LAPPEENRANTA UNIVERSITY OF TECHNOLOGY
School of Technology
Master's Degree Program in Chemical and Process Engineering

Ismo Pekkanen

CONCENTRATION OF HYDROGEN PEROXIDE AND IMPROVING ITS ENERGY EFFICIENCY

Examiners: Professor Marjatta Louhi-Kultanen
D.Sc. (Tech.) Harri Niemi
D.Sc. (Tech.) Nina Salmela-Mäkelä

ACKNOWLEDGEMENTS

An energy savings project Solwatt was carried out at the Solvay Voikkaa Plant in 2013. As a result of this project, a number of ideas to improve the energy efficiency of the concentration unit of the factory was formed. These, and new ideas regarding the energy savings of the distillation, were required to be studied more deeply in the form of Master's Thesis. This challenge was offered to me and I decided to take this opportunity. I am very grateful to the Solvay Voikkaa Plant for this opportunity and the possibility to work at the same time with the thesis. I did my best and I hope that the results of this work are useful and profitable for the Solvay Voikkaa Plant.

The experience of doing this work has been very rewarding. I have learnt much about engineering work and the combining of theoretical knowledge with practice. The working days have been long at times, but I think they have been worth of it. The feedback from the work has been positive and encouraging, not forgetting the constructive criticism.

First, I would like express my gratitude to the whole personnel of the Solvay Voikkaa Plant. I am especially thankful to the supervisor of my thesis at Solvay: Production Engineer Nina Salmela-Mäkelä. Moreover, I am grateful to the Site Manager Juha Piipponen and Production Manager Teppo Myohanen. In addition, I am thankful to Supervisor engineer Timo Orava, who has done a large part of the experiments regarding to the optimization of the reflux flow, which were used in this work. I would also like to thank shift supervisors and operators of the Solvay Voikkaa Plant.

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ABSTRACT

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Concentration of hydrogen peroxide and improving its energy efficiency

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100 pages, 41 figures, 28 tables and 1 appendix

Examiners: Professor Marjatta Louhi-Kultanen
D.Sc. (Tech.) Harri Niemi
D.Sc. (Tech.) Nina Salmela-Mäkelä

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Distillation is a unit operation of process industry, which is used to separate a liquid mixture into two or more products and to concentrate liquid mixtures. A drawback of the distillation is its high energy consumption. An increase in energy and raw material prices has led to seeking ways to improve the energy efficiency of distillation. In this Master's Thesis, these ways are studied in connection with the concentration of hydrogen peroxide at the Solvay Voikkaa Plant.

The aim of this thesis is to improve the energy efficiency of the concentration of the Voikkaa Plant. The work includes a review of hydrogen peroxide and its manufacturing. In addition, the fundamentals of distillation and its energy efficiency are reviewed. An energy analysis of the concentration unit of Solvay Voikkaa Plant is presented in the process development study part. It consists of the current and past information of energy and utility consumptions, balances, and costs. After that, the potential ways to improve the energy efficiency of the distillation unit at the factory are considered and their feasibility is evaluated technically and economically. Finally, proposals to improve the energy efficiency are suggested.

Advanced process control, heat integration and energy efficient equipment are the most potential ways to carry out the energy efficient improvements of the concentration at the Solvay Voikkaa factory. Optimization of the reflux flow and the temperatures of the overhead condensers can offer immediate savings in the energy and utility costs without investments. Replacing the steam ejector system with a vacuum pump would result in savings of tens of thousands of euros per year. The heat pump solutions, such as utilizing a mechanical vapor recompression or thermal vapor recompression, are not feasible due to the high investment costs and long pay back times.

TIIVISTELMÄ

Lappeenrannan teknillinen yliopisto
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Ismo Pekkanen

Vetyperoksidin väkevöinti ja sen energiatehokkuuden parantaminen

Diplomityö

2014

100 sivua, 41 kuvaa, 28 taulukkoa ja 1 liite

Tarkastajat: Professori Marjatta Louhi-Kultanen
TkT Harri Niemi
TkT Nina Salmela-Mäkelä

Hakusanat: vetyperoksidi, tislaus, väkevöinti, energiatehokkuus

Tislaus on prosessiteollisuuden yksikköoperaatio, jota käytetään erottamaan nestemäinen seos kahdeksi tai useammaksi tuotteeksi sekä nesteseoksien väkevöimiseen. Yksi tislauksen haitoista on sen suuri energiankulutus. Nousseet energian ja raaka-aineiden hinnat ovat johtaneet tislauksen energiatehokkuutta parantavien keinojen kartoittamiseen. Tässä diplomityössä tutkitaan näitä keinoja vetyperoksidin väkevöinnin yhteydessä Solvayn Voikkaan vetyperoksiditehtaalla.

Työn tavoitteena on parantaa Voikkaan tuotantolaitoksen väkevöinnin energiatehokkuutta. Työ sisältää katsauksen vetyperoksidiin, sen valmistamiseen, tislauksen perusteisiin ja sen energiatehokkuuteen. Väkevöintiyksikön energia-analyysi on esitetty työn prosessinkehittämisen osassa. Se koostuu tämän hetkisistä ja aikaisemmista energia- ja hyödykekulutuksista, taseista ja kustannuksista. Energia-analyysin jälkeen on esitetty potentiaaliset väkevöintiyksikön energiatehokkuutta parantavat keinot. Näiden keinojen toteutettavuutta on arvioitu sekä teknisesti että taloudellisesti. Lopuksi annetaan ehdotuksia väkevöintiyksikön energiatehokkuuden parantamiseksi.

Kehittyneet prosessisäädöt, lämpöintegrointi ja energiatehokkaat laitteistoratkaisut ovat potentiaalisimmat keinot parantaa väkevöinnin energiatehokkuutta Voikkaan tuotantolaitoksella. DM-vesivirran ja lauhduttimien lämpötilojen optimointi voi tarjota välittömiä säästöjä energia- hyödykekulutuksissa ilman investointeja. Höyryejektorin korvaaminen alipainepumpulla mahdollistaisi kymmenien tuhansien eurojen vuosittaiset säästöt. Lämpöpumppuratkaisut, kuten mekaaninen lämpöpumppu ja termokompressori, eivät ole järkeviä suurien investointikustannuksien ja pitkien takaisinmaksuaikojen takia.

SYMBOLS

B	molar flow of bottom product, mol h^{-1}
D	molar flow of overhead product (distillate), mol h^{-1}
E	exergy flow, J h^{-1}
E_{feed}	exergy flow of feed, J h^{-1}
$E_{product}$	exergy flow of product, J h^{-1}
E_0	standard electrode potential, V
F	mass flow of feed, kg h^{-1}
H	enthalpy flow, J h^{-1}
H_{Bottom}	enthalpy flow of bottom product, J h^{-1}
H_{Feed}	enthalpy flow of feed, J h^{-1}
$H_{Ovh.}$	enthalpy flow of overhead product, J h^{-1}
L	mass flow of liquid, kg h^{-1}
L_R	molar flow of liquid in rectifying section, mol h^{-1}
$L_{R.flux}$	molar flow of reflux, mol h^{-1}
L_S	molar flow of liquid in stripping section, mol h^{-1}
m	an equilibrium stage in stripping section
n	an equilibrium stage in rectifying section
n_D^{20}	refractive index, -
P	pressure, Pa
pK_a	logarithmic acid dissociation constant, -
Q	heat flow, J h^{-1}
Q_c	cold utility target, J h^{-1}
Q_C	heat flow removed, J h^{-1}
$Q_{Cond.}$	heat flow removed in condenser, J h^{-1}
$Q_{Cool.}$	heat flow removed in cooler, J h^{-1}
Q_h	hot utility target, J h^{-1}
Q_H	heat flow supplied, J h^{-1}
Q_i	opportunity for process heat integration, J h^{-1}
$Q_{P.heat}$	heat flow supplied in preheater, J h^{-1}
Q_{Vap}	heat flow supplied in vaporizer, J h^{-1}
R	gas constant, J K^{-1}mol^{-1}
R^2	coefficient of determination, -
R_D	reflux ratio, -
S	entropy flow, J h^{-1}
T	temperature, °C
T_a	reference temperature, °C
T_C	temperature at which heat removed, °C
T_h	heat temperature, °C
T_H	temperature at which heat supplied, °C

