepsilon = \frac{Q}{Q_{max}} \tag{6.55}$$

The *number of transfer units* (NTU) can now be determined. There are two different relations for the equations used in this study. The first is for counterflow heat exchange

$$NTU = \frac{1}{\left(C_{ratio}-1\right)} \ln\left(\frac{\varepsilon-1}{\varepsilon C_{ratio}-1}\right) \tag{6.56}$$

The second is when the $C_{ratio} = 0$

$$NTU = -\ln(1-\varepsilon) \tag{6.57}$$

If the UA is known the NTU is determined by

$$\mathrm{NTU} = \frac{\mathrm{UA}}{C_{\mathrm{min}}} \tag{6.58}$$

The effectiveness can now be calculated for counterflow heat exchange

$$\varepsilon = \frac{1-\exp\left[-\mathrm{NTU}\left(1-C_{\mathrm{ratio}}\right)\right]}{1-C_{\mathrm{ratio}}\exp\left[-\mathrm{NTU}\left(1-C_{\mathrm{ratio}}\right)\right]} \tag{6.59}$$

The second is when the Cratio = 0

$$\varepsilon=1-\exp\left(-\mathrm{NTU}\right) \tag{6.60}$$

The heat exchanger model is used to determine the heat exchanger size. This will play a vital part in the cost analysis of the TSHHP system. The transport properties of the mixture were not calculated in this study. For that reason the overall transfer coefficient was selected from experimental and calculated values in literature. The heat transfer could then be calculated.

6.8 Summary

In this chapter the model for the *two stage hybrid heat pump* was described in detail. The model will enable a thermodynamic study to be done on the features of the cycle. The different configurations for the compressor will be tested. The influence such as mass flow, pressure level and temperature glide over the heat exchanger will also be studied in the model. A model for the heat exchanger is also given and will also be evaluated.

In the next chapter the results of the simulation will be given and discussed. The model has to be tested with another program to verify if the model is correctly simulated. This verification will also be done in the next chapter.

The result of the simulation will provide the data necessary to do a economic evaluation of the TSHHP in comparison with conventional systems. This will be done in chapter 7.

Chapter 7 - Model results and discussion

7.1 Introduction

In this chapter the results from the model developed in chapter 5 will be discussed. Investigations on the model was done for the following

- A base model was created to satisfy the requirements
- The compression types were investigated (paragraph 6.4.6)
- The thermodynamic property diagrams of the base model is discussed
- The model characteristics are studied to obtain a better understanding of TSHHP
- External heat transfer control to the ethanol plant is also discussed.

At the end of the chapter an optimized model was simulated that is used in the ethanol plant integration in the next chapter. The model was also validated with an industry standard simulation program, ASPEN (paragraph 7.8.).

7.2 Base model

A base model was simulated to create a starting point, from where a study of the characteristics of the TSHHP could be conducted due to changes of the inputs parameters. The base model was simulated with a temperature lift of 104°C over the average temperatures in the desorber and absorber. The rest of the parameters were set according to the simulation strategy in paragraph 6.2. A quick recap will be given.

The OP (paragraph 6.4.1) at the exit of the absorber (Point 20, Figure 6.1), was first to be set. The high pressure of each cycle was set to approximately 10 bar. The concentration was then adjusted to reach the temperature at the exit of the absorber of 105°C (378 K). The temperature at the outlet of the desorber was also fixed, to 25°C (298 K). This is done to maintain a temperature gradient in the heat exchangers. These temperatures were chosen, because the maximum temperature of external heat transport fluid (HTF) to the absorber will never exceed the absorber outlet temperature. This due to the fact that the maximum temperature requirement of the ethanol plant is 105°C (paragraph 6.2) and losses can be assumed in the HTF system, due to the high temperature of the pipes.

The same was done in the desorber, where the outlet temperature was fixed to 25°C (298 K) at the outlet. Temperatures in the ethanol plant are never below 25°C (paragraph 6.2.) and the selection of this temperature will maintain a temperature gradient. The pressure on the low pressure side of the desorption processes in the absorber/desorber was adjusted to maintain a minimum temperature difference of approximately 4-5℃ between the desorption side of the HT cycle and absorption side of the LT cycle. The pressures were also adjusted to maintain a temperature lift in the respective cycles between 50 – 60℃. The low pressures were found to be in the region of 1.5 bar, keeping them above 1 bar to prevent intrusion into the heat exchangers as mentioned in paragraph 4.8.

The efficiencies of the heat exchanger never exceed 85%, especially at the critical conditions where a high temperature fluid has to be heated, or cool liquid cooled. The efficiencies of the compressors was set to 60%. This was lower than the efficiencies obtained from equation 5.30. The equation resulted in efficiencies of up 75% for certain pressure ratios. This was too optimistic. With liquid injection, the research of Infante Ferreira et al. mentioned efficiencies of 55 %, but with high losses through labyrinth flow. This value could easily be improved upon, so it was decided to use a 60% isentropic efficiency throughout the study, to give realistic answers.

The end result was a model with a temperature lift of around 104℃, with around 120 kW of heating and 65 kW of cooling available. The COP however still depended on the compression type used. The different compression types and thermodynamic property diagrams will now be discussed in the next paragraphs to get a better understanding of the TSHHP.

7.3 Compression type

The different types of compressions mentioned in paragraph 5.4 were implemented into the base model. Dry compression, injection into the compression and multistage compression with intercooling was considered. The result of the simulation is in Table 7.1.

Table 7.1 - Different types of compression implemented on the base model.

Type of	**Maximum discharge temperature**		**Work**	**COP$_{heating}$**
compression	[℃]	[K]	[kW]	
Dry	330.75	603.9	61.21	2.03
Multistage	188.25	461.4	56.85	2.107
Injection	142.45	415.6	56.74	2.111

The first model was that of dry compression. The problem encountered was that compression of the vapour in the HT cycle resulted in temperatures of over 300℃. This is beyond the maximum temperatures of dry compressors (Howden compressors: maximum temperature of 225°C) and will cause overheating and even seizing of compressors. The compression power consumption was also higher, which in turn lowered the COP (paragraph 4.3).

The second model was that of multistage compression. This was done with dry compression of the vapour, but by desuperheating the vapour that is discharged from the compressor. This could be done with an intercooler or a liquid spray that is enough to desuperheat the vapour to a saturated vapour. The maximum discharge temperature decreased to 188°C, and with an improvement in COP. Multistage dry reciprocating compressors could suffer catastrophic failure if liquid droplets enter the compression chamber, if it is used for multistage compression. A separation system should then be incorporated into the design. Using more than one compressor is also an option, or using intercooling heat exchangers between stages. The problem with this setup is that it is impractical in small heat pumps and would increase the cost of the TSHHP considerably.

Liquid injection into the compression was then considered. The setup improved the maximum discharge temperatures to 142°C. The injection should be just enough to ensure that the vapour is saturated at the end of compression. The setup also increased the COP and decreased the maximum work input. This setup would be the most practical since the concept has been proved by Infante Ferreira et al. (2005) with reasonably high efficiencies (55%). They used dry screw compressors with total wet compression. Using only partial injection with twin screw compressors, will prove to be more practical, with higher efficiencies and tolerance to liquid carryover. Due to this, liquid injection is chosen as the best option and will be the only configuration considered further in the chapter.

The results and temperature-concentration diagrams of the different compressor configurations are given in Appendix B.

7.4 Thermodynamic property diagrams

Understanding the T-s, T-x and P-h diagrams is fundamental to understanding the thermodynamic relationship of a cycle and its properties. Diagrams were created in EES for the TSHHP cycle base model. The following relationships will be discussed in the figures:

- Temperature vs. concentration diagram (Figure 7.1)
- Temperature vs. entropy diagram (Figure 7.2)
- Pressure vs. enthalpy for the low temperature cycle (Figure 7.3)

As mentioned in the thermodynamic model (paragraph 6.4), the OP pressure and concentration were adjusted to get the necessary temperatures in the cycle. This can be seen in Figure 7.1, 7.2 and 7.3, where point 1 and 20 are on the saturated liquid line (bubble point line), at 10 bar.

The cycle starts at the OP of each cycle, point 1 for LT cycle and point 20 on the HT cycle. The stream decreases in temperature by exchanging heat in the economizers from 1-3 and 20 – 22. The working fluid passes through the expansion valve from 3 - 5. The temperature at the exit of the expansion valve decreases due to the lower pressure, as can be seen in figure 7.1 and 7.2. Note in Figure 7.3 that the expansion is isenthalpic from points 3-5, with the decrease in pressure.

Heat is transferred from the external heat transfer fluid to the cooler two phase mixture. (point 5: Figures 7.1 and 7.2). The temperature in the desorber increases to point 6. Note in Figures 7.1 and 7.2 that the temperature in the desorber increases due to the zeotropic nature of the HHP working fluid. This is done at constant pressure, Figure 7.3.

After heat transfer the mixture is in separate phases and the separator produces a phase split. The one part exits as a saturated vapour at points 7 and 26 and the other as saturated liquid, at points 15 and 34. Note the concentration difference of the two saturated streams in Figure 7.1.

The pressure of the saturated liquid is increased with the pump from points 12-15 in Figure 7.3. The temperature of the liquid stream increases as it passes through the economizer from point 15-16 and 34-35. The saturated vapour enters the compressor, but is mixed in the compression chamber with some of the recirculated liquid exiting the economizer. This results in a two phase mixture from points 7-9 and 26-28. The amount of liquid injection is just enough to ensure that all of the liquid evaporates in the compressor and exits the compressor as a saturated vapour, as can be seen in the figures. The vapour from the exit of the compressor is now mixed with the remaining liquid from the economizers at points 11 and 30. Note in Figure 7.1 that the concentration of the mixture is back to the original concentration.

Point 11 and 30, is at the inlet of the absorber. Heat is transferred to the external working fluid. The temperature decreases as heat is transferred from the absorber indicated from points 11-1 and 30-20. Note the temperature glide during the absorption process in the figures.

Also shown in Figure 7.3 is that there is a pressure drop throughout the system, especially at the heat exchangers. The low isentropic efficiency that was selected for the compressor can also be seen with the entropy generated in the compression process in Figure 7.2, from points 9-10 and 28-29.