$T_{Condenser}$	temperature at condenser, °C
$T_{Vaporizer}$	temperature at vaporizer, °C
T_0	ambient temperature, °C
T_1	temperature of the bottom of the distillation column, °C
T_2	temperature of the middle part of the distillation column, °C
T_3	temperature of the top of the distillation column, °C
V	mass flow of vapor, kg h^{-1}
V_R	molar flow of vapor in rectifying section, mol h^{-1}
V_S	molar flow of vapor in stripping section, mol h^{-1}
W	minimum work consumption per mole of feed, J mol^{-1}
W_{heat}	theoretical minimum work required for the distillation, J h^{-1}
W_{lost}	heat lost during the distillation, J h^{-1}
x	mole fraction of more volatile component in liquid phase, -
x_B	mole fraction of more volatile component in bottom product of distillation column, -
x_D	mole fraction of more volatile component in overhead product of distillation column, -
x_F	mole fraction of component in feed, -
x_m	mole fraction of more volatile component in liquid phase, which flows to the stage *m*+1 of distillation column, -
x_n	mole fraction of more volatile component in liquid phase, which flows to the stage *n*+1 of distillation column, -
$x_{bottoms}$	mole fraction of component *i* in bottom product, -
$x_{distillate}$	mole fraction of component *i* in distillate, -
x_{Fi}	mole fraction of component *i* in feed, -
x_{H_2O}	mole fraction of water in liquid phase, -
y	mole fraction of more volatile component in vapor phase, -
y_{H_2O}	mole fraction of water in vapor phase, -
y_{n+1}	mole fraction of more volatile component in vapor phase, which flows from the the stage *n*+1 of distillation column, -
y_{m+1}	mole fraction of more volatile component in vapor phase, which flows from the stage *m*+1 of distillation column, -
z_{feed}	mole fraction of more volatile component in liquid phase in feed, -

Greek symbols

$\Delta H_{melt.}$	heat of fusion, J mol^{-1}
$\Delta H_{vap.}$	heat of vaporization, J mol^{-1}
$\Delta T_{ac.pre.}$	temperature difference across preheater, °C
$\Delta T_{\min}$	minimum allowable temperature difference, °C
ΔT_{1-2}	temperature difference of the lower part of distillation column, °C
γ_i	activity coefficient of component *i*, -

ABBREVIATIONS

AO	auto-oxidation
B	bottom product flow
cc	concentration
CW	cooling water
D	distillate flow
DC	distillation column
ds	distillation
DIBC	diisobutyl carbinol
DIST	distillation unit
DMW	demineralized water
DWC	divided wall column
E	reboiler
EXT	extraction
F	feed flow
HIDiC	internally heat integrated column
HPPO	hydrogen peroxide to propylene oxide
HYDR	hydrogenation
MiMo	Micro Motion
MIBK	methyl isobutyl ketone
MVR	mechanical vapor recompression
NG	natural gas
ppm	parts per million
R	reflux
S	motive steam flow
SMR	steam reforming
TOC	total organic carbon
TVR	thermal vapor compression
VC	vapor compression
VLE	vapor-liquid equilibrium
VSD	variable speed drive
WS RED	reduced working solution

TABLE OF CONTENTS

1 INTRODUCTION

Hydrogen peroxide is a chemical, which is widely used in many industrial areas. It is mainly used in bleaching of pulp and paper but its uses in environmental applications and in the chemical industry have also been increased in the last decades. [1, 2] Nowadays, hydrogen peroxide is industrially manufactured almost exclusively by the anthraquinone auto-oxidation (AO) process in which crude aqueous hydrogen peroxide solution (~ 40 wt%) is formed. This crude solution is further concentrated into more concentrated solutions usually by vacuum distillation. [3]

Distillation is a well-known and efficient concentration method but at the same time, it is one of the most energy consuming unit operations in the process industry. The rise of energy and raw material prices has created a need to develop more energy and cost efficient distillation systems. The increase of the environmental awareness has also led to considering, how distillation should be designed and operated in a more energy efficient way. [4, 5] In this Master's Thesis, the ways to improve energy efficiency of distillation are studied closely. The aim of this thesis is to evaluate and improve the energy efficiency of the concentration of hydrogen peroxide. The thesis is divided into literature and process development study parts. In the literature part, the theoretical basic knowledge of hydrogen peroxide, distillation, and energy efficiency of distillation are introduced. This knowledge is used in the process development study part in which the energy efficiency of distillation is evaluated at a practical level at the hydrogen peroxide plant Solvay Voikkaa.

A short review of hydrogen peroxide, including the most important chemical and physical properties, is given in the beginning of the literature part. The main manufacturing process (the anthraquinone-process), together with its unit operations, are briefly introduced. Moreover, the safety factors and the uses of hydrogen peroxide are briefly discussed. The basic features of concentration of hydrogen peroxide are described.

The basic fundamentals of distillation theory, continuous distillation processes, process control, and distillation columns are dealt with in the chapter on distillation. The energy efficiency of distillation is considered at a theoretical level at the end of the literature part in which the methods to improve the energy-efficiency of distillation are studied.

In the process development study part, the energy-analysis of the concentration of hydrogen peroxide at the Solvay Voikkaa Plant is carried out. The energy analysis includes the current information of the energy efficiency of the distillation unit: energy and utility consumptions, balances, and costs. After this, the potential ways to improve the energy efficiency of the distillation unit at the plant are considered and their feasibility is evaluated technically and economically. Finally, proposals to improve the energy efficiency are suggested.

LITERATURE PART

2 HYDROGEN PEROXIDE

Hydrogen peroxide, H_2O_2, is a chemical compound, which is available in the environment in small concentrations. Commercially, it is manufactured for industrial use with a wide range of concentrations. Most often hydrogen peroxide is sold in concentrations 35, 50, 60 and 70 wt%, and these concentrated solutions can be further diluted for different applications. In addition, the distillates of hydrogen peroxide, which are purer than industrial grades, are manufactured for special uses. [1, 3]

Nowadays, hydrogen peroxide is almost exclusively manufactured by the anthraquinone auto-oxidation (AO) processes. The development of the anthraquinone auto-oxidation processes made the construction of large-scale plants possible since 1950. [3] The global production capacity of hydrogen peroxide was estimated to be 3.8 million t/a in 2012, calculated as 100 % H_2O_2 and it is predicted to rise to 5 million t/a by the year 2017 [6, 7]. An interest towards cleaner, cheaper and more simple manufacturing processes of hydrogen peroxide has been increased during the last years. An example of these kinds of processes is a Mini AO-process in which a small amount of hydrogen peroxide is produced locally where it is needed. The process is cheap compared to the large-scale AO-process and at the same time, the amount of impurities is small. [8] Another example is a direct combination of hydrogen and oxygen. In this process hydrogen peroxide is manufactured directly by combining these compounds. Some patents on this process have been published but large scale processes have not yet been developed [3].

2.1 Physical properties

Hydrogen peroxide, molar mass 34.016 g/mol, is a clear and colorless liquid, which is miscible with water in all proportions. It is also soluble in many organic solvents, such as carboxylic esters. Hydrogen peroxide does not form an azeotropic mixture with water and, in theory, they can be separated completely by distillation. Fractional crystallization can be used to manufacture 100 wt% hydrogen peroxide from highly concentrated aqueous solutions. However, crystallization is not used on an industrial scale. [1, 9]

Eul et al. state [1] that the structure of the hydrogen peroxide molecule is nonpolar H-O-O-H and the hydrogen bonding between the molecules is less than found in water. In aqueous solutions, the association between water and hydrogen peroxide molecules is more stable than between the individual species. Some physical properties of pure hydrogen peroxide and aqueous hydrogen peroxide solutions can be seen in Table I. The comparison between physical properties of hydrogen peroxide and water is introduced in Table II.

Table I Physical properties of hydrogen peroxide solutions [1].

	Concentration of hydrogen peroxide, wt%					
	10	35	50	60	70	100
Density at 20 °C, kg/m^3	1.034	1.113	1.195	1.236	1.288	1.450
Freezing point,°C	-6.0	-33.0	-52.2	-55.5	-40.3	-0.41
Boiling point,°C	102	108	114	119	125	150.2
Viscosity at 20 °C, mPa·s	1.01	1.11	1.17		1.24	1.245
$\Delta H_{vap.}$ at 25 °C, kJ/mol	2.357		2.017	1.928	1.832	1.517

Table II Physical properties of pure hydrogen peroxide and water [1, 3].

	H_2O	H_2O_2
Density at 20 °C, kg/m^3	1.288	1.450
Freezing point,°C	0	-0.41
Boiling point,°C	100	150.2
Viscosity at 20 °C, mPa·s	1.002	1.245
$\Delta H_{melt.}$ at 25 °C, kJ/mol	0.334	0.368
$\Delta H_{vap.}$ at 25 °C, kJ/mol	2.443	1.517
Critical temperature, °C	374.2	457
Critical pressure, MPa	21.44	20.99
Refractive index n_D^{20}	1.3330	1.4084

2.2 Chemical properties

Hydrogen peroxide is a weak acid, which dissociates in water as follows:

$$H_2O_2 + H_2O \rightarrow H_3O^+ + HO_2^- \quad (1)$$

The pK_a of hydrogen peroxide is 11.75 at 20 °C and as weak acid it forms salts with various metals. The dissociation of the second proton of hydrogen peroxide molecule is insignificant. [1]

Hydrogen peroxide decomposes by releasing heat, water and oxygen

$$2H_2O_2 \rightarrow 2H_2O + O_2 \quad (2)$$

The decomposition of hydrogen peroxide can occur both in the vapor and in the liquid phase. The enthalpy of the exothermic reaction is -105.26 kJ/mol in the vapor phase and -98.20 kJ/mol in the liquid phase. [1]

According to Eul et al. [1] the decomposition may occur due to many factors. Temperature, pH or presence of impurities may initiate the decomposition and the mechanism and the rate of the decomposition depend on these factors. Commonly, impurities are metals which are used as catalysts in the manufacturing process of hydrogen peroxide. The decomposition can occur homo- or heterogeneously. Dissolved ions, such as metals: iron, copper, manganese and chromium can catalyze the homogeneous decomposition. The heterogeneous decomposition can occur due to metals, suspended metal oxides, and metal hydroxides. Examples of these metals are platinum, palladium, mercury, osmium, and silver.

The decomposition of hydrogen peroxide has to be especially prevented in commercial hydrogen peroxide solutions. These commercial solutions may contain or may be exposed to slight amounts of catalytic impurities, which can cause the decomposition. These impurities have to be removed or deactivated. Various purification steps, control of contaminants, and stabilization are ways to carry this out.

The stability is the most important quality parameter for commercial hydrogen peroxide solutions and this is a measure which implies how easily hydrogen peroxide decomposes. The stability is checked before the shipment by using a decomposition test at elevated temperatures. The stability of hydrogen peroxide solutions can be controlled by reagents and stabilizers, which can deactivate the impurities either by adsorption or complex formation. Sodium pyrophosphate $Na_2H_2P_2O_7$ is a common stabilizer, which is added to hydrogen peroxide solutions where it acts as a complexing agent. Another stabilizer is sodium stannate trihydrate $Na_2SnO_3 \cdot 3H_2O$, which adsorbs the impurities in hydrogen peroxide solutions. [1]

Hydrogen peroxide is used in several industrial applications. Eul et al. [1] state that these applications may need hydrogen peroxide which is extremely pure. Thus, several stabilizer systems have been developed for different industrial needs and particular hydrogen peroxide grades. Some distillates, for instance, may also need additional stabilizing. Special stabilizers have been targeted to uses, such as metal etching, detergents, electronics, cosmetics, food processing, cleaning semiconductor chips, and electronic components.

2.3 Reactions

The reactions of hydrogen peroxide are complex and they are not completely known. However, most of the reactions are oxidizing reactions in which hydrogen peroxide acts as an oxidizing agent. Hydrogen peroxide can also be a reducing agent if stronger oxidizers react with it. The reducing and oxidizing reactions are following:

$$H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O \qquad E_0(pH0) = +1.80\ V \qquad (3)$$

$$H_2O_2 \rightarrow 2H^+ + O_2 + 2e^- \qquad E_0(pH0) = -0.66\ V \qquad (4)$$

In the oxidizing reactions hydrogen peroxide can react as molecule H_2O_2 or as hydroxyl radicals $OH^\cdot$. Hydroxyl radicals are formed from hydrogen peroxide by cleavage of either O-H or O-O bond

$$HOOH \rightarrow H^\cdot + OOH^\cdot \qquad (5)$$

$$HOOH \rightarrow 2OH^\cdot \qquad (6)$$

Hydrogen peroxide is a strong oxidant but the hydroxyl radical is one of the strongest. The oxidation potential of hydrogen peroxide is 1.81 V and hydroxyl radical is 2.80 V. Most of the uses of hydrogen peroxide are based on that oxidation potential and hydroxyl radical formation. Hydrogen peroxide can oxidize many organic and inorganic compounds and these reactions can be utilized in many applications. [1, 3]

2.4 Safety factors

The most important safety factors for hydrogen peroxide are related to its decomposition. Hydrogen peroxide has a high energy and oxygen content, which may cause explosion and combustion reactions during the decomposition. Then, pressure and temperature may rise considerably and break equipment or cause other hazards. Thus, the decomposition should be taken into account when hydrogen peroxide is treated and stored. The significant decomposition and explosive hazards concerning hydrogen peroxide are the following: [1, 3]

1. Formation of unrelieved pressure when hydrogen peroxide decomposes
2. Combustion reactions of hydrogen peroxide and readily combustible material
3. Decomposition of hydrogen peroxide due to contacting of incompatible materials

4. Formation of an oxygen-rich vapor phase during the decomposition of hydrogen peroxide
5. Detonation of a liquid-phase mixture of H_2O_2 and organic compounds initiated by shock or thermal effects
6. Explosion of hydrogen peroxide vapor
7. Explosion of hydrogen peroxide liquid solution

Gustaf et al. [3] state that pure, highly concentrated hydrogen peroxide solutions have a risk of exploding. This risk has been investigated in many research studies, but contradictory findings have been achieved. However, decisive factors, which seem to lead to the explosions, are occlusions and initiation energy. For example, it has been proved that 86 wt% hydrogen peroxide solution in a tube of 4.09 cm internal diameter exploded when the temperature was raised over 50 °C.

According to Gustaf et al. [3] explosive vapor mixtures are formed when the hydrogen peroxide content of vapor phase is increased over 26 mol% at atmospheric pressure. This has to be paid especial attention when industrial concentrations of hydrogen peroxide solutions are handled at reduced pressures. This is because the concentration of hydrogen peroxide in the vapor phase may exceed the critical limit.