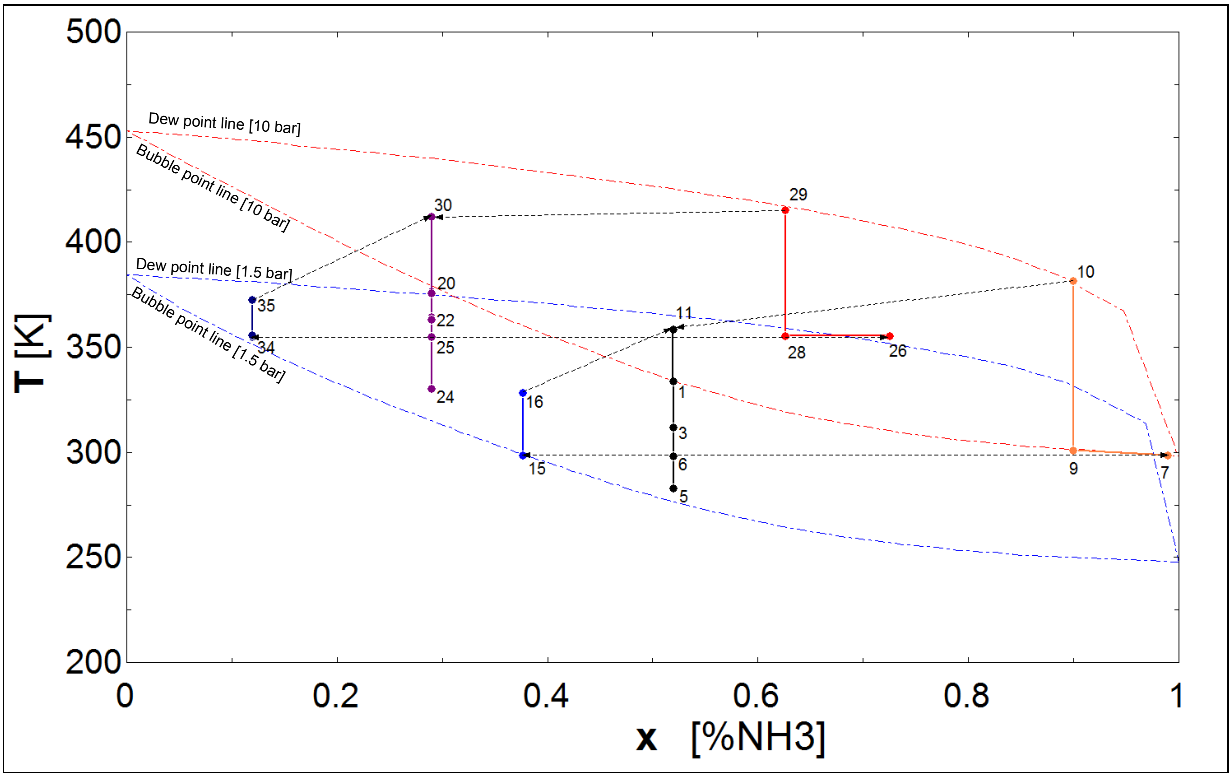

Figure 7.1 - Temperature vs. concentration diagram

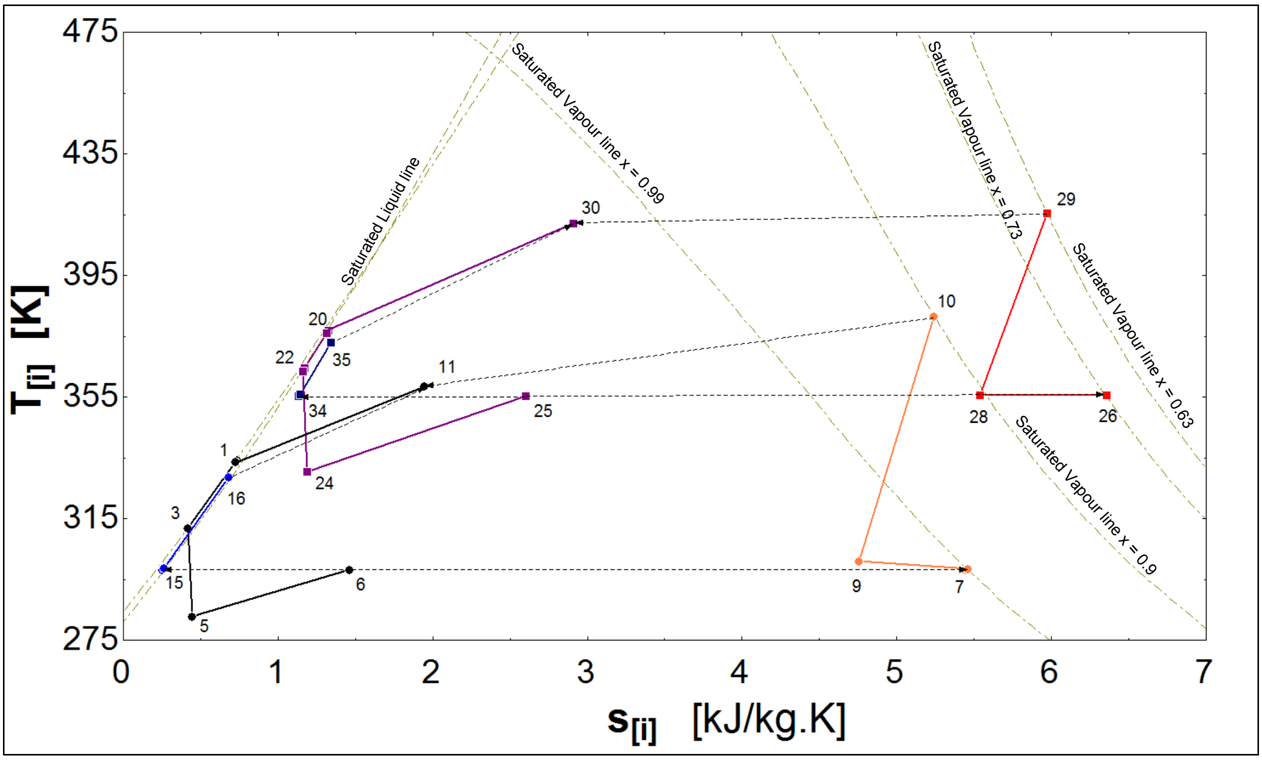

Figure 7.2 - Temperature vs. entropy diagram

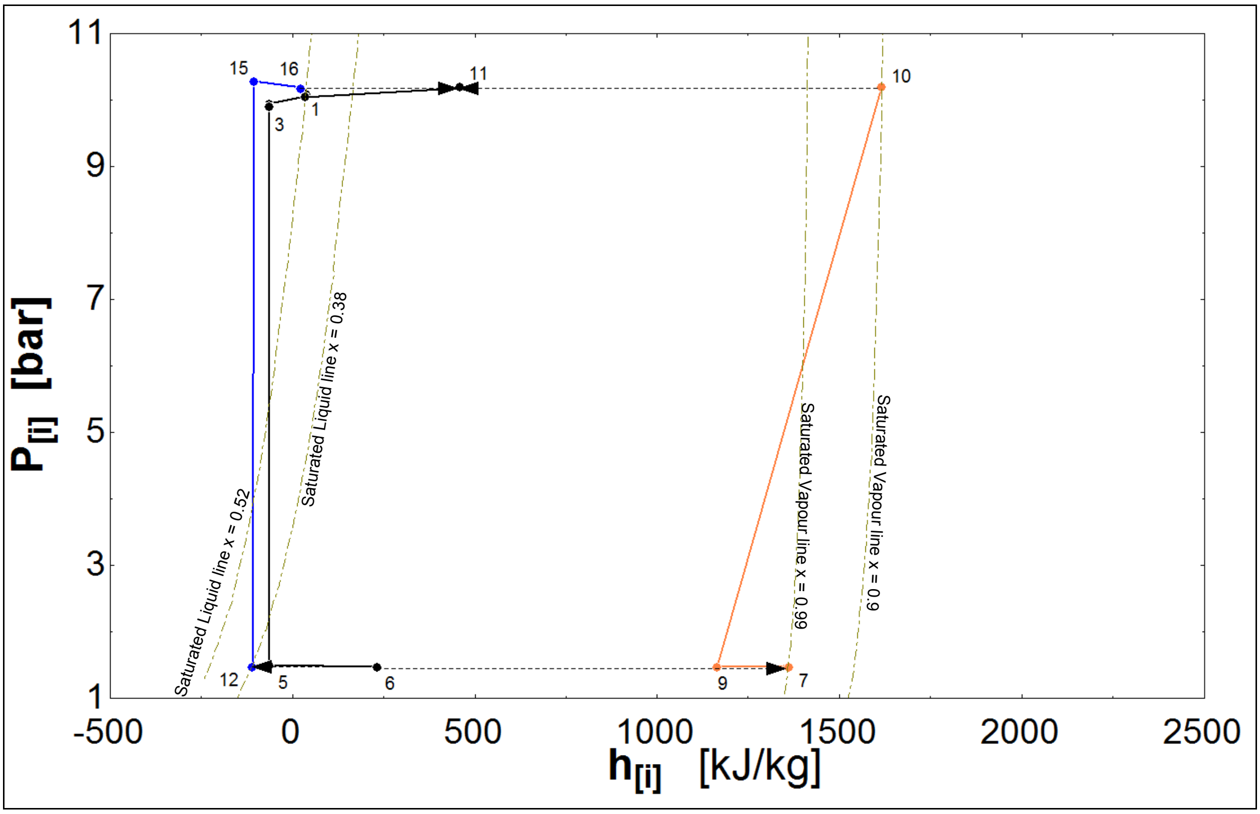

Figure 7.3 - Pressure vs. enthalpy diagram for LT cycle (HT cycle looks the same)

7.5 Model characteristics

Hultén mentioned that the absolute level of pressure should always be at a maximum. In this section it will be investigated. The pressures were increased incrementally from 10-20 bar and the relationships tabulated. A maximum pressure of 20 bar was chosen as the limit, due to cost implications of the heat exchangers at too high pressures (paragraph 7.3). As the pressure was increased the concentration was changed to keep the temperatures of the different operating points, at the absorber and desorber outlets, within 0.5℃. The heat transfer of the desorber, absorber and absorber/desorber were kept close to constant. The results are discussed in the following paragraphs. The results are presented in Appendix C.

7.5.1 Concentration change

When the pressure of each cycle was increased the temperatures in the cycle increased. This relationship is also shown in Figure 7.1. Note the difference in boiling temperature of a constant concentration mixture with different pressures.

In order to lower the temperatures to its original state the concentration had to be increased as the pressure increased. In Figure 7.4 and 7.5 the concentration increase of the LT and HT cycles are shown at the following operating points:

- Overall cycle concentration at the operating point
- Saturated vapour concentration to the compressor
- Mixture concentration during compressing, after injection of liquid
- Saturated liquid to the pump, after the desorption process

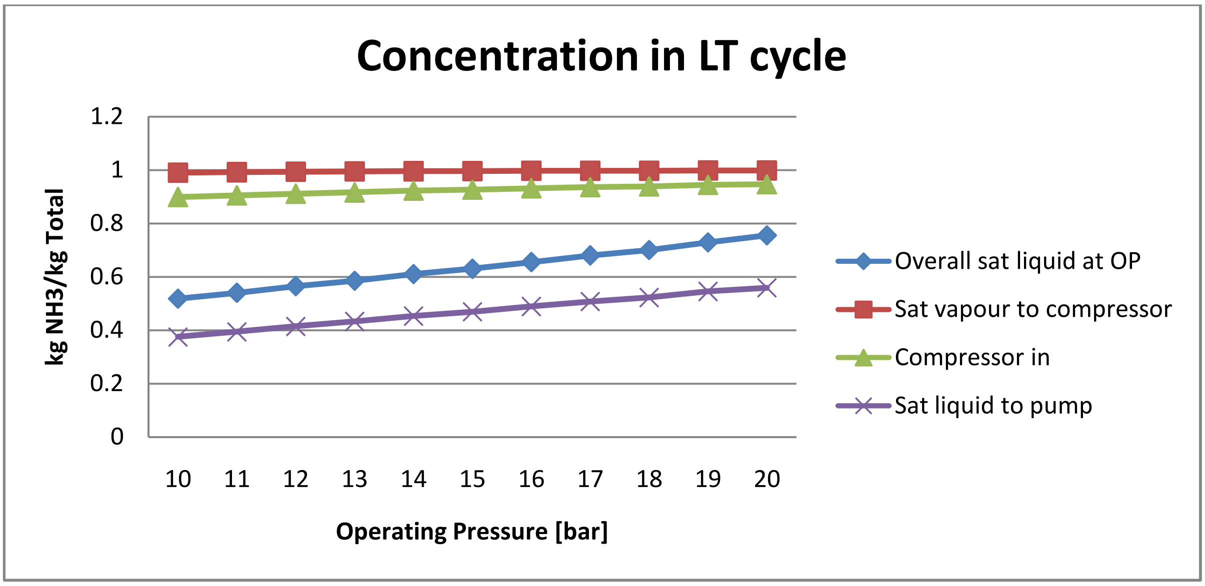

Figure 7.4 - Concentration vs. operating pressure in the low temperature cycle

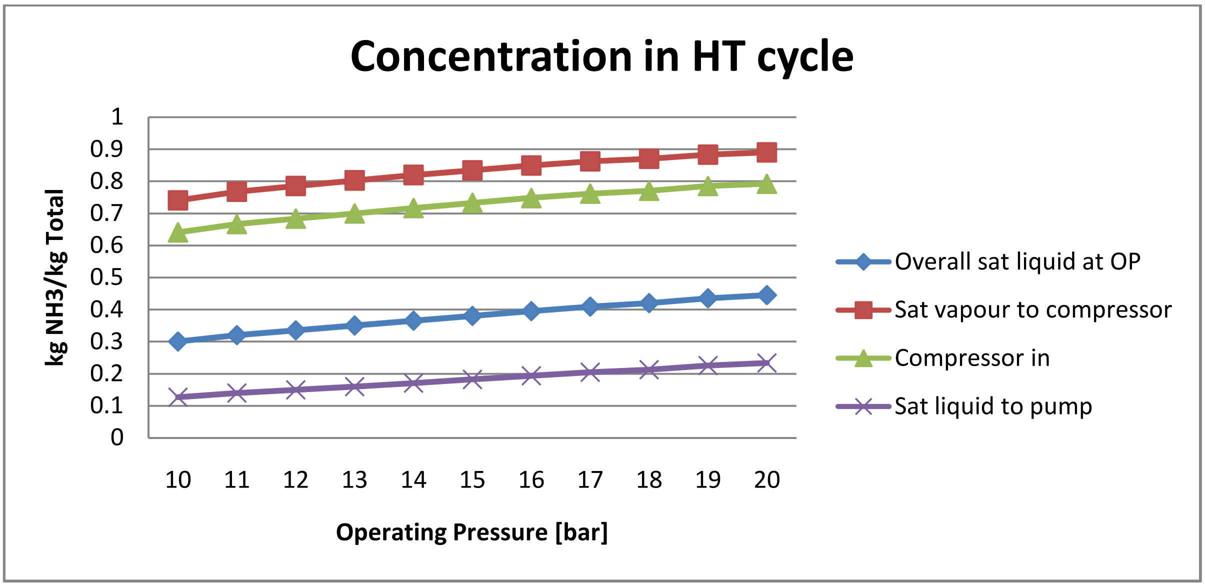

Figure 7.5 - Concentration vs. operating pressure in the high temperature cycle

7.5.2 Pressure ratio

The change in concentration at the OP decreased the temperatures in the desorbers. The pressure then had to increase on the desorption side. This is shown in figure 7.6. The higher the inlet pressures to the compressors, the more the density of the working fluid will increase and make it possible for the compressor to work easier. It was however found that the pressure ratios in the respective cycles decreased as the OP pressure increased. This is also shown in Figure 7.6. This aspect could be favourable, because it can help with compressor selection. Twin screw compressors also a have built in pressure ratios for maximum efficiency. This means that the pressure ratio could be adjusted to match a compressor maximum efficiency pressure ratio.

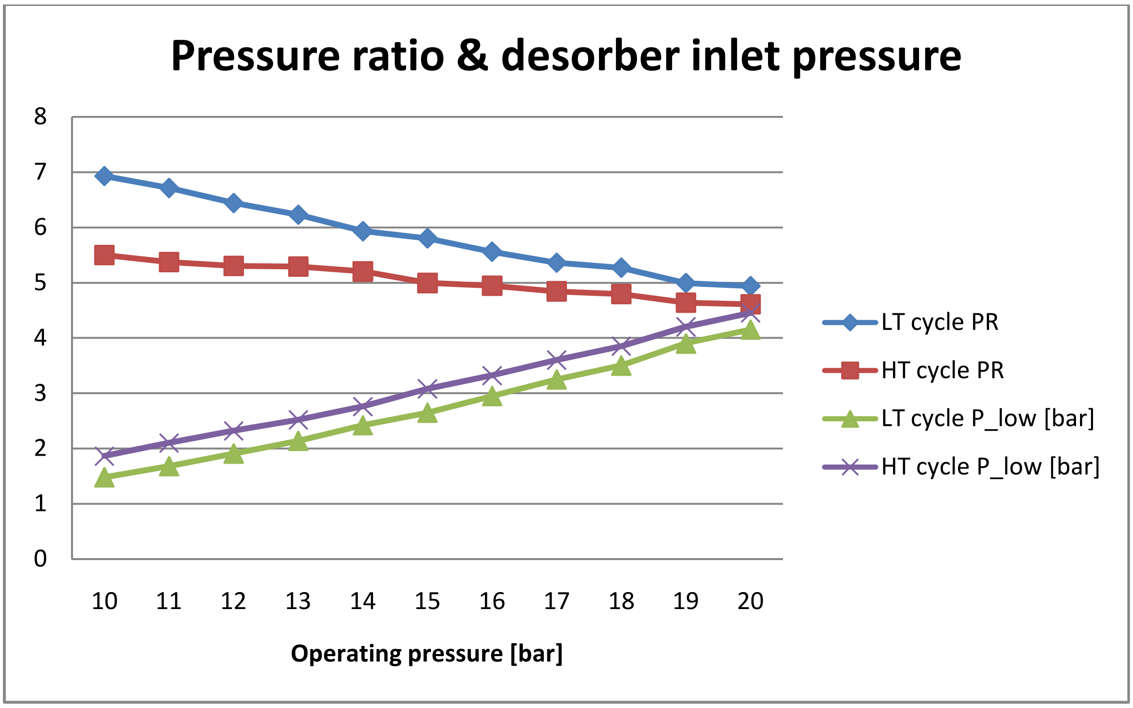

Figure 7.6 - Change in pressure ratio and desorber inlet pressure vs. operating pressure

7.5.3 Flow rate

The increase in pressure has an impact on the mass flow and volume flow in the cycles. Two different configurations were used in the HT and LT cycles respectively. In the LT cycle in Figure 7.7, the mass flow varied due to the increase in pressure. This is due to concentration change as mentioned in paragraph 7.5.1. The flow was allowed to vary, because it did not increase the temperature glide as much as in the HT cycle.

The overall mass flow in the LT cycle reduced even though the mass flow through the compressors increased slightly. The LT cycle has a high concentration of ammonia, and the increase in pressure increased the mass of ammonia in the cycle even more. Most of the ammonia is desorbed in the desorbers, leaving only a small quantity of liquid to be recirculated. An increase in pressure reduced the mass to be recirculated even more. The decrease in liquid mass flow will also decrease the work of the pumps.