Hydrogen peroxide forms explosive mixtures with organic chemicals if the concentrations of the compounds of the mixture are specific. These specific concentrations for hydrogen peroxide-acetone-water system can be seen in Figure 1. This figure shows the explosive area of the system. The specific concentrations of the explosive area vary with different organic compounds. [3]

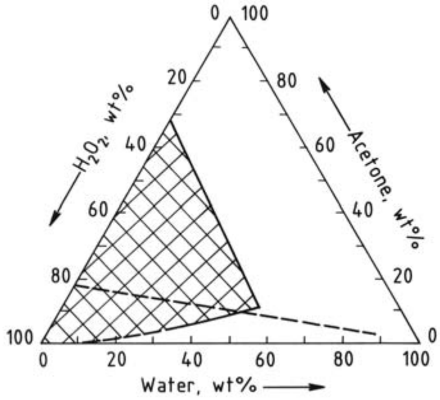

Figure 1. Explosive area of hydrogen peroxide-acetone-water system [3].

2.5 Manufacturing

The majority of hydrogen peroxide is manufactured by an anthraquinone auto-oxidation (AO) process, which makes it possible to manufacture hydrogen peroxide on a large industrial scale. In this process, anthraquinone is dissolved in a suitable solvent or in a solvent mixture. This combination is called a working solution and it is hydrogenated by the presence of a catalyst. In the hydrogenation step, which can be seen in Figure 2, anthraquinones are hydrogenated to corresponding hydroquinones. [1, 3] The hydrogenation reaction is exothermic and it is carried out in a hydrogenation reactor. The excess heat formed during the reaction can be removed by internal cooling systems of the reactor or by heat exchangers, which are located before or after the reactor. [1] With the heat exchangers, it is possible to utilize the heat formed in other parts of the process where heat is needed. This kind of heat integration increases the energy efficiency of the process.

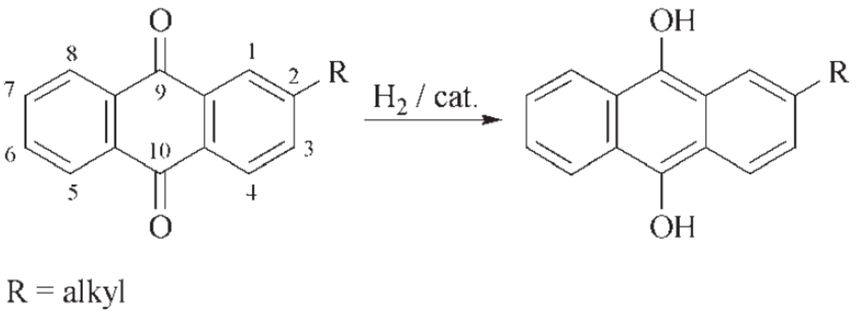

Figure 2. Hydrogenation of anthraquinones [3].

The hydrogenated working solution, which has been filtered in order to remove the catalyst, is oxidized by the oxygen-containing gas, which is usually compressed air. The oxidation reaction occurs so easily that a catalyst is not needed to initiate the reaction. Therefore, the reaction is called an auto-oxidation reaction. As a result of this, hydroquinones are oxidized to corresponding anthraquinones and hydrogen peroxide, as shown in Figure 3. The oxidation reaction is also exothermic and the temperature of the oxidation step should be controlled by different cooling systems. [1] The utilization of the formed heat is also possible in this step of the AO-process.

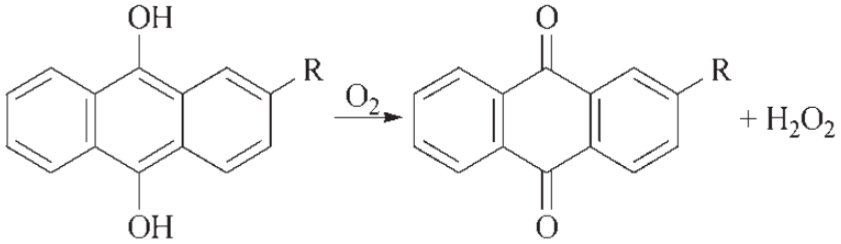

Figure 3. Oxidation of hydroquinones [3].

After the oxidation, hydrogen peroxide is extracted from the working solution by using demineralized water (DMW) in an extraction column. After the extraction, the aqueous hydrogen peroxide solution is purified and concentrated to the desired concentration. The working solution, from which hydrogen peroxide is extracted, is circulated back into the hydrogenation step and the process cycle begins again. [1]

Several by-products, which are useful or unusable in the manufacturing of hydrogen peroxide, are formed in the hydrogenation and in the oxidation steps. Some of the unusable by-products can be converted back to the useful products in a regeneration step, which is a part of AO-process. Some of the working solution is circulated through this step during the process cycle. [3]

2.6 Applications

The main use of hydrogen peroxide is bleaching and mostly, it is used to bleach pulp, paper, and textiles. The pulp and paper industry has been the primary consumer of hydrogen peroxide, but the share used for this purpose has decreased in the last years. However, a growing sector, in which hydrogen peroxide is applied, is manufacturing of propylene oxide. In the hydrogen peroxide to propylene oxide (HPPO) process, hydrogen peroxide and propylene are used as raw materials to manufacture propylene oxide. The production of propylene oxide via the HPPO process will be the driving force behind the industrial hydrogen peroxide markets in the future. This has led to the construction of high-capacity hydrogen peroxide plants over the world. [2, 10]

Gustaf et al. [3] state that hydrogen peroxide is also widely used as an oxidizer. Environmental applications and the mining industry are sectors in which the ability of hydrogen peroxide to oxidize is applied. In addition, hydrogen peroxide is also an important chemical in the other sectors of the chemical industry. For instance, it is used to produce many peroxy compounds, such as percarboxylic acids, sodium percarbonate, and metallic peroxides.

2.7 Concentration

In concentration, crude hydrogen peroxide solution is distilled by heat to more concentrated solutions. The crude solution (~ 40 wt%), which is manufactured by the AO-process, is concentrated to products typically in the range of 50 to 70 wt% [1, 11]. According to Myohanen [12] the main purpose of the concentration is to decrease the storing and the transportation costs of hydrogen peroxide. The storage and the transportation capacity can be kept high when the concentrated solutions are treated, which decreases the costs. Moreover, the concentration removes some amounts of impurities, such as organic solvents in hydrogen peroxide. At the same time, distillation makes it possible to produce purer distillates for special uses. Some applications, such as rocket fuels, also prefer concentrated solutions rather than crude solutions [13].

There are many different industrial distillation configurations of hydrogen peroxide but some common features occur in all of them. These features are safety factors which extensively control the distillation system. [12] An example of the hydrogen peroxide distillation system can be seen in Figure 4. Its features are described more precisely in the process development study part of this work.

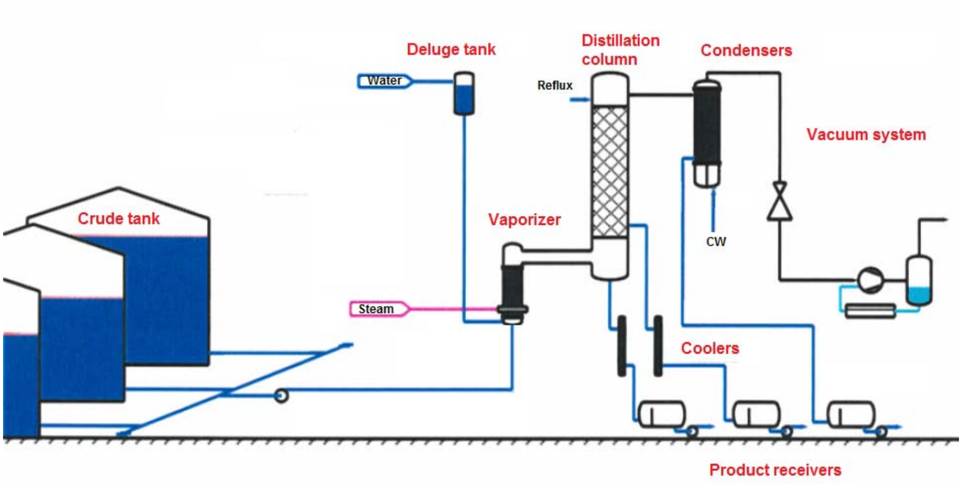

Figure 4. A common flowsheet of distillation of hydrogen peroxide [11].