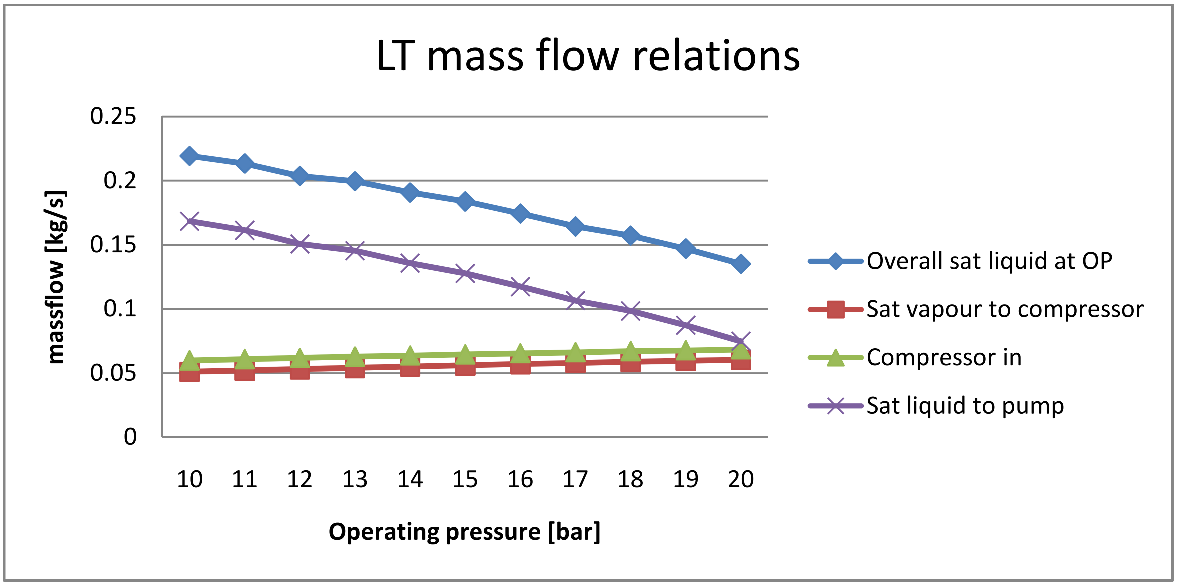

Figure 7.7 - Change in mass flow vs. operating pressure in LT cycle

In the HT cycle in figure 7.8, the mass flow was kept constant with the increase of pressure. The concentration increase also leads to an increase in desorption and subsequent increase in vapour through the compressors. Here the liquid recirculated also decreased.

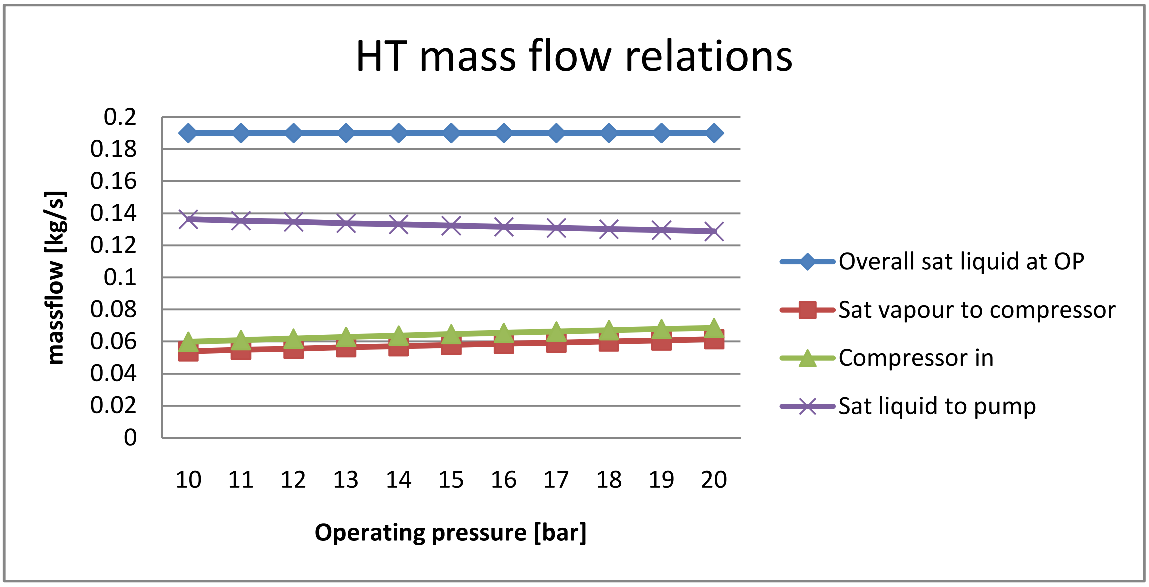

Figure 7.8 - Change in mass flow vs. operating pressure in HT cycle

The biggest impact was on volumetric flow rate as shown in figure 7.9. Even though the mass flow rate through both cycle compressors remains relatively constant, the volumetric flow rate decreased substantially. This is due to the fact that the higher pressures increased the density of the vapour. The decrease in volumetric flow rate will have a big impact on the compressor selection. Lower volumetric flow rate will result in smaller compressors for the same work and mass flow.

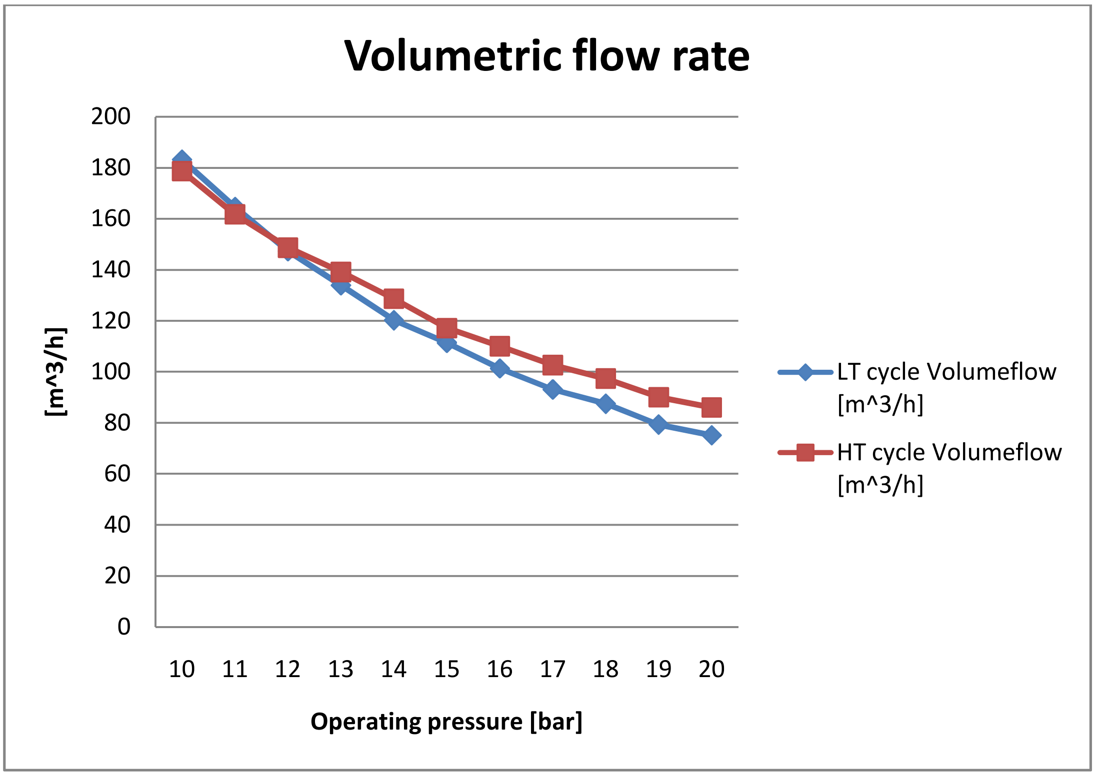

Figure 7.9 - Volumetric flow rate vs. Operating pressure

7.5.4 Economizer heat duty

The decrease in liquid mass flow also results in a smaller amount of liquid to be recirculated. When the overall mass flow decreased as in the LT cycle in Figure 7.10, the heat transfer in the economizers reduced dramatically. This is due to the lower amount of liquid that exchanges heat. On the other side, the total mass flow exiting the absorber also decreased which reduces the necessary heat to be exchanged.

With the HT cycle, where the mass flow was kept constant, the heat duty also decreased due to lower recirculated liquid mass flow. The overall mass flow from the absorber remained constant and still needs to be cooled to give a good system performance.

It was found best to control the mass flow in the HT cycle. A higher liquid mass flow decreases the temperature glide and maximum discharge temperatures from the compressor. The higher mass flow recirculated, also helps with the cooling of the hot stream exiting the absorber. As mentioned in paragraph 6.4.2 cooling of the stream is important to achieve lower working temperatures in the desorber. Thus the economizer size in the HT cycle should not be decreased too much.

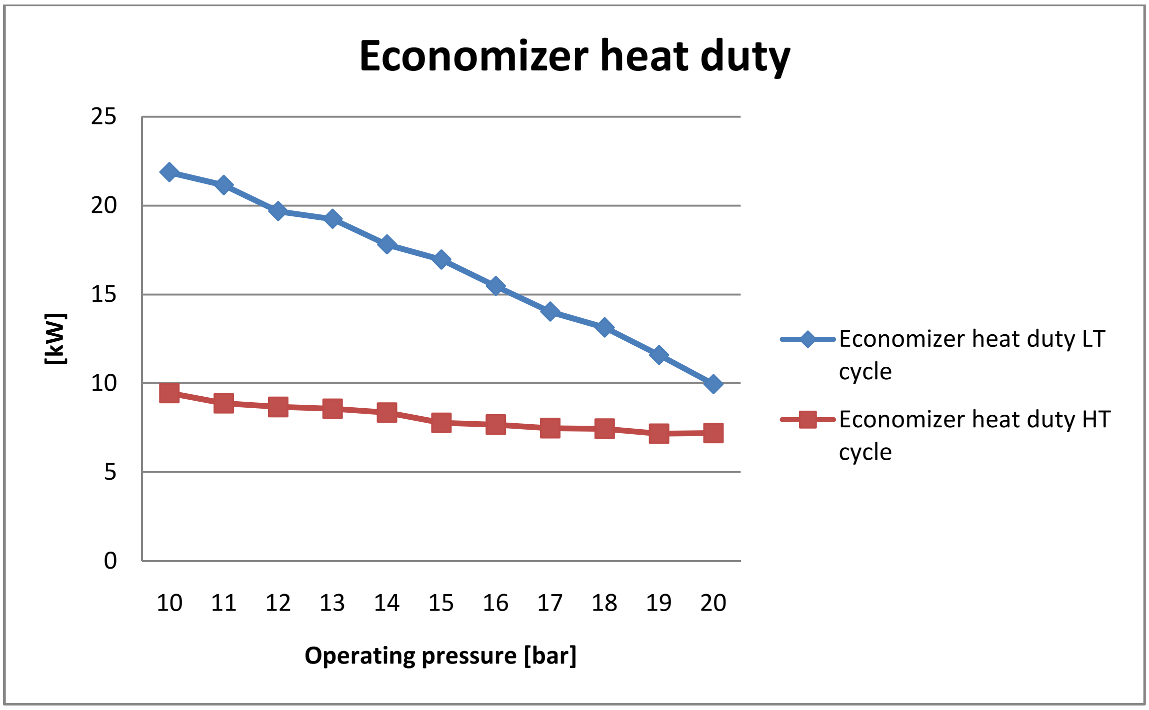

Figure 7.10 - Economizer heat duty vs. operating pressure

7.5.5 Other characteristics

The heat duties in the desorber, absorber and absorber/desorber remained relatively constant with the pressure change. The total compressor work also remained constant, even though the individual compressor work varied a little. Due to the heat duties not changing, the COP also remained relatively constant. The COP changed from 2.11 to 2.14, which is a very small improvement.

Temperature lift in the cycle also remained constant at ±105℃. The maximum discharge temperature of the compressor did increase with the increase in pressure and concentrations of the cycles. An increase of up to 10℃ was observed. The maximum temperature at the HT cycle of 151.4℃ at 20 bar, is still significantly lower than the limitations of the dry screw compressors (paragraph 5.5.2).

Temperature glide also increased as the maximum temperature increased. A maximum change was 5℃, which increased the glide in the HT cycle from 35 to 40℃. However, it was found that increasing the total mass flow of the cycle will result in a decrease in maximum temperatures and temperature glide.

Liquid injection into the compressor was also investigated. The maximum injection into the compression was about 15% of the compression mass. But because positive displacement twin screw compressors was used, the volume of the liquid-to-vapour is more important. It was found that with the liquid injection, the vapour still accounted for a minimum volume of 98% in the LT cycle and 99.4% in the HT cycle. Even with none of the liquid evaporating, the compressor would still be able to tolerate such a small volume of water compared to the vapour.

The effectiveness-NTU and LMTD methods (paragraph 6.7.) were used to construct heat exchanger models in the cycle. According to Zatsev and Itard, the LMTD method is too inconsistent if there are temperature glides in the system. The effectiveness-NTU method was then used for the absorber and desorber. Problems were encountered in the absorber/desorber due to evaporation and desorption on the respective sides of the heat exchanger. This caused the validity of the assumption of $C_{ratio} = 0$ for a condensing and evaporation to come into question, because both sides are changing phase with the additional exothermic and endothermic reactions due to the affinity of mixing of the zeotropic mixture of ammonia and water. Thus, no detail model was developed for the investigation into the individual heat exchangers' characteristic.

The validity of the absorber and desorber overall heat transfer was investigated if the heat exchangers were modelled as black box heat exchangers, where only the input and output parameters were considered. The results of the heat exchanger models are discussed in paragraph 7.8.

7.6 External heat transfer

The method of controlling the external heat transfer was also investigated. The heat transfer in the desorber and absorber were kept constant, while the heat transfer fluid (HTF) mass flow is adjusted to transfer the heat. It can be seen in Figure 7.11 that as the HTF inlet temperature approaches the minimum temperature in the absorber, the mass flow of the HTF increases while the efficiency of the heat exchanger decreases. Lower temperature HTF through the absorber will then result in more efficient heat transfer, while still achieving good efficiencies when the temperature of the HTF came closer to the minimum temperature of the absorber.

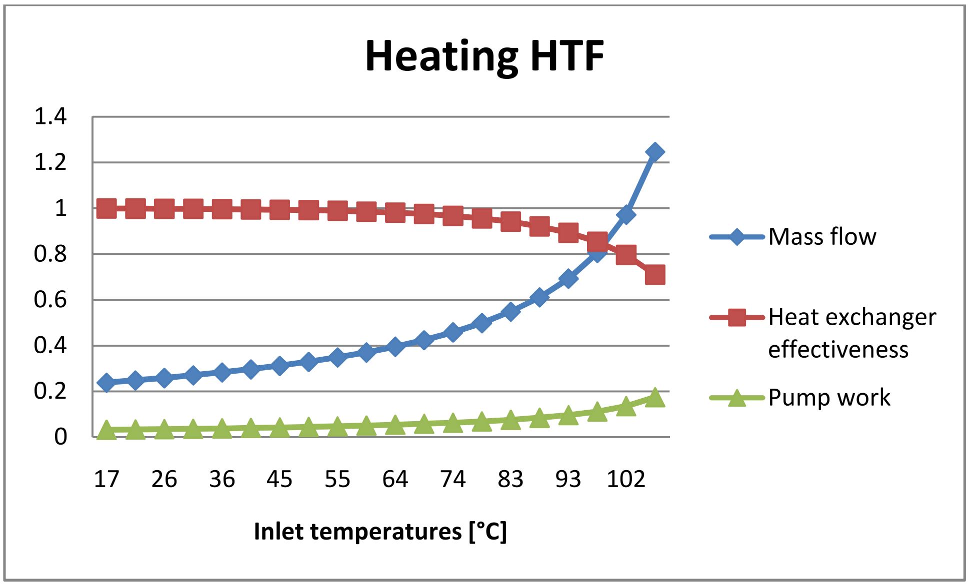

Figure 7.11 - Heating heat transfer fluid vs. absorber external Inlet temperatures

In Figure 7.12, it can be seen that as the inlet temperature of the HTF approaches the maximum temperature in the desorber, the mass flow also increases, with a reduction in heat exchanger efficiency. Higher temperature HTF through the desorber will then result in more efficient heat transfer, with good efficiencies as the temperatures of the HTF approaches the maximum desorber temperatures.

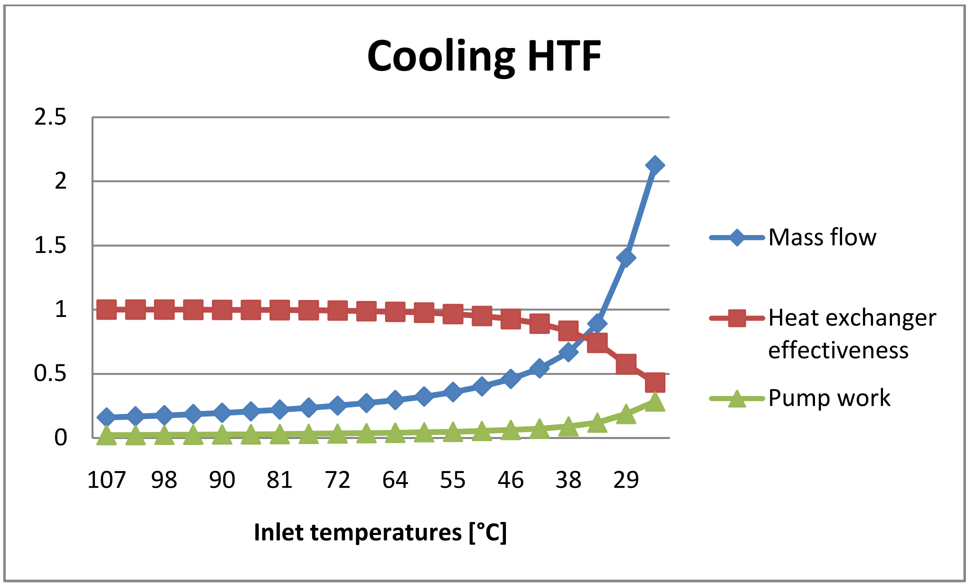

Figure 7.12 - Cooling heat transfer fluid vs. desorber external Inlet temperatures

In Figure 7.13, the change in temperatures of the external HTF can be seen as the mass flow through the heat exchangers increase. Due to the temperature glide in the absorber, high temperatures of up to 142℃ can be achieved in the hot HTF. When the incoming hot HTF temperature approaches the inlet temperatures at the absorber inlet (105℃), the mass flow increases with a reduction in efficiency (Figure 7.11), which decreases the outlet temperature of the HTF.

In the desorber temperatures as low as 9℃ can be achieved for the cold HTF. When the cold incoming HTF temperature approaches the outlet temperature at the desorber outlet (25℃), the mass flow also increases with a reduction in efficiency, which increases the outlet temperatures of the HTF.

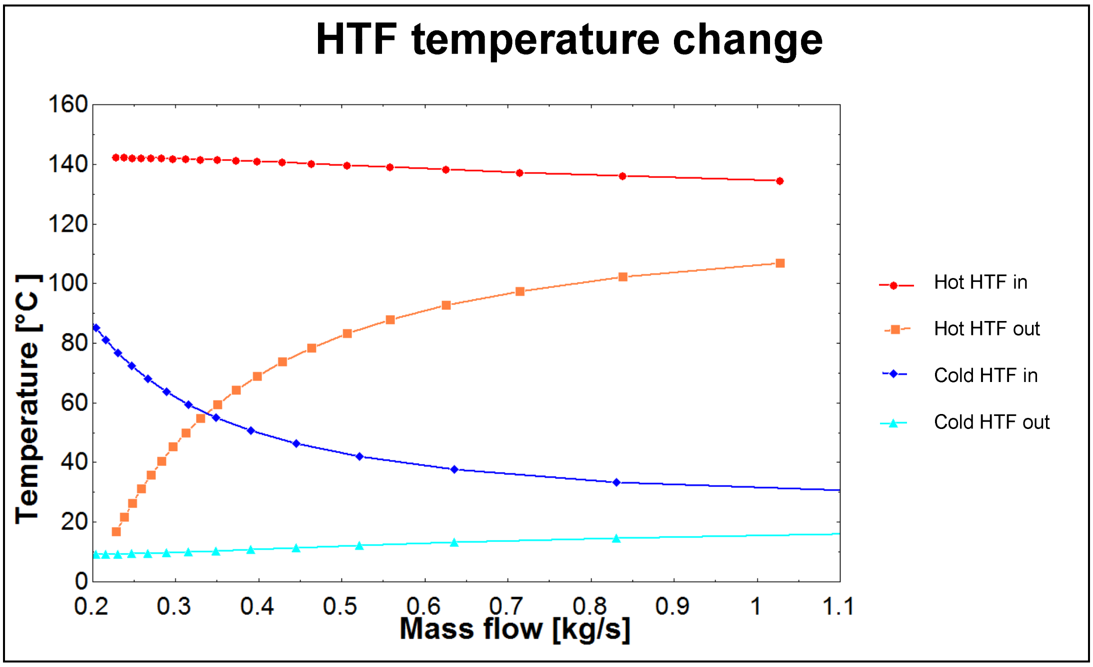

Figure 7.13 - Change in temperature over desorber and absorber

7.7 Optimized model

From the knowledge gained in the model characteristics it was possible to calculate the conditions for an optimized model. The result that will have an impact on the economic evaluation of the model is given in Tables 7.2 and 7.3. The results of the model are presented in Appendix D.

Table 7.2 - Heat exchanger duties

Heat Exchangers	Heat duty [kW]
Absorber	119.2
Absorber/Desorber	92.0
Desorber	65.0
LT Economizer	11.7
LT Economizer	7.5

Table 7.3 - Compressor and pump work

Compressor & pump	Volume flow [m^3/h]	Work [kW]
LT compressor	83.2	27.03
LT pump	0.37	0.33
HT compressor	82.4	28.29
HT pump	0.57	0.51
Total		**56.16**

The conditions of the cycle were adjusted to optimize the model. A $COP_{heating}$ of 2.123 was achieved for the overall TSHHP, with COP's for the respective cycles ($COP_{heating;LT} = 3.36$ $COP_{heating;HT} = 4.14$)

A maximum pressure of 20 bar was used. The concentrations were adjusted to achieve the necessary temperatures. The low pressures were then adjusted for the desorption temperatures in the desorbers. The low pressures can also be adjusted to help with compressor selection. The pressure difference between the desorber and absorber of the respective cycles can be maintained with back pressure regulating expansion valves.

With the compressors, the volume flow was adjusted to about the same levels by adjusting the desorption pressure and keeping the absorption pressure to a maximum. The result makes it possible to use relatively similar compressor sizes for the LT and HT cycles. This could be beneficial to future designs, where a single compressor could be used that has to displace the same volume for both LT and HT cycles, like in the prototype of Radermacher (paragraph 5.4).

The glide in the absorber/desorber for the HT cycle desorption and LT cycle absorption was adjusted to keep a temperature gradient of 4℃ throughout the heat exchange. Because no detail heat exchanger design is done, the presence and location of the pinch point is not known.

The mass flow of the HT cycle was increased, relatively to the base model, to decrease the temperature glide and maximum discharge temperatures of the compressor. A temperature lift of 106℃ was also achieved.

7.8 Validation of model

In order to accept the results, it was necessary to validate the base model in another simulation program. The heat exchange especially was in question due to the zeotropic nature of the working fluid. The program ASPEN was used to validate the heat transfer of the base model, over the same temperature range and with the same mass flows. ASPEN is an market leading process modelling tool for conceptual design, optimization, and performance monitoring (ASPEN, 2008)

The program is for simulating chemical reactions and is useful due to the exothermic reaction when the ammonia and water is mixed.

Table 7.4 - Deviation in heat duties of the heat exchangers

Heat Exchangers	EES	ASPEN	Deviation
	[kW]	[kW]	[%]
Absorber	119.8	122.5	2.23%
Absorber/Desorber	92.3	93.6	1.40%
Desorber	65.0	65.0	-0.03%
LT Economizer	21.9	21.6	-1.33%
HT Economizer	9.8	9.4	-4.18%

In Table 7.4 the different results for the heat transfer over the heat exchangers are presented. The simulations in ASPEN resulted in a good correlation of the result obtained in EES for the base model. Thus it can be assumed that the results are valid for the study. The ASPEN model outputs for the heat exchangers are presented in Appendix E.

7.9 Summary

In this chapter the results of the model of the two stage hybrid heat pump was discussed. The injection into the compressor is the best way to overcome high discharge temperatures of the compressors in the TSHHP. The property diagrams were also created and discussed.

The pressures were then increased to get a better understanding of the TSHHP cycle. This lead to an overall concentration increase in the cycles. It was found that the higher pressures in the cycle have several advantages like:

- Decreasing economizer heat transfer;
- Decreasing compressor volumetric flow rate.

These advantages could be fundamental in the economic aspects of evaluating the TSHHP against conventional system. Smaller compressors can be selected due to lower volumetric flow and smaller economizer sizes due to lower heat transfer. This could decrease the cost of a TSHHP.

An optimized model was then created. The cycle has a high temperature lift of 106℃ and a COP of 2.12. This means that at least 2.12 kW of useful heat is rejected from the absorber for each kW used, with the additional cooling effect on the desorber side. This is ideal for the implementation in processes where simultaneous heating and cooling is needed. The result also correlated well with results from Radermacher (paragraph 5.4) for high temperature lift application. The temperature glide over the heat exchangers during heat transfer, result in temperatures of the outlet HTF of up to 142℃ at the absorber and as low as 9℃ at the desorber.

The result for the base model was also validated in another simulation program, ASPEN. The result was that the model simulated in EES is a good representation of the overall cycle performance.

Chapter 8 - Implementation into ethanol plant

8.1 Introduction

In this chapter the implementation of the TSHHP into the ethanol plant will be discussed. In the previous chapter the performance and heat transfer duties of the heat pump was calculated. These heating and cooling duties can now be used in the implementation of the TSHHP into the ethanol plant. In this chapter the following will be discussed:

- Implementation of simultaneous heating and cooling;
- Conventional plant components heat transfer, selection and control;
- TSHHP components selection and control;
- Economic comparison between the different plants configurations.

The initial work identified that heat pumps are alternatives to conventional heating and cooling systems. Now the work can concentrate on the implementation of the TSHHP in the ethanol plant.

8.2 Simultaneous heating and cooling

In this section, a method that is suitable for managing the simultaneous heating and cooling demand, will also be discussed.

8.2.1 Energy requirements

The energy requirements of each vessel were calculated in Chapter 3. In Figure 8.1 it can be seen that the processes in the cook tank and distillation column have high energy fluctuation, which results in high heating and cooling requirements. This is due to the high temperatures to which the cook tank and distillation column have to be heated.

It is proposed that simultaneous heating and cooling could be applied to the cook tank and distillation column. The one tank could be heated, while the other is cooled. This would reduce the overall time of the ethanol production process. The plant could then be used as a continuous batch process, with multiple batches at different stages of the Ethanol production process.

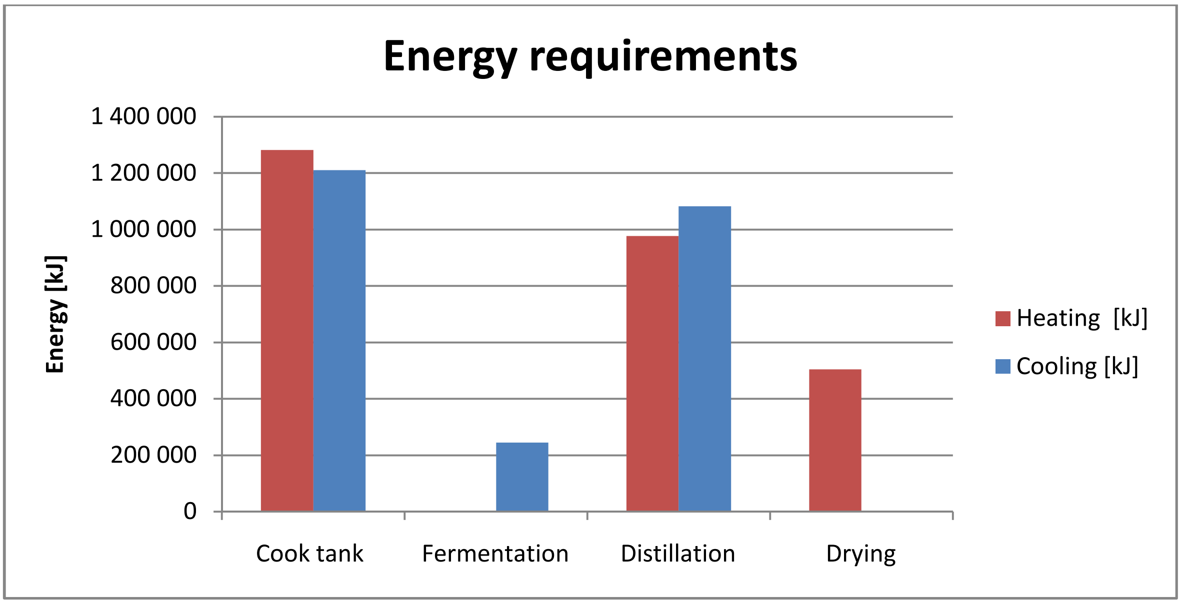

Figure 8.1 – Energy requirements during ethanol production

In Table 8.1, the energy exchange for the different processes is indicated. Positive values indicate heating and negative values indicate cooling. The time of the heating or cooling actions were calculated according to the rate at which the TSHHP can provide cooling (65 kW) and heating (120 kW). All the values are calculated for adiabatic tanks with no losses.