3 FUNDAMENTALS OF DISTILLATION

Distillation is a unit operation and separation method of the chemical industry, which is usually used to separate a liquid mixture into two or more products. In some cases, distillation can also be applied to concentrate liquid mixtures. The concentration of hydrogen peroxide is an example of this. [12, 14] Separation or concentration by distillation is based on the boiling of liquids. Thus, it is possible only if the boiling points of the separable components are different. The vapor of a boiling mixture will be enriched with components which have lower boiling points, and consequently the residual liquid phase is concentrated with the high-boiling components. [14, 15] The theory of distillation is explained more precisely by the theories of vapor pressure and vapor-liquid equilibrium.

3.1 Vapor pressure

Vapor pressure is a physical property of a pure chemical. It is a pressure, which is produced by a pure chemical component at a particular temperature when liquid and vapor phases are at present. More precisely, the vapor pressure is caused by the molecules of this pure chemical that leaves and enters the liquid surface. [16] According to Luyben [17] vapor pressure data has been determined for most chemical components with industrial importance by laboratory experiments.

Vapor pressure is related to the boiling and the volatility of a chemical compound. A liquid boils when its vapor pressure reaches the ambient pressure. In turn, volatility is a measure which describes how easily this happens. Liquids, which have high vapor pressures have correspondingly low boiling points and vice versa. [16] The vapor pressures of some chemicals are shown in Table III.

Table III Vapor pressure of some pure chemicals at 20 °C [16, 18, 19, 20].

Chemical component	Vapor pressure, bar
Carbon dioxide	57.0000
Formaldehyde	4.35700
Methyl isobutyl ketone (MIBK)	0.26500
Water	0.02335
Hydrogen peroxide	0.00181
Heavy aromatic solvent naphta (Solvesso)	0.00040
Diisobutyl carbinol (DIBC)	0.00013

Vapor pressure depends only on temperature and the dependency is usually strongly exponential. The pure compound has a specific vapor pressure at a given temperature and an increase in temperature means exponentially increasing vapor pressure. This can be seen in Figure 5, in which the vapor pressure of pure hydrogen peroxide and water are represented as a function of temperature. [16]

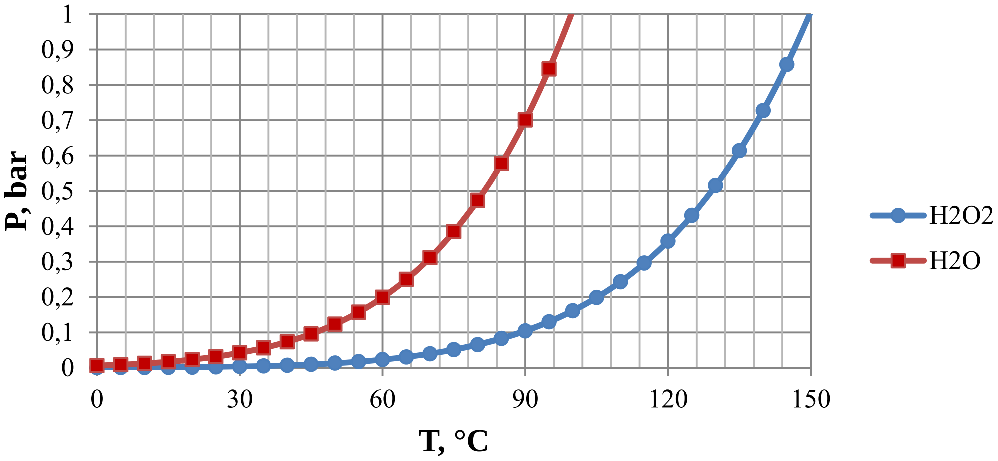

Figure 5. Vapor pressure of pure hydrogen peroxide and water [20].

Figure 5 shows that water has a higher vapor pressure than hydrogen peroxide at a constant temperature. For this reason, water is a more volatile component than hydrogen peroxide. Correspondingly, water boils at a lower temperature than hydrogen peroxide at constant pressure. When the binary-mixture of water-hydrogen peroxide is distilled, the concentration of the lighter (more volatile) water will be higher in the vapor phase than that in the liquid phase. Conversely, the concentration of hydrogen peroxide is higher in the liquid phase than in the vapor phase. As a result of this, hydrogen peroxide solution can be concentrated by distillation. The product at the bottom is concentrated hydrogen peroxide solution, and the upper product is almost pure water vapor.

3.2 Vapor-Liquid Equilibrium

Separation of chemical components by distillation is only possible when the compositions of liquid and vapor phases in equilibrium are different for each component. This mixture component composition at a thermodynamic equilibrium is called the vapor-liquid equilibrium (VLE), which if favorable is a driving force for distillation. [14] Typically, the VLE is represented by vapor-liquid equilibrium diagrams, which can be determined by laboratory measurements or by literature data. One of these diagrams is a boiling point diagram, which is also called (T-xy)-diagram. It shows, how the mole composition of the components in a liquid and vapor phases (x,y) vary with temperature T at a constant pressure P. In addition of (T-xy)-diagram, (P-xy)- and (xy)-diagrams are used to describe the equilibrium between vapor and liquid phases. [21]

Figure 6 shows the boiling point diagram for the water-hydrogen peroxide system at atmospheric pressure. Because water and hydrogen peroxide are not identical compounds, the non-ideality of VLE is taken into account. The lower curve of the diagram is the bubble-point curve (saturated liquid curve) and the upper is the dew point curve (saturated vapor curve). The saturated liquid curve gives the mole fraction of water in liquid phase, whereas the saturated vapor curve gives the mole fraction of water in vapor phase. When water-hydrogen peroxide mixture is boiled, the vapor produced during the boiling is richer in water than the original mixture. This difference is the basis for the distillation.

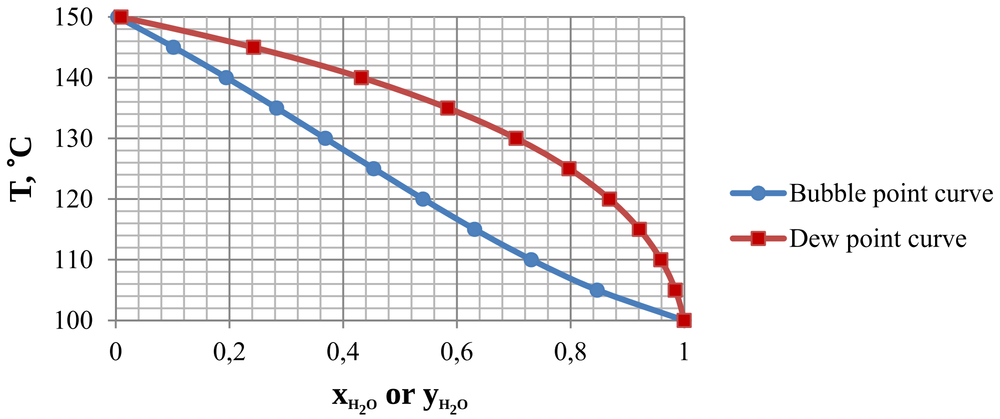

Figure 6. Vapor-liquid equilibrium of water-hydrogen peroxide mixture at 1 bar pressure [20].

3.3 Continuous distillation processes

When distillation is accomplished with a continuous feed of material and continuous removal of products, the process is called the continuous distillation process. [14] Usually, continuous distillation processes are applied in industry when high throughputs of feed are required to distill without interruptions. The opposite to the continuous process is a batch process, in which distillation is charged with a specific amount of feed, which is distilled. The continuous distillation processes are more common in industry than the batch processes. [21]

According to McCabe et al. [22] continuous distillation processes can be carried out by two principal ways. The first one comprises the production of a concentrated solution and vapor by boiling the liquid mixture and condensing the vapor without returning any condensate back to the solution mixture. The second method is based on the returning of some amount of the condensed vapor back to the mixture. The first process is called flash distillation and the second rectification. Both flash distillation and rectification can be used to separate binary and multicomponent solutions, however, rectification is a better distillation method for a solution that contains several components. In practice, real distillation processes may have features from both flash distillation and rectification. In this thesis distillation of binary-mixtures is mainly considered.