Table 8.1 - Energy exchange during heating and cooling in the ethanol production process.

Heating steps	End Temperature [°C]	Transfer [kW]	Duration [h]	Energy [kJ]	Energy [kWh]
Mixing	60	120	0.8	350 138	97
Liquefaction	95	120	0.8	355 206	99
Cooking	105	120	1.3	576 891	160
Saccharification	60	-65	4.0	-932 096	-259
Cooling	33	-65	1.2	-278 729	-77
Fermentation	37	-2	36.0	-245 010	-68
Distillation Heating	101.5	120	2.3	977 081	271
Distillation Cooling	25	-65	4.6	-1 082 931	-301
Drying	100	120	1.2	504 630	140

8.2.2 Heat loss

Due to a temperature difference between the tank and the environment, as well as the large size of the tanks, it is necessary to determine what the losses for the tanks would be. The losses were calculated for the 3000 kg tanks of the batch process, at the maximum temperature gradient of the tanks during the processes in them. The volume needed for the tanks was calculated as 4000 litres, by using the density of the effluent mixture in an 80% full tank (Oberholzer, 2008). From this the heat transfer area for the exposed surfaces was calculated.

The average ambient temperature was taken as 20℃ for the calculation. The losses were calculated for bare surface heat losses and for tanks insulated with typical glass fibre, with a thickness of 50 mm. The results from the heat loss calculations are given in Table 8.2. The calculation for the heat loss is presented in Appendix F.

Table 8.2 - Tank losses with bare surface or Insulation

Heat losses	**Bare surface**	**Insulation**
	[kW]	**[kW]**
Cook Tank	13.97	0.07
Fermentation tank	2.54	0.01
Distillation Column	13.33	0.07

In Table 8.2 it can be seen heat losses from the cook tank and distillation column are high if the tanks are not insulated. Losses of up to 14 kW would be significant if compared to the maximum heating of the heat pump of 120 kW. If insulation is applied the losses are very low and could be assumed negligible for the calculations in this study. From the result, it would be required to insulate the tank with high temperature processes.

The losses in the fermentation tanks are however much lower. This is due to the smaller temperature difference between the fermentation tank and the environment. In Table 8.1 it was shown that the cooling needed during fermentation is at a very low rate. This is because the fermentation takes place over a 36 hour period.

If the fermentation tank was left without insulation, no cooling would not be needed. If left uninsulated, the temperature of the fermented material in the tank would not rise to levels that would start degradation of the yeast performance. Therefore, cooling calculations for the fermentation would be *unnecessary in this study*. It should however be noted that changes in the ambient temperature, would change the temperature gradient of the tanks. It would however still be wise to include insulation and heat exchangers into the design of fermentation tanks, to prevent overheating of the tanks due to the exothermic reaction. The low rate of cooling that is needed, makes it possible to use low cost cooling options like a small cooling tower or circulating cool water through the fermentation tanks.

With the fermentation cooling not needed or considered further, the overall plant requirements are given in Table 8.3. The energy needed for heating and cooling of the system is given, as well as the time it would take for these operations, if the rate of cooling and heating of the TSHHP is applied.

Table 8.3 – Overall plant heating and cooling requirements

Overall plant requirements	Energy [kJ]	Energy [kWh]	Heat Transfer [kW]	Time [h]
Heating	2 763 946	767.76	120	6.4
Cooling	-2 293 756	-637.15	-65	9.8

8.2.3 Heat storage tank

Conventional systems have boilers for heating and evaporative cooling towers for cooling. The high temperature steam generated in the Boilers would be used to heat the tanks. When cooling the tanks, with evaporative cooling towers, energy is rejected to the atmosphere via condensers. Thus, there exists the opportunity to reuse that lost energy. However, this energy is of a low grade due to the low temperature.

To stabilize the amount of energy requirements and absolute temperature level of the whole ethanol plant, a *heat storage tank* (HST) could be implemented. The tank can be implemented to cool distillate to a certain level by passing the effluent through the tank, which would heat the tanks. The heat storage tank would then serve as an energy reservoir. This would make it possible of supplying warm water to the mixing process, reducing the amount of initial heating for the cooking processes.

When using the TSHHP, the high temperature water could serve as a source of energy. The tank at intermediate temperature (40 – 65 ℃) would be cooled, while energy is upgraded to supply high temperature heating of over 100℃. Heat could also be supplied to the drying process by passing hot water from the HST through coils in the DDGS storage vessel with direct heat exchange or using the TSHHP to provide higher temperature heating.

The difference in the cooling (65 kW) and heating (120 kW) of the proposed system, makes it difficult to balance the cooling and heating requirements. The HST could simplify this and makes it possible to achieve a zero net energy balance over the system.

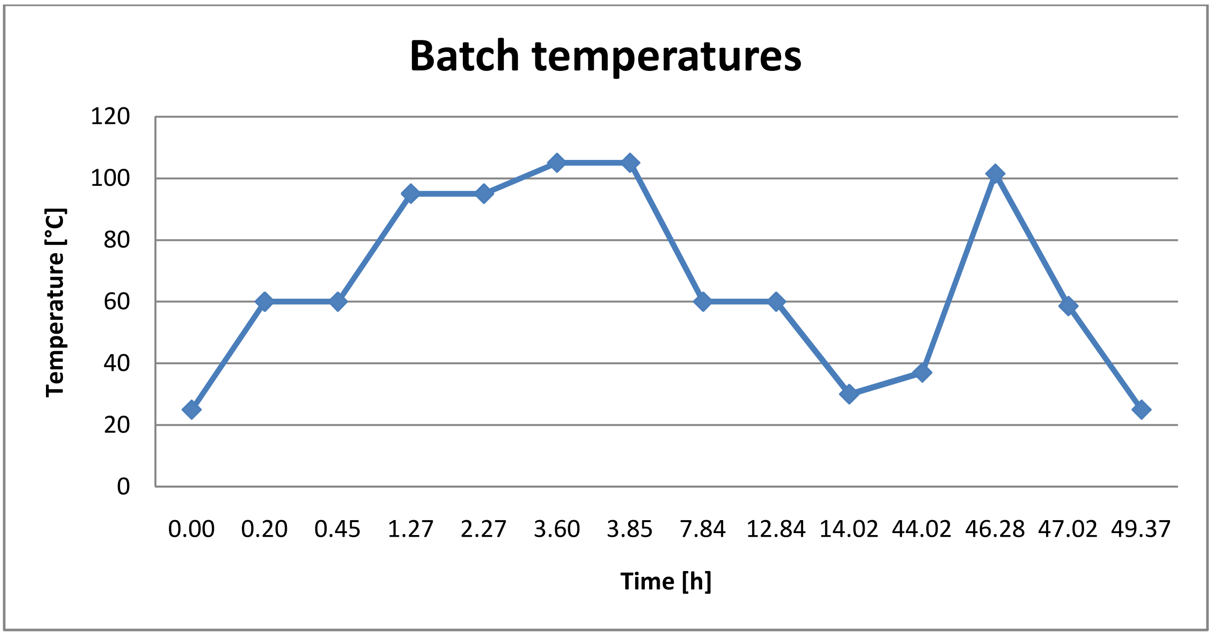

Figure 8.2 - Batch temperature profile with Heat storage tank

In Figure 8.2 the batch temperature profile with the implementation of the heat storage tank is given. When compared to Table 8.1, it can be seen that the overall time for the mixing, liquefaction, saccharification and distillation has decreased. There is also an extra temperature during the distillation tank cooling.

The heat integration of the system is implemented in the following way:

- Effluent from the distillation process is cooled with the water in the HST to a certain temperature. This can be done by passing the distillate through the HST and/or circulating the water in the HST through heat exchangers in the distillation column.
- The temperature, to which the distillation effluent is cooled, is just enough that sufficient energy is left to do simultaneous cooling of the effluent in the distillation process, while heating the effluent in the mixing and cooking process. This is done by matching the time required for the cooling, with the time required for the heating of the effluent.
- Cooling of the effluent in the cook tank, can then be done. During cooling energy is supplied to heat effluent in the beer boiler and distillation column to the boiling temperature required.
- Further cooling of the cook tank, supplies high temperature energy for drying of the DDGS.
- Final cooling of the effluent in the cook tank provides excess energy to the system. This could either be used for heating the HST or discharged in the dryer for further drying, since the drying process has low energy efficiency.

In Table 8.4 the changes in temperature of the HST can be seen. In the first step, warm water is supplied to the mixing in the cook tank. Then makeup water at 18℃ is mixed with hot water, reducing the tank temperature. The cooling of the distillate then heats the water in the tank to 57℃. Excess energy from cooling the cook tank is then used to heat the tank even further to 66.5℃. At the end, if the tank should be cooled back to its original temperature, there is a lot of energy that can be reused or rejected in the dryer.

Table 8.4 - HST energy and temperature levels

Energy storage tank	Start Mass	End mass	End Temperature	Energy	Energy
	[kg]	[kg]	[℃]	[kJ]	[kWh]
Water to Cook tank	20000	17887	55.0	0	0
Makeup water (18℃)	17887	20000	51.1	0	0
Cooling of distillate	20000	20000	57.4	532 094	148
Excess heating	20000	20000	66.5	753 658	209
Available energy	20000	20000	55.0	**-958 542**	**-266**

A new heat balance with the implementation of a HST is given in Table 8.5. Note the temperature during the distillation process of 58.6℃, after it is cooled with the HST. Important to note is that the total energy balance of the entire process is the same as the energy available in Table 8.4, if the HST is cooled to its original temperature. This means that there were no energy losses in the system and that the net energy balance of the system is zero.

Table 8.5 - Heating and cooling requirements with HST

Heating steps	End Temperature	Transfer	Duration	Energy	Energy
with HST	[℃]	[kW]	[h]	[kJ]	[kWh]
Mixing	60	120	0.2	84 832	24
Liquefaction	95	120	0.8	355 206	99
Cooking	105	120	1.3	576 891	160
Saccharification	60	-65	4.0	-932 096	-259
Cooling	33	-65	1.2	-278 729	-77
Distillation Heating	101.5	120	2.3	977 081	271
Distillation Cooling_tenk	58.5	-200	0.7	-532 094	-148
Distillation Cooling_HP	25	-65	2.4	-550 836	-153
Drying	100	120	1.2	504 630	140
Heating tank	66.5	120	1.7	753 658	209
Total energy balance				**958 542**	**266**

During the mixing, liquefaction and saccharification in the cook tank, there are four constant temperature steps. This can be seen in Figure 8.3 and it amounts to 6.5 hours. It would be wise to implement the heating and cooling in such a way that more than one batch could pass through the plant during the residence time of 36 hours it takes for fermentation.

Table 8.6 - Simultaneous heating requirements

Overall plant requirements	Energy [kJ]	Energy [kWh]	Heat Transfer [kW]	Time [h]
Heating	3 252 298	903	120	7.5
Cooling	-1 761 662	-489	-65	7.5

Implementing the heating and cooling in a simultaneous manner with the HST, will have a reduction in the overall process time. In Table 8.6 it can be seen that the duration of heating and cooling are now matched perfectly, because of the zero net energy balance.

8.3 Batch management

In paragraph 2.3, Fong (1983) stated that the fermentation of raw material in the tanks takes 36 hours. From the constant temperature stages and cooling and heating, the overall time of the processes excluding fermentation is 14 hours. This means that two batches could easily be cooked and distilled, in the same residence time of fermentation. The extra four hours could provide the extra time needed for loading, unloading, maintenance and cleaning of the cook tank and distillation column.

In Figure 8.3 a schematic of a proposed batch management system is illustrated. If the plant is started at zero hours, the first batch of effluent is being prepared in the cook tank for fermentation. After 18 hours, the first batch of 3000 kg enters the fermentation tank and starts the fermentation process. At 36 hours the next batch enters the fermentation tank. The first fermentation tank is now full and is left for 36 hours to fermentate to the required ethanol concentration. At 54 hours, the next batch then enters a second fermentation tank. This is halfway through the residence of the first tank. At 72 hours, the second tank is also full and the fermentation process in the first tank is complete.

At 90 hours, the mass in the first tank is halved, by supplying effluent to the distillation column, where the first ethanol can be recovered. The second tank is now halfway through fermentation. A third tank is introduced to accept the effluent from the cook tank, and is filled halfway. At 108 hours, the second tank has reached its maximum concentration in the fermentation process. The first tank supplies the last of its contents to the distillation column, and is emptied. The third tank is now full.

The first tank can now be cleaned, after the whole cycle for that tank is complete. At 126 hours, the first tank receives the next batch from the cook tank and is filled halfway. The second tank transfer's its first batch to the distillation column. And the third tank is halfway through the fermentation. The cycle continues and repeats itself.

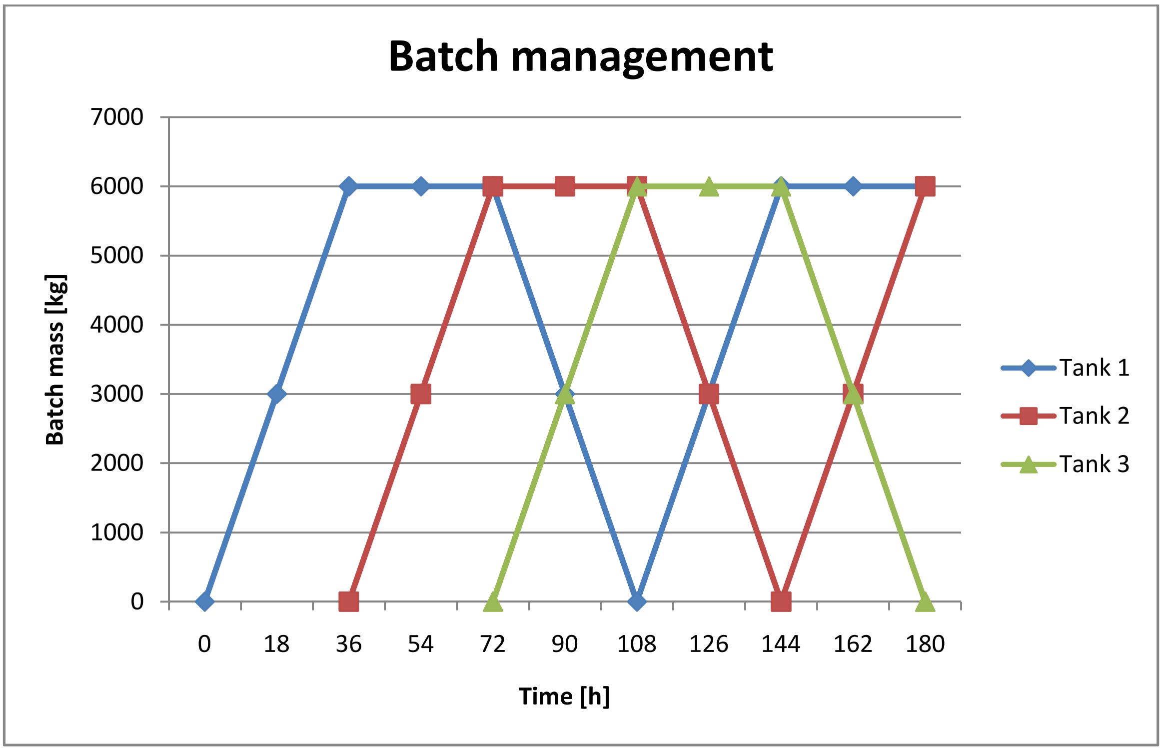

Figure 8.3 - Fermentation tank batch management

Managing the fermentation with three Fermentation tanks will make it possible for the cook tank and distillation column to work almost continuously. This will make it easier to implement the ethanol production in the small scale plant as a continuous process, with almost no stoppages.

8.4 Economic evaluation

The economics of the installation of the TSHHP will depend on the way it is implemented/applied in the ethanol production process. Identification of a feasible installation is of crucial importance. This was done in the previous paragraphs. The procedure is given as:

- To do the economic evaluation, the criteria of the process characteristics were determined. This was needed to compare the TSHHP with a feasible installation alternative.
- Conventional systems have different operating characteristics and different possible operating temperature ranges. Thus it was decided to compare the conventional system configurations directly, in the same way that is proposed in the previous paragraph for the TSHHP.
- Component sizing was done for the different configuration. Specialists in the field were then contacted to get component information for implementation of the systems as well as cost for installation of the systems into the small scale ethanol plant.

8.4.1 Conventional system

The conventional system consist of a boiler cycle for heating and the evaporative cooling tower cycle for cooling. The selection method of the components is discussed below.

8.4.1.1 Boiler cycle

The boiler is the heart of the steam generation system. The layout of the boiler cycle is shown in Figure 8.4. Steam is generated by supplying energy to the boiler feedwater in the form of electricity or combustion of a fuel. Water is evaporated in the boiler, by supplying latent heat to the water. Boilers always work under high pressures (5 to 15 bar) to accommodate a large mass of steam in a small volume. (Spyrax-Sarco, 2007)

Selection of the boiler size was determined by calculating the amount of steam needed to supply 120 kW of heating. The constraints were set at the cook tank where a temperature of 105℃ is needed, the same as for the TSHHP. In the heat exchanger, the steam is condensed and leaves the tank as a saturated liquid. According to Beckley (2008) the following assumptions can be made for the boiler system:

- The saturated liquid temperature is the same as the tank temperature at 105℃.
- A 10% mass flow loss for the blowdown and condensate losses.
- The mass flow was calculated to determine the Boiler Rating. The results are given in Table 8.7. The calculations are shown in Appendix G. From the Boiler rating and mass flow of steam, the selection of a steam boiler could be made.

Table 8.7 - Boiler selection criteria

Mass flow	Boiler rating
[kg/h]	[kW]
211.75	146.63

8.4.1.2 Evaporative cooling tower cycle

The evaporative cooling tower is used to cool the effluent in the respective tanks. The layout of the evaporative cooling tower cycle is shown in Figure 8.5. Cooling towers work on the principle that the evaporation of water absorbs the latent heat energy from the system and causes a cooling effect. Heat is transferred from high temperature processes to the cool working fluid in the cooling tower cycle.

A closed circuit was selected, because it isolates the cooling fluid from the atmosphere. Heat is rejected with a heat exchanger to the external water due to the cool temperatures provided by the evaporation. Closed circuits provide more flexibility at operational conditions.

Selection of the cooling tower was determined by calculating the mass flow for the working fluid with a cooling heat transfer of 65 kW. The constraint was set by the minimum temperature in the ethanol plant of 25℃.

Table 8.8 - Cooling tower selection criteria

Volume flow	Energy consumption
[m^3/s]	[kW]
0.001563	5.87

8.4.2 TSHHP

The layout of the TSHHP in the ethanol plant is shown in Figure 8.6. It shows both the cooling and heating cycles. The external HTF steams, from the absorber and desorber, are connected to the equipment like the cook tank and distillation column. Three port control valves are used, to change between heating and cooling streams for the individual components.

The external heat transport fluid was chosen as either water or an ethylene glycol/water mixture. If water in the cycle is kept under pressure (over 4 bar), it is possible to prevent any vaporization of water. Glycol mixtures are mainly known for their anti-freezing capabilities, but also increase the boiling point of working fluids. Sufficiently high concentrations (80%) of glycol in the water will increase the boiling point beyond the maximum temperatures (142℃) in the external working fluid transport system. Radermacher (1991) also used glycol/water solutions in their plant (paragraph 5.4).

Pump selection was done according to the volume flow requirement and pressure difference in the system. The ammonia/water mixture is corrosive to coppers. Thus pumps had to be used that are not susceptible to corrosion.

Compressor selection for cost estimation was done for ammonia compressors. According to Infante Fereira et al. (2006) dry compressors should be used with liquid injection. Well known refrigeration screws compressors were selected, according to their volume displacement and work requirements. These parameters were calculated from the model of the TSHHP developed in chapter 6.

The cost comparison was done for both the base model and optimized model, to evaluate the difference in total cost due to the change in parameters of the cycle discussed in paragraph 7.5.

A specialist in heat exchanger design, Bester (2008), was contacted to assist with heat exchanger cost analysis. The input and output parameters from the TSHHP model were used to determine the cost of the base model heat exchangers. The change in heat transfer in the economizers, changed their sizing and cost. According to Bester, the material cost can be estimated as having a linear relationship to the UA value (paragraph 6.7). This relationship was used to determine the cost of the economizers if the heat transfer changed. Calculations are shown in Appendix H.