3.3.1 Typical distillation process (rectification)

A typical continuous distillation process is shown in Figure 7. This rectification process consists of several pieces of equipment which are used either to transfer heat or mass. The process includes a feed preheater, a vaporizer, a distillation column, a condenser, and a product cooler. The actual separation or concentration of liquid components is carried out in the distillation column that contains internal items such as plates, bubble caps, or packings to enhance the separation [21]. If a liquid mixture contains components, which have comparable boiling points, distillation with reflux in several equilibrium stages is needed. In such cases the application of rectification is recommended.

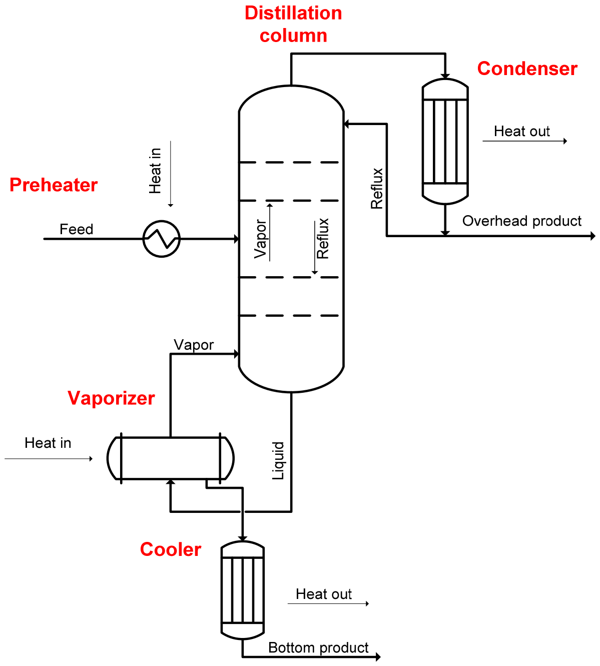

Figure 7. A schematic figure of rectification distillation.

The liquid mixture to be distilled is continuously fed into the distillation column. Before the column, the liquid mixture flows through a preheater, in which the temperature of the mixture is increased. The feed mixture flows down to the bottom of the column and further to the vaporizer by gravity. In the vaporizer the mixture is partially vaporized by heat-transferring of steam. The released vapor flows to the top of the column counter-currently with a down flowing liquid which is called reflux. The function of the reflux is to enrich the rising vapor with the more volatile component, and thus increase the purity of the overhead product. Usually, the reflux is obtained by condensing the overhead vapors in a heat exchanger and returning a part of the condensate back to the column. The rest of the condensate is recovered as the overhead product. [22]

The enrichment of the rising vapor can occur if the concentration of the reflux is related high enough to the more volatile component. The vapor is enriched since the rising vapor to a stage contains less more volatile component than that would be in equilibrium with the reflux fed to the stage. Hence, the more volatile component is transferred from the reflux to the vapor and at the same time, the reflux is enriched with the less volatile component. A concentrated solution, related to the less volatile component, is formed at the bottom of the column. This solution is called the bottom product. [22]

McCabe et al. state [22] that in the rectification, the feed solution is usually fed to the central area of the column in order that both the overhead and the bottom products are obtained as nearly pure as possible. If the column is equipped with plates, the plate on which the feed enters is called the feed plate. It divides the column into two sections. The section, which is located above the feed plate, is a rectifying section and the section below the feed plate is a stripping section. In the rectifying section the vapor is enriched with more volatile components and in the stripping section the liquid is progressively stripped of them.

According to Fair, [14] rectification or the multiple equilibrium stage distillation can be visualized by a graphical McCabe-Thiele diagram, which can be seen in Figure 8. This diagram contains knowledge of the material balances of the distillation with vapor-liquid equilibrium relationship. The McCabe-Thiele method is used to determine how many ideal equilibrium stages are needed to achieve a desired separation. When the efficiencies of the column are known, it is possible to further evaluate the number of real stages. These stages can be regarded as plates when a plate column is considered. In the McCabe-Thiele diagram, the material balances of the distillation column are represented by operating lines of the rectifying and the stripping sections. When an arbitrary equilibrium stages *n* and *m* in the rectifying and in the stripping sections are considered, the operation lines for these sections are following:

$$y_{n+1} = \frac{L_R}{V_R} x_n + \frac{D x_D}{V_R} \tag{7}$$

where	y_{n+1}	mole fraction of more volatile component in vapor phase from the stage *n*+1
	x_n	mole fraction of more volatile component in liquid phase to the stage *n*+1
	x_D	mole fraction of more volatile component in overhead product
	D	molar flow of overhead product
	L_R	molar flow of liquid in rectifying section
	V_R	molar flow of vapor in rectifying section

$$y_{m+1} = \frac{L_S}{V_S} x_m + \frac{B x_B}{V_S} \tag{8}$$

where	y_{m+1}	mole fraction of more volatile component in vapor phase from the stage *m*+1
	x_m	mole fraction of more volatile component in liquid phase to the stage *m*+1
	x_B	mole fraction of more volatile component in overhead product
	B	molar flow of bottom product
	L_S	molar flow of liquid in stripping section
	V_S	molar flow of vapor in stripping section

The ratio between reflux and the overhead product is called reflux ratio and usually it is defined as follows:

$$R_D = \frac{L_{R.flux}}{D} \tag{9}$$

where	$L_{R.flux}$	molar flow of reflux

When the reflux ratio is high, fewer theoretical stages are needed for a specific separation. In accordance, when the reflux ratio is low, infinite theoretical stages are needed for the separation. The equation for the operating line of the rectifying section can be presented with the reflux ratio:

$$y_{n+1} = \frac{R_D}{R_D + 1} x_n + \frac{x_D}{R_D + 1} \tag{10}$$

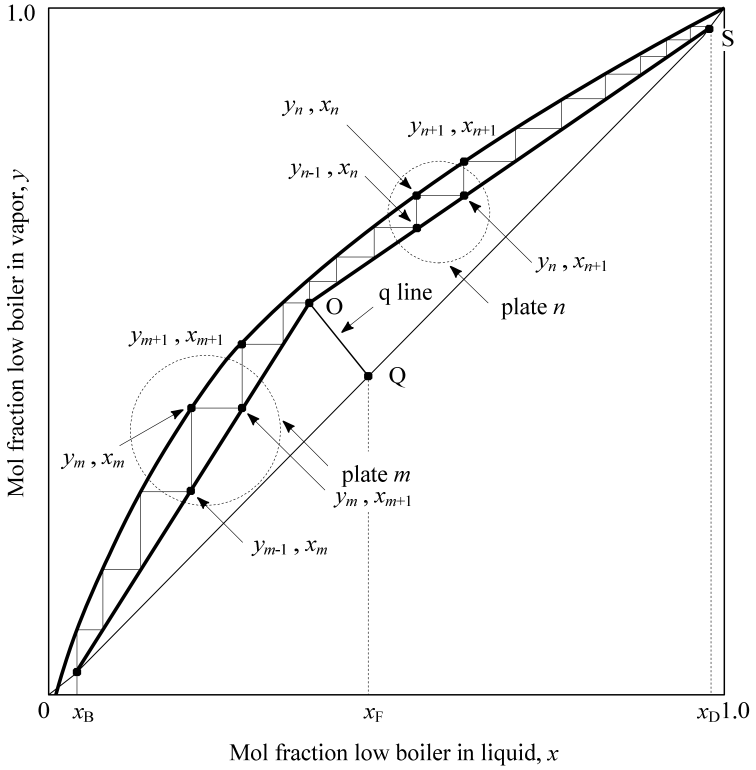

Figure 8. Multiple equilibrium stage distillation represented by McCabe Thiele diagram [14].