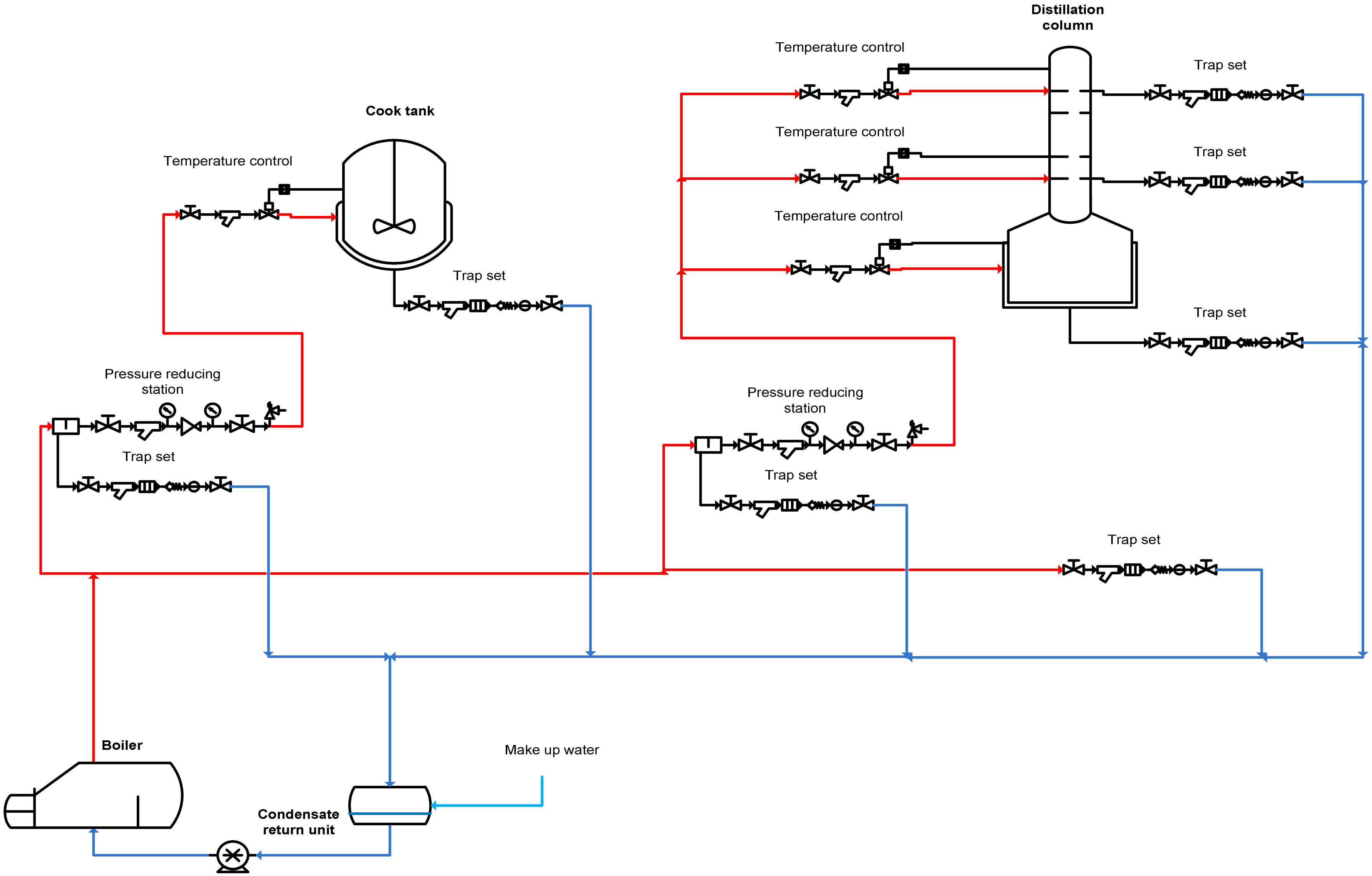

Figure 8.4 - Conventional steam heating cycle with boiler

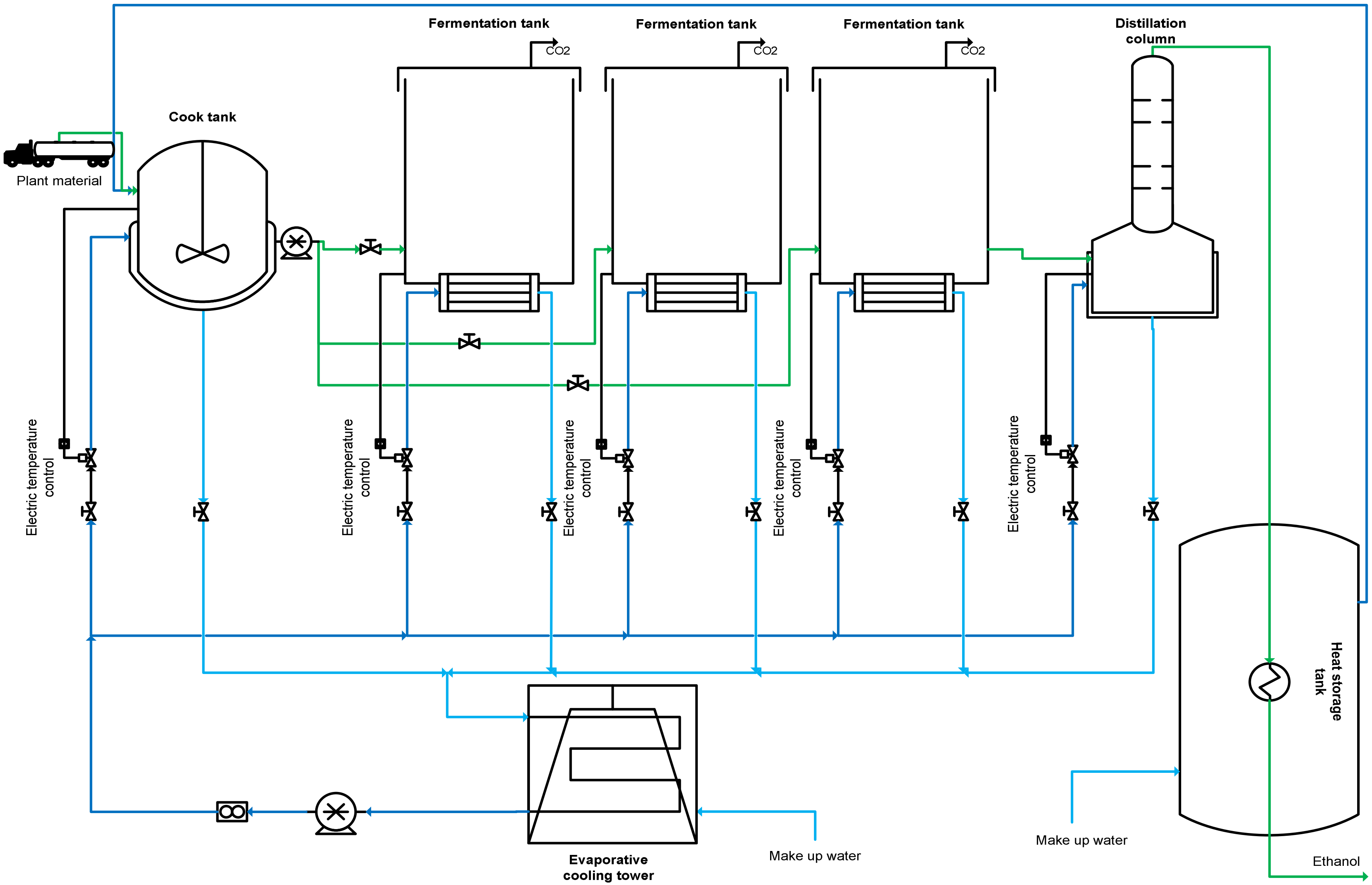

Figure 8.5 - Conventional cooling tower cycle implementation into the plant

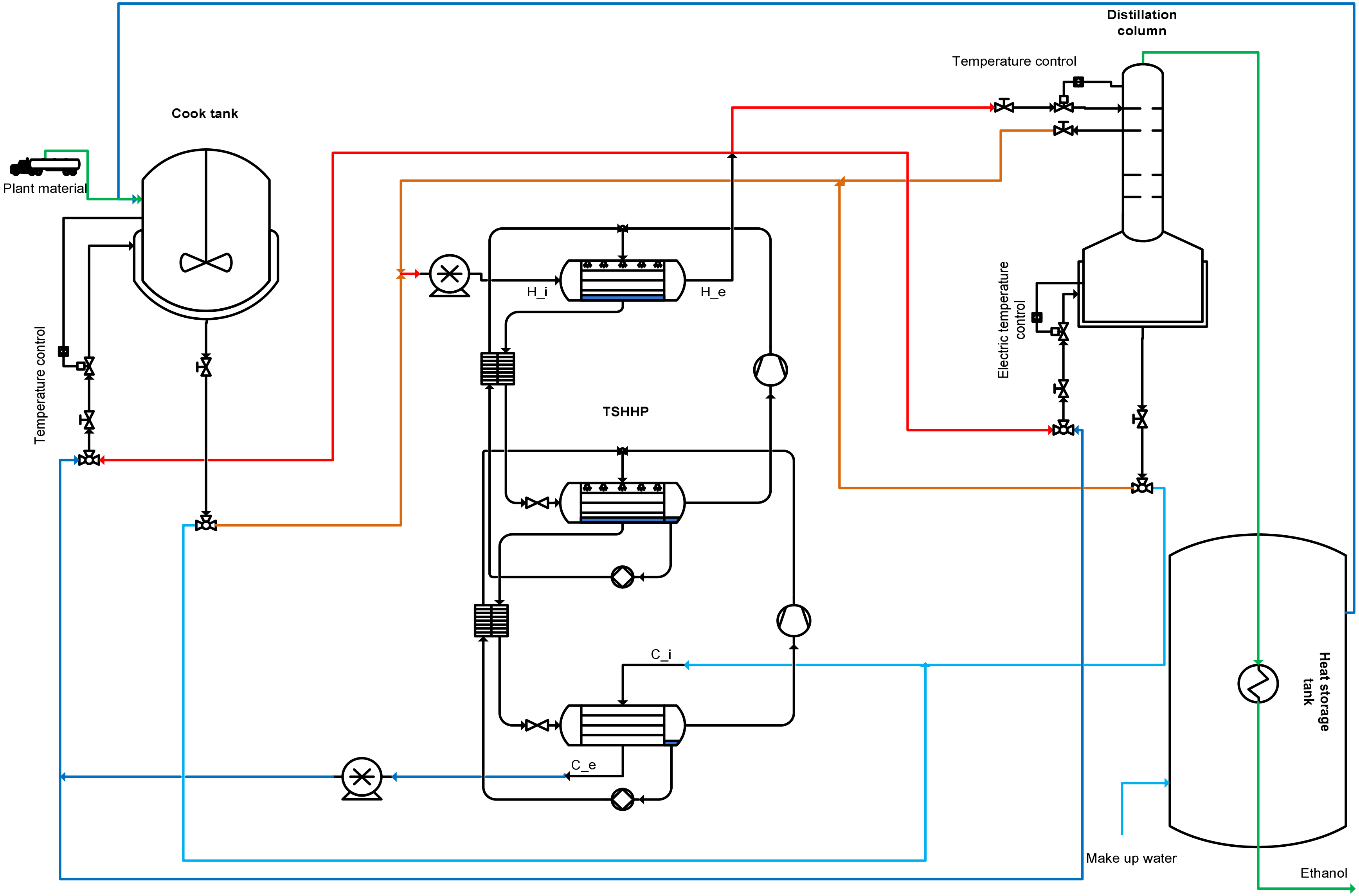

Figure 8.6 - TSHHP implementation into the plant

8.4.3 Pipe line system controls

The controls and configurations has a big influence on the overall cost of a heating and cooling system. The required information for components were obtained from Spyrax-Sarco (2007). The following controls were used in the system.

- **Pressure Reducing Valve** is needed to reduce the temperatures at which heat transfer from the steam takes place, by lowering the pressure. The higher the pressure of the steam, the higher the temperature. Because the maximum temperature requirement is 105℃, pressure is reduced to 2 bar, with condensate leaving at 1.2 bar. The reduction in pressures also reduces the cost of the heat transport system.
- **Steam trap sets** are used to remove water in the system. Steam traps releases condensate without allowing steam to escape. Water is formed when steam releases its latent energy when it condenses. In this process it will provide warming to equipment and pipes, and due to the temperature gradient with the atmosphere, it will cause losses. This happens throughout the system and water has to be removed from the steam, because it inhibits the heat transfer of the steam and causes corrosion and water hammering.
- **Strainer** is a kind of sieve in the pipeline that contains a mesh through which steam must pass. Any debris or scale in the cycle is retained in the mesh. Debris needs to be removed from a steam cycle, because it can be damaging to a plant and could contaminate the steam or final product.
- **Separator** is used to remove droplets of moisture in the steam. It has a series of plates or baffles in the flow path of the steam. Droplets hit the baffles and are collected on them, before being drained to the bottom of the separator. This is necessary to keep the steam as dry as possible, to ensure effective heat transfer.
- **Control valves** are used to control the flow of heat transfer fluid or steam. Constant flow at the same temperature and pressure is not always required. Electric control valves can be used to gradually increase or decrease the flow, according to the requirement of the heating or cooling process. It has an actuator that applies a force to open or close the valves. A sensor monitors condition in the processes, and transmits information to the controller. The controller compares the information to a set value, sends a signal to the actuator and adjusts the valve to apply a certain correction. Al the control valves in the selection is electronically controlled.
- **Isolation valves** are used to stop the flow of fluid into a particular system. It can be used to divert flow into another direction or isolate processes for maintenance,

removal of equipment and shut down purposes. These valves are controlled manually or electronically.

- **Pumps** also play an important role in the control system. Condensate return pumps in the steam heating systems it is used to return the condensate to the boiler. Circulation pumps in the cooling tower and TSHHP cycles, are used to circulate the external working fluid in the cycle. The pump flow rate can be adjusted to specific needs or to regulate the heat transfer needed in a particular system.

8.4.3.1 Boiler cycle control

The configuration of the control components in the steam heating cycle is shown in Figure 8.4.

After the boiler the line is split into two main lines for the cook tank and distillation column. Each of the main lines passes through a **pressure reducing station**. The components in the reducing station are a separator, isolation valve, strainer, pressure gauge, pressure reducing valve, pressure gauge, isolation valve and a safety valve. Pressure is reduced from 10 to 2 bar according to the temperature requirements in the plant.

Trap sets are used to remove the condensed water from the steam system. Condensate is recovered and returned to the boiler. The trap set consists of an isolation valve, strainer, steam trap, non-return valve, sight glass and another isolation valve. Trap sets are located at:

- The boiler main outlet stream;
- Pressure reducing stations, where is connected to the separator;
- Outlet of heat exchangers in the cook tank, beer boiler and the valve trays in the distillation column.

Temperature control units are located at the heat exchanger inlets of the cook tank, beer boiler and the valve trays in the distillation column. It consist of a isolation valve, strainer and electric temperature control valve. It is used to manage the temperatures and heat transfer at the particular components.

Condensate unit is used to accumulate liquid condensate and recirculate it back to the boiler with the condensate pump. The condensate pump is selected according to the high temperatures and mass flow of the condensate.

8.4.3.2 Evaporative cooling tower cycle control

The configuration of the control components in the evaporative cooling tower cycle is shown in Figure 8.5.

Temperature control valve is used to control the temperatures and amount of cooling needed. Adjusting the mass flow from the pump would also contribute to heat transfer management. It is found at the cook tank and beer boiler to control the cooling. Even though cooling of the fermentation tanks is not required, the possible set up is also shown. **Circulation pump** was also selected for the working fluid circulation.

Isolation valves are located before the temperature control valve and after the cook tank and beer boiler. **Three port control** valves are not shown in the Figures 4 and 5, but would be used to connect the conventional systems together and then switch between heating and cooling according to the different process needs.

8.4.3.3 TSHHP control

The TSHHP control system in figure 8.6 is similar to that of the evaporative cooling tower. It also has **temperature control valves** and **isolation valves** at the cook tank, beer boiler and the valve trays in the distillation column. **Three port control valves** are also used to switch between heating and cooling mode. The only difference is that a liquid is used as working fluid throughout the system, with pumps circulating and managing mass flow for the respective cooling and heating sides.

Circulation pump selection was done for each of the two solution circulation pumps in the TSHHP control cycle. Selection was done according to the volume flow that had to be displaced, for the different inlet temperatures and heat transfer in the heat exchangers.

8.4.4 Installation and running cost analysis

From the selection of the components discussed in the previous paragraph, a realistic cost analysis could be done for the respective systems. Cost analysis was done by acquiring cost for each component from the market (2008).

The installation cost analysis was done for the conventional heating and cooling system as well as the TSHHP system. For the cost analysis of the TSHHP, two configurations were used to compare the difference in cost, due to the different component sizing when using the TSHHP at different pressure ranges. The TSHHP was evaluated on the base model and

Optimized model discussed in paragraph 7.7. The detailed selection, calculation of cost for the components in the systems is in Appendix I.

Table 8.9 – Direct cost for the cooling and heating systems in the small scale ethanol plant

Heating and cooling system	Direct cost
Conventional Model	R 876 497
TSHHP Base Model	R 689 284
TSHHP Optimized Model	R 549 496

In Table 8.9 the different costs for the respective systems can be seen. The conventional system is more expensive than the other systems. The cost of the boiler and evaporative cooling tower compared well with the TSHHP base model.

The big difference is the cost of the steam control system, which is more expensive than the cost of a liquid external heat transfer system used in the TSHHP. Two separate systems had to be evaluated for the boiler steam and cooling tower water system. The assumption was made that they could be coupled with three port electronic control valves and use the same heat exchangers after purging the steam from the cycle. This could however still be an unrealistic assumption, and using separate heat exchangers will increase the cost of the steam cycle even more.

The TSHHP heating and cooling processes will work with a glycol/water mixture or pressurized water throughout the system. Because the external working fluid is in liquid phase throughout the system, it decreases the cost. The higher pressures in the optimized cycle also proved to decrease the cost of the TSHHP system, due to smaller and cheaper compressors and economizers.

When the running cost of the conventional system was compared with the TSHHP, the following criteria were used to make an evaluation:

- In both systems the heat storage tank was used to lower the overall duration of heating and cooling.
- The systems were compared with the same energy transfer to the external working fluid for cooling and heating.
- Both systems use electrical power input. Electric efficiency of 98% was used for the boiler and electric motors. These values were obtained from the manufacturers.

Table 8.10 - Conventional system energy needs

Conventional system	Run Time	Power input	Total Power input
	[h]	[kW]	[kWh]
Cook tank heating	2.4	146.6	345.2
Distillation cooling	2.4	5.9	13.8
Distillation heating	2.3	146.6	331.6
Cook Tank cooling	2.3	5.9	13.3
Drying	1.2	146.6	171.3
Further cooling of cook tank	1.2	5.9	6.9
Final cooling of cook tank	1.7	146.6	255.8
Other heating requirements	1.7	5.9	10.2
Total	**15.1**		**1148.1**

Table 8.11 - Two stage hybrid heat pump energy needs

TSHHP	Run Time	Power input	Total Power input
	[h]	[kW]	[kWh]
Cook tank heating & distillation cooling	2.4	57.3	134.9
Distillation heating & Cook tank cooling	2.3	57.3	129.6
Drying & further cooling of Cook tank	1.2	57.3	66.9
HST heating & final cooling of Cook tank	1.7	57.3	100.0
Total	**7.5**		**431.4**

In Table 8.10 it can be seen that the conventional system has higher energy needs than the TSHHP system in Table 8.11 for the same running period. This is mainly due to the fact that the TSHHP can use less energy by simultaneously providing heating and cooling. The boiler also uses more than 120 kW of energy for the heating. This is because of high losses due to condensation and blowdown, which causes the boiler to produce more steam than the actual requirements.

Table 8.12 - Difference in running cost

Overall Energy Cost	Usage	Tarif	Cost	Annual Cost
	kWh	c/kWh	R	R
Conventional	1148.09	36	R 413.31	R 165 325.20
TSHHP	431.43	36	R 155.31	R 62 125.54
Savings	**716.66**		**R 258.00**	**R 103 199.66**

The difference in running cost for the two systems is shown in Table 8.12. Both systems use electricity as the main source of energy. When the running cost of the cycles are compared for a single batch process, the TSHHP uses 717 kWh less energy , which is only 38% of the energy used by the conventional system. This amounts to R258 savings per batch if a tariff of 36 c/kWh is used

If the plant is operated for 300 days a year, with two batches produced every 36 hour interval, up to 400 batches could be produced each year. This would result in a R 103 200 saving if the heat pump is used.

8.5 Conclusion

In this chapter a method for simultaneous heating and cooling was investigated. It was important to investigate the different possibilities in the ethanol plant for decreasing the cost of the heating and cooling system installation and running cost.

The result was that the introduction of a heat storage tank could reduce the duration of the entire batch process. The processes in the cook tank and distillation column including the constant temperature steps, take 14 hours to complete, which means that two batches could be prepared for fermentation and distilled during the residence time of the fermentation.

An economic evaluation was then discussed. The conclusion is that using a TSHHP will cost only 63% of a conventional system. When the running cost is compared, the TSHHP will use only 38% of the energy for heating and cooling in the ethanol production process. This lower energy consumption will contribute to considerable savings in the future.

If a combustion engine is used to drive the compressors, extra heating could be supplied to the system, from the cooling water of the engine. Another method of implementing the TSHHP, might be to manage the energy requirements in such a way, that the LT and HT cycle could work in *series and parallel*. This would decrease the energy requirements of the system even more, by using the high COP (up to 4.2) individual cycles in parallel when the temperature gradient is sufficient over the heat exchangers. The TSHHP would only be coupled in series if there is no high temperature energy source available, to achieve the high discharge temperatures.

For the heat exchanger cost analysis by Bester, the overall heat transfer coefficient was considerably lower than mentioned in paragraph 5.6 for experimental plant already constructed. Better design of the heat exchangers could increase the overall heat transfer coefficient more, which will decrease the size and cost of the heat exchangers.

Chapter 9 - Closure

9.1 Conclusions

This study set out to evaluate the feasibility of using a hybrid heat pump in a small scale ethanol plant. The plant should make it possible for farmers to produce their own ethanol. Ethanol is a renewable fuel that is a viable alternative to fossil fuels, with the advantage of reducing greenhouse gas emissions. The production of ethanol should be as energy efficient as possible, to reduce the cost of ethanol production process.

Hybrid heat pumps combine the features of vapour compression heat pumps and absorption heat pumps. The combination gives hybrid heat pumps the advantage of working at high temperature levels with a zeotropic mixture, which result in high COP's (over 4). To achieve the high temperature lift needed in the ethanol production process, the hybrid heat pump was coupled in a cascade to form a two stage hybrid heat pump (TSHHP). The TSHHP has the additional advantage of high temperature lift (over 100℃) and low pressure ratios when compared to other heat pump systems over the same operating conditions.

To determine the energy efficiency potential of TSHHP in the ethanol production process, a small scale ethanol plant was simulated. The ethanol production process is achieved through a number of steps, of which liquefaction, cooking, saccharification and distillation is the most energy intensive. Temperatures in the process varied between 105℃ and 25℃ in the plant. The plant was modelled for a 3000 kg batch process, with 882 kg raw material input and 402 kg of 92 wt% ethanol output. The high temperature lift capability and efficiency of the TSHHP made it a viable and attractive alternative to conventional heating and cooling systems in ethanol plants.

A TSHHP model was then developed to determine the operating temperatures and features of the system. An ammonia/water mixture was used due to its stability and proven operation in AHT at high temperatures. The zeotropic nature of the ammonia/water mixture used, gave the TSHHP an extra degree of freedom in the design. Temperature is a function of pressure and concentration of ammonia in the mixture. This made it possible to adjust the concentration or pressure to achieve the temperature lift needed in the ethanol production process.