3.3.2 Flash distillation

Flash distillation, also known as equilibrium distillation, occurs in a single equilibrium stage in which a liquid mixture is partially vaporized. The vapor and the liquid are allowed to reach an equilibrium and after that, they are separated. The vaporized part of the feed is not returned back to the column as reflux. Instead, it is totally condensed and recovered. [23] If a liquid mixture contains components, which have widely differenting boiling points, flash distillation can be used for separation [22]. Usually, flash distillation is applied to separation or concentration of binary-mixtures. The features of flash distillation are represented in Figure 9 [23].

Feed solution flows at a specific flow rate into a vaporizer. In the vaporizer, the mixture is partially boiled and then it is allowed to return to the equilibrium. The released products are the condensed vapor and the concentrated liquid solution. The condensate is enriched with the more volatile component and the liquid with the less volatile component. [23]

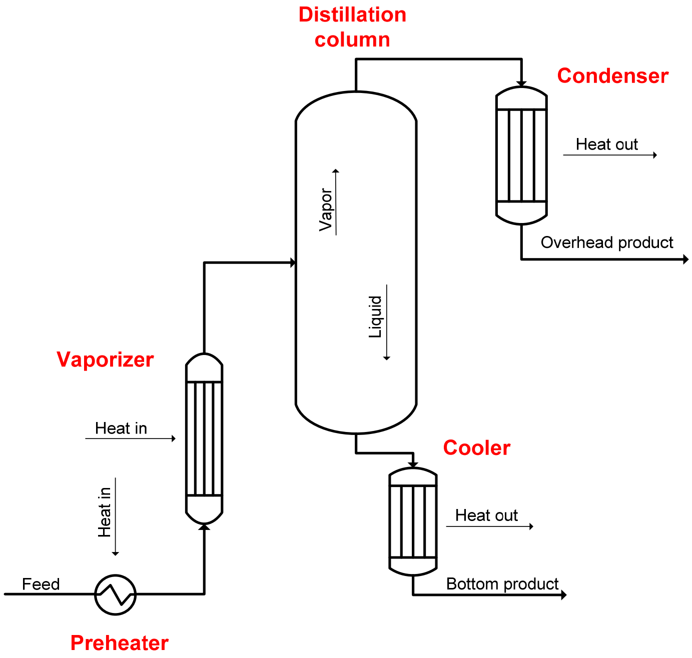

Figure 9. A schematic figure of flash distillation.

Mass and energy balances of distillation are important when the energy requirements and the usage are evaluated [24]. For flash distillation the mass and energy balance equations can be evaluated as follows:

$$F = V + L \tag{11}$$

where F mass flow of feed solution
V mass flow of vapor
L mass flow of liquid

$$H_{Feed} + Q_{P.heat} + Q_{Vap.} = H_{Ovh.} + H_{Bottom} + Q_{Cond.} + Q_{Cool.} \tag{12}$$

where H_{Feed} enthalpy flow of feed solution
$Q_{P.heat}$ heat supplied in preheater
$Q_{Vap.}$ heat supplied in vaporizer

$H_{Ovh.}$	enthalpy flow of overhead product
H_{Bottom}	enthalpy flow of bottom product
$Q_{Cond.}$	heat removed in condenser
$Q_{Cool.}$	heat removed in cooler

3.3.3 Process control

The purpose of a control system for any process is to maintain the desired state of operation without human actions. A process control system consists of several control loops which may interact with each other. For distillation columns a large number of different control configurations and loop systems have been developed due to the high variation in the different separation tasks. [25]

Usually, distillation processes include control variables and tasks for flow rates, liquid levels, pressure, and product concentrations. These variables can be controlled, manipulated, or loaded. The controlled variables have to be maintained at a specific value in order to achieve the distillation objectives. Typical controllable variables are concentrations of the products, column temperature, pressure, and liquid levels. In turn, manipulated variables are those, which must be changed in order that the controlled variables can be maintained at their precise values. These kinds of variables are reflux flow, reflux ratio, steam flow, cooling water flow, and product flows. The loaded variables are those that disturb the distillation, such as feed concentration and environmental conditions. [26]

White [27] describes typical controls of a two-product distillation system. These controls are shown in Figure 10. In this system feed solution (F) is separated into two products: distillate (D) and bottoms (B). At least one of these products and especially its quality is controllable. The quality of the bottoms can be controlled by reboiler duty (steam flow) or in some cases by feed flow. Whereas, the quality of the distillate is usually adjusted by reflux flow or by reflux ratio. The liquid level of the column is maintained at a specific value by the bottoms flow and the level of the reflux tank is controlled by distillate flow. Other controllable variables are pressure and temperature of the column.

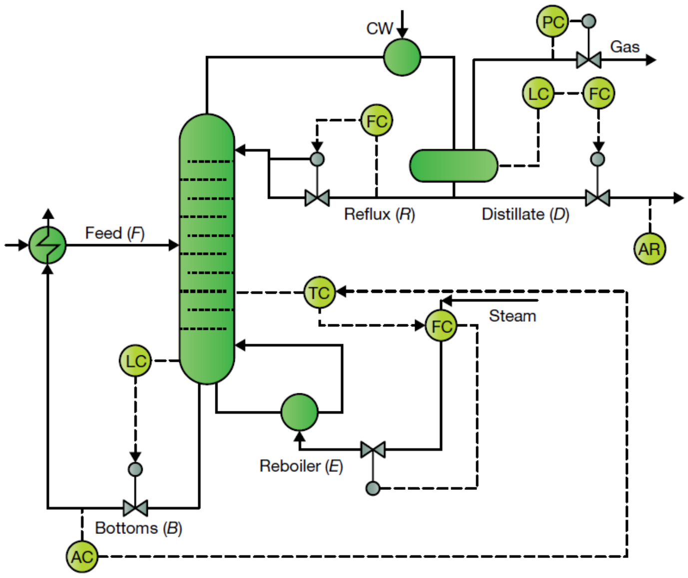

Figure 10. Typical controls of a two-product distillation column [27].

The temperature of the column can be adjusted by the steam flow of the reboiler. Thus, temperature also depends on the required product quality. Moreover, the temperature at the top of the column can be adjusted by the reflux flow rate. In many cases, the reflux flow rate is then controlled by the temperature controller in the overhead vapor outlet. An increase in the column top temperature causes an increase in reflux flow and vice versa. In a two-product distillation column the temperature profile should be such that the temperature increases towards the bottom of the column. An increase in pressure and the increasing concentration of the high boiling component towards the bottom of the column causes this kind of profile. If side-stream products, such as distillates, are removed from the column, the temperature profile should be controlled even more precisely. Then, if the temperatures of the feed and the bottom are too high, too much heavy vapor (less volatile component) will rise up the column and this may cause side-stream products to be off the specifications. These kind of conditions with high reflux rate may further cause flooding and poor separation in the column. Respectively, the opposite conditions may lead to liquid starvation and again inefficiency of the column. Thus, the careful control of the top temperature, the feed and the reboiler temperatures with pressure control is important. [22, 27, 28]

The distillation pressure used depends on the separable components of liquid mixture and their volatilities. Liquid boils at higher temperature when the pressure is increased and lower when the pressure is decreased. This phenomenon can be utilized when easily volatile and heat sensitive chemicals are distilled. Easily volatile chemicals, such as ethane and propane have to be distilled by pressure which is over atmospheric pressure, in order that the compounds can be liquefied. In turn, some liquid mixtures tend to decompose at high temperatures at atmospheric pressure. In these cases, an atmospheric distillation is not a suitable method to distill these mixtures. Instead, distillation with a vacuum (under atmospheric pressure) is then necessary. [29]

According to Stichlmair and Fair [25], distillation pressure can be adjusted by many ways depending on the distillation nature. A simple method to control the pressure of an atmospheric column is to control the draw-off of the inert gases from the collector drum, as in Figure 10. The column pressure can also be affected by manipulating the temperature of the condensate. This can be carried out by adjusting the cooling water flow rate in the condensers. When the cooling water flow is increased, then more vapor is condensed and the vapor pressure is decreased, which decreases the column pressure. In vacuum columns a vacuum pump or a steam jet ejector system can be used to form the vacuum conditions.