The TSHHP was modelled for 120 kW of heating, while providing simultaneous cooling of 65 kW. Average temperature lift over the heat exchangers of 106℃ is achieved in the TSHHP model with a COP of 2.1. Due to the temperature glide in the absorption and desorption processes during counter-flow heat transfer, a maximum temperature of heat delivery to external working fluid as high as 142℃ could be achieved with cooling water as low as 9℃. These values varied due to changes in inlet temperature of external working fluid, while keeping the heat transfer at the heat exchangers constant. The compressor of the TSHHP was modelled as a partial wet compression with liquid injection into the compression cavity. This reduced the superheating of the vapour exiting the compressor.

TSHHP system was evaluated against conventional heating and cooling systems in the ethanol plant model developed. Different methods of integrating the multiple batch process were investigated with simultaneous heating and cooling. The implementation of a heat storage tank (HST) proved to be a viable method of stabilizing the energy input into the plant. The HST will make it possible for the ethanol plant to achieve zero energy balance if the TSHHP is used, due to energy that is recycled in the plant. Shortcoming of conventional systems is that energy is dumped into the atmosphere and provides no opportunity for the reuse and integration of energy in a system.

The economic evaluation related to the installation and running cost of the TSHHP and a conventional system was done. The conventional system with boiler and evaporative cooling tower proved to be more expensive than the TSHHP. The installation cost of the TSHHP was only 63% than that of a conventional system. The main advantage of the TSHHP is the reduction in energy use. The TSHHP uses only 38% of the energy a conventional system uses for heating and cooling in the plant. This could contribute to substantial saving in the future running cost of the plant and reduce the expenses related to the final ethanol product.

To conclude, the TSHHP technology described in this dissertation offers the farming community the possibility of producing ethanol on their own farms in a small scale ethanol plant. The implementation of the TSHHP compared to conventional systems, will reduce the cost related to installation and the cooling and heating processes in the ethanol plant. It will also reduce the power input and increase the overall energy efficiency of the plant.

9.2 Recommendation for further work

Based on the results of this study the following was identified as areas that need further attention.

- Detail simulations of the heat exchanger models should be developed to better understand the temperature profiles and pinch points in the absorption and desorption of the ammonia/water mixture.
- Prototype of the TSHHP should be constructed to obtain experimental data. This would also help identifying the characteristics of screw compressors with the liquid injection into the compression cavity.
- Implementation of the TSHHP technology into an ethanol plant should be investigated and tested in an experimental plant, to evaluate its potential in high temperature applications.
- Managing of the energy requirements and the potential of a Heat storage tank should be further investigated in cooperation with the TSHHP in the ethanol plant.
- Managing the heating and cooling requirements of the TSHHP in such a way, that it is possible to use the stages of the TSHHP in series and parallel according to what is needed in the plant. This would increase the energy efficiency of the plant even further.

BIBLIOGRAPHY

Åhlby L, Hodgett D. 1990. **Compression–absorption heat pumps**. In: Proc of the 3rd International Energy Agency Heat Pump Conference. Tokyo, 1990.

Albers, E., Larsson, C., Liden, G. Niklasson, C., Gustafsson, S. 2002. **Continious estimation of product concentration with calorimetry and gas analysis during anaerobic fermentation of Saccharomyces cerevisiae**, Thermochima Acta vol. 394 pp. 185 – 190,

Alefeld, G. Radermacher R. 1994. **Heat Conversion Systems.** CRC Press.

ASPEN. 2008. **Aspen Plus** - http://www.aspentech.com [Date of access: 19 Jun. 2008].

Beckley, M. 2008. **Spirax Sarco South Africa (Pty) Ltd. Personal communication.** Gauteng. South Africa

Bergmann, G., Hivessy, G. 1990. **Main features and operational experience of the hybrid heat pump pilot plant**. Proceedings of the 3rd International Workshop on Research Activities on Advanced Heat Pumps, University of Technology Graz, Graz, Austria, p. 111–120.

Berk, J. 2005. **Everything you wanted to know about direct thermal drying but were afraid to ask**. USFilter, Holland,

Bester, F. 2008. **ELROX design and management service. Personal communication.** Hatfield, South Africa.

Bohlmann, G.M. 2002. **Biotechnology Separation Process.** SRI Consulting Report no. 188B, California.

Botha, P. 2008. **Hoeveel gaan dit jou regtig kos om hierdie seisoen te plant?** Senior Landbounavorsings - Kundige, SA GRAAN SA September 2008 http://www.graansa.co.za/ [Date of access: 15 Sep. 2008].

Brunin, O., Feidt, M., Hivet, B. 1997. **Comparison of the working domains of some compression heat pumps and a compression–absorption heat pump**. Int J Refrig 1997;20(5):308–318.

Buchheit, J.K. 2002. **Production of Ethanol**. Rural Enterprise and Alternative Agricultural Development Initiative. Report 13.

Butzen, S. & Hobbs, T. 2002. **Maize Processing**. Crop Insights, 12(10):1-6.

Crever 2006. **Report on Energy Efficient and Renewable Energy Systems** Planning and Recommendations for their Successful Application. http://six6.region-stuttgart.de [Date of access: 8 Aug. 2007].

Demirbas, A. 2004. **Bioenergy, Global Warming, and Environmental Impacts**. Energy Sources, 26(3):225-236.

Demirbas, M.F. & Balat, M. 2006. **Recent advances on the production and utilization trends of biofuels: A global perspective**. Energy Conversion and Management, 47(15-16):2371-2381.

Department of Minerals and Energy (DME) 2005. **The energy efficiency strategy for the Republic of South Africa**. http://www.dme.gov.za/ [Date of access: 11 Mar. 2008].

Department of Minerals and Energy (DME) 2006. **Draft Biofuels Industrial Strategy of the Republic of South Africa.** http://www.dme.gov.za/ [Date of access: 21 Jul. 2007].

Energy Information Administration. (EIA) 2005. **International Energy Outlook 2005**. Online at: http://www.eia.doe.gov [Date of access: 14 Jan. 2008].

Felder, R.M. and Rousseau, R.W. 2000. **Elementary Principles of Chemical Processes**. 3de ed., John Wiley & Sons, Inc, New York.

Fong, W.S. 1982.**Ethanol for Gasohol**. SRI Consulting Report no. 149, California.

Genchap. 2007. **Chapter 3. Heat Pumps and Related Plant** – p 373-392 WEB: http://www.caenz.com/info/downloads/publications [Date of access: 16 March 2008].

Groll, E.A. 1997. **Current Status of Absorption/Compression Technology**. In ASHRAE Transactions: Symposia. Philadelphia.

Heat Pump Centre (IEA). 2007. **About Heat Pumps**. IEA Heat Pump Centre Website 2006 [cited 2007 May 24]; Available from: URL: www.heatpumpcentre.org [Date of access: 28 Jul. 2008].

Herold, K. E., Radermacher, R., Klein, S. A. 1996. **Absorption Chillers and Heat Pumps**. Boca Raton : CRC Press LLC.

Howden Compressors Ltd. 2008. **Oil free screw compressors** http://www.howden.com [Date of access: 3 Aug. 2007].

Hultén, M., Berntsson, T. 1998.**The compression/absorption cycle – influence of some major parameters on COP and a comparison with the compression cycle** International Journal of Refrigeration 22 (1999) 91–106

Hultén, M., Berntsson, T. 2002. **The compression/absorption heat pump cycle—conceptual design improvements and comparisons with the compression cycle.** International Journal of Refrigeration 25 (2002) 487–497

Ibrahim, Klein. 1993. **"Thermodynamic Properties of Ammonia-Water Mixtures,"** ASHRAE Trans.: Symposia, 21, 2, 1495 (1993).

Incropera, F.P., De Witt, D.P. 2002.**Fundamentals of heat transfer**. 5th ed. Canada: John Wiley & Sons :641-680)

Infante Ferreira, C.A., Zamfirescu, C., Zaytsev, D. 2005. **Twin screw oil-free wet compressor for compression–absorption cycle.** International Journal of Refrigeration 29 (2006) 556–565

Itard, L.C.M. 1995. **Wet compression versus dry compression in heat pumps working with pure refrigerants or non-azeotropic mixtures** Int. J. Refrig. Vol. 18, No. 7, pp. 495-504, 1995

Itard, L.C.M. 1998. **Wet compression–resorption heat-pump cycles:thermodynamic analysis and design**. PhD Thesis. Delft University of Technology, Delft.

Itard, L.C.M., Machielsen, C. H. M. 1994. **Considerations when modelling compression/resorption heat pumps.** Int. J. Refrig.. vol. 17, no. 7, s. 453-460.

Jancík, L., Bašta, J. 2007. **Hybrid heat pump optimization. WEB** http://www.fsid.cvut.cz [Date of access: 15 Feb. 2008].

Jenkins, B.M., Soroka, B. 2007. **Energy Systems Heat Pumps.** Power Quality & Utilisation Guide . Section 7: Energy Efficiency www.leonardo-energy.org. [Date of access: 15 Feb. 2008].

Kotas, T.J. 1995. The **Exergy Method of Thermal Plant Analysis,** USA, Krieger Publishing Company.

Kwiatkowski, J.R., McAloon, A.J., Taylor, F. & Johnston, D.B. 2006. **Modelling the process and costs of fuel ethanol production by the maize dry-grind process.** Industrial Crops and Products, 23(3):288-296.

Magneti Marelli. 2008. **Flexfuel SFS** http://www.magnetimarelli.com [Date of access: 7 June 2008].

Mehendale, S.S., Radermacher, R. 1996. **Simulation of hybrid heat pumps with two- and three-stage solution circuits for high lift applications**. ASHRAE Trans 1996;102(1):1101–1109.

Meyer, F., Strauss P.G. 2005. **Bio-ethanol production in South Africa: An objective analysis.** Bureau for Food and Agricultural Policy.

Minea, V., Chiriac, F. 2006. **Hybrid absorption heat pump with ammonia/water mixture : Some design guidelines and district heating application.** International Journal of Refrigeration vol. 29 (2006) 1080-1091

Noll, S. L., C. Abe, and J. Brannon, 2003. **Nutrient composition of corn distiller dried grains with solubles**. University of Minnesota, USA. *Poultry Sci.* 82 (Suppl. 1): 71.

Oberholzer, A.L. **Personal communication.** School of Chemical Engineering. North West University, Potchefstroom Campus, South Africa.

Piskur, J. and Langkjaer, R.B. 2004. **Yeast genome sequencing: The power of comparative genomics**. Molecular Microbiology, vol. 53, pp. 381–389.

Punwani, D.V., Ryan, W.A., Kalensky, D.C. 2005. **Natural Gas-Fired Cooling Technologies and Economics.** Developed for Cooling Solutions for Customer Choice Mutual Fund. Gas Technology Institute (2005)

Radermacher, R. 1991. **Advanced heat pump cycle for district heating and cooling systems** http://www.osti.gov [Date of access: 26 Sep. 2007].

Radermacher, R., Hwang, Y. 2005. **Vapour compression heat pumps with refrigerant mixtures** - Boca Raton: Taylor & Francis.

Rane, M. V., Radermacher, R., Herold, K. E., 1990. **Experimental Investigation of a Single Stage Vapour *C*ompression Heat Pump with Solution Circuit** .ASME Winter Annual Meeting, December 10-15, San Francisco, US*A*.

Renewable Fuels Association (RFA). 2005. **Home grown for the Homeland: Ethanol Industry Outlook 2005**. http://www.ethanolrfa.org/objects/pdf/outlook/outlook_2005.pdf. [Date of access: 21 Jul. 2007].

Risberg, T., Horntvedt, B., Madland, D., Nordtvedt, S.R. 2004. **Process dynamics in an industrial prototype compression/absorption heat-pump**, **Natural working fluids 2004**, Proceedings of the 6th IIR Gustav Lorentzen Conference, Glasgow, United Kingdom, International Institute of Refrigeration, Paris, [session 7b].

Rousseau, P.G. 2007. **Advanced Thermal-Fluid Systems.** School of Mechanical Engineering. North West University, Potchefstroom Campus, South Africa.

Sasol. 2008. **Gauteng Fuel Prices - Fuel price history** http://www.sasol.com/ [Date of access: 8 April 2008].

Satapathy, P.K., Gopal, M.R., Arora, R.C. 2004. **Studies on a compression–absorption heat-pump for simultaneous cooling and heating**, Int J Energy Res 28 (2004) 567–580.

Shapouri, H., Gallagher, P., Graboski, M.S. USDA's 1999. **U.S Ethanol Cost-of-Production Survey. U.S Department of Agriculture**. Agricultural Economic Report Number 808.

Sonntag, R.E., Borgnakke, C., Van Wylen, G.J. 2003. **Fundamentals of Thermodynamics** 6th ed. John Wiley & Sons Inc

Spyrax-Sarco. 2007. **The steam and Condensate loop,**1st ed, Spyrax-Sarco Limited, Gloucestershire, England

Tait, B. 2005. **Requirements and viability for biofuels in South Africa**. FSSA Annual Congress, May [Web:] www.fssa.org.za [Date of access: 23 October 2008].

UNEP. 2002. **Report of the refrigeration, air conditioning and heat pumps.** Technical options committee 2002 assessment: http://ozone.unep.org/ [Date of access: 12 May 2007].

Utria, B.E. 2004. **Ethanol and gelfuel: clean renewable cooking fuels for poverty alleviation in Africa**. Energy for Sustainable Development, vol.8, no.3.

Van der Veen, M.E., Veelaert, S., Van der Groot, A.J., Boom, R.M. 2006. **Starch hydrolysis under low water conditions: A conceptual process design**. Journal of food Engineering, vol. 75, pp. 178-186.

Vorster, P.P.J., Meyer, J.P. 1999. **Wet compression versus dry compression in heat pumps working with pure refrigerants or non-azeotropic binary mixtures for different heating applications.** International Journal of Refrigeration 23 (2000) 292-311

Walsh, J.H. 2000. **Projection of cumulative world conventional oil production, Remaining resources and Reserves to 2050**.

White, S.D., Cleland, D.J., Cotter, S.D., Stephenson, R.A., Kallu, R.D.S., Fleming, A.K. 2001. **A heat pump for simultaneous refrigeration and water heating** Proc. IPENZ Conf., Wellington, New Zealand, vol. 2. 1997. p. 117–22

Wilson, S. C., Matthew, M., Austin, G., Von Blottnitz, H. 2005. **Review of the Status of Biodiesel Related Activities in South Africa**. Report for the City of Cape Town, South Africa. pp 76.

Zaytsev, D., Infante Ferreira, C.A. 2004. **Profile generation method for twin screw compressor rotors based on the meshing line.** International Journal of Refrigeration 28 (2005) 744–755

Zhou, Q., Radermacher, R. 1996. **Development of a vapor compression cycle with a solution circuit and desorber/absorber heat exchange** Int J. Refrig. Vol. 20, No. 2, pp. 85-95

Ziegler, F., Spindler, U. 1993. **An ammonia refrigerator with an absorption circuit as economizer**. Int J Refrig 1993; 16(4):230–239.