3.4 Distillation columns

Distillation columns are the main parts of the continuous distillation processes. They are vertical vessels where distillation occurs often with the intimate contact between the rising vapor and the down flowing liquid. The contact between vapor and liquid can be caused by discrete steps by plates or differentially by packings. [14] These plate and packed columns are the most frequently used industrial distillation equipment [25]. According to Stichlmair and Fair [25], the advantages of plate and packed columns are a counter current flow and a large overall height. Moreover, these internals effectively increase the mass transfer between the vapor and liquid phases. The choice between plate and packed column is not always simple because both column types can be modified to fulfill many requirements.

3.4.1 Plate columns

Plate columns, also called tray columns, are equipped with perforated horizontal plates. These plates allow the vapor to flow upwards through the perforations at the same time as the liquid flows downwards, mostly with downcomers [14]. Figure 11 shows a cross-sectional figure of a plate column construction.

Although the main flow in the plate column is countercurrent, the vapor and the liquid cross flow on the plates. The rising vapor goes through the perforations into the liquid, which flows across the plate. Subsequently, the liquid flows over the weir into the segmental downcomer and some of the liquid is accumulated there. Then the liquid flows onto the following plate below. [25] A schematic figure of the typical flow pattern in a plate column can be seen in Figure 12.

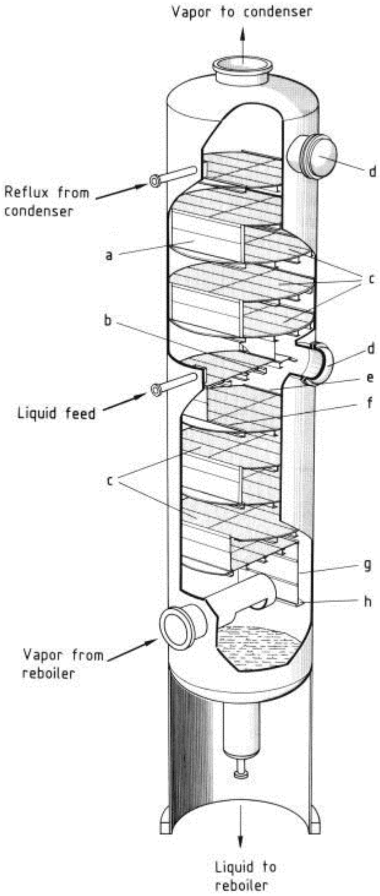

Figure 11. A construction of a typical plate column. a. downcomer, b. plate support, c. sieve plates, d. manhole, e. outlet weir, f. inlet weir, g. side wall, h. liquid seal [25].

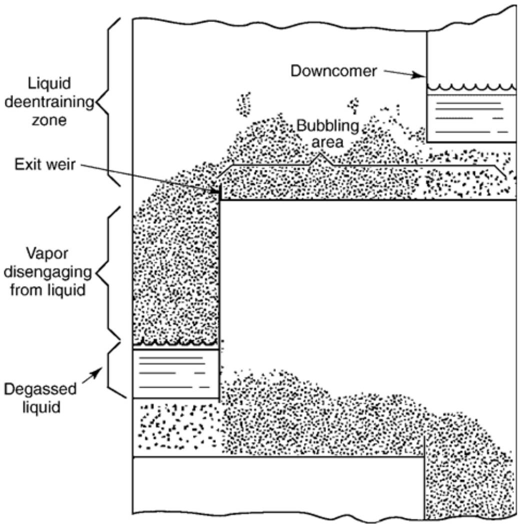

Figure 12. A typical flow pattern in a plate column [14].

Stichlmair and Fair [25] state that an advantage of the plate columns is a liquid load, which can be adjusted with a wide range. As a result of this, the plate columns can be operated efficiently both at very low and high liquid loads. Instead of a liquid load, the vapor load has to be kept within a quite narrow range. Inaccurately adjusted vapor and liquid flows may lead to the flooding of the column and poor separation efficiency. [22] Other advantages of the plate columns are the resistance to impurities in the liquid and the controlled liquid flow, which cannot form channels in the column [22, 25]. A disadvantage of the plate columns is a high pressure drop that may limit the capacity of the column. Another disadvantage is the high liquid holdup, which results in a high residence time in the columns. This may further cause the decomposition of unstable chemicals due to thermal effects. [25]

The types of the perforation plates have various models: bubble caps, sieve and valve plates. According to Stichlmair and Fair [25], bubble caps have been used for long time and their design prevents the leakage of the liquid through the plates. However, bubble caps are quite expensive and have a high pressure drop which limits their use. Sieve plates have become a common type of plates. Their separation efficiency is high, the pressure drop is low and their construction is cheap. Valve plates are a quite new and widely used technology for the perforated plates and they can provide a large operational flexibility when adjusting the vapor load.

3.4.2 Packed columns

In packed columns, random or structured packings are used to enhance the mass transfer between vapor and liquid phases. Usually, the vapor enters at the bottom of the column and flows upwards through the packings. The liquid flows down counter currently to the up flowing vapor. The aim is to wet the packings as extensively as possible. Stichlmair and Fair [25] recommend that the height of the individual packing sections should not exceed over 6 m because the liquid may distribute poorly and form channels when the height of the packing section increases. However, the packing section should be over 3 m high in order for the separation to occur. The uniform and extensive distribution of the liquid can be achieved by different liquid distribution solutions.

In addition to the liquid distributor, packed columns also contain other packing supplements. The other most important supplements are the liquid collector, the liquid redistributor, the support grid, the hold down plate, and the gas distributor. These packing supplements should be designed such that they prevent as much as possible the counter current flow of vapor and liquid. The most common packing supplements can be seen in Figure 13 where a cross-sectional figure of a packed column construction is shown. This packed column contains two discrete packing sections and the liquid is redistributed between these sections. [25]

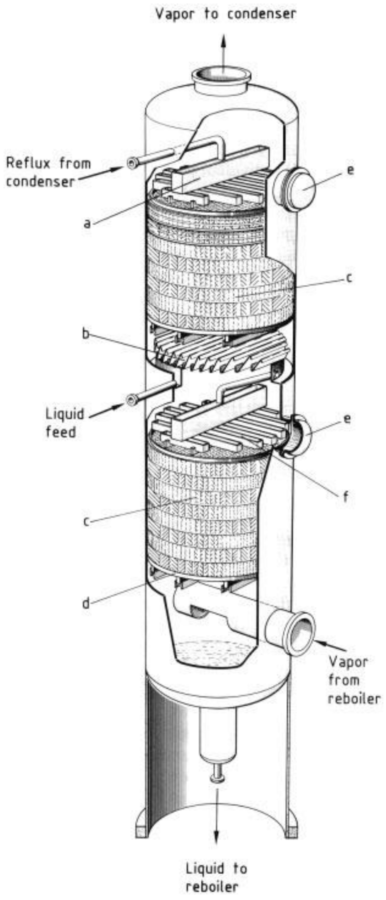

Figure 13. A construction of a packed distillation column. a. liquid distributor, b. liquid collector, c. structured packing, d. support grid, e. manhole, f. liquid redistributor [25].

The efficiency of the column is influenced by the type of packings. The packings can be discrete or structured. Discrete packings are composed of a large number of particles, which are randomly organized in the column. The types of the discrete packings vary and they can be metal rings or ceramic saddles, for example. [25] However, structured packings are usually corrugated metal sheets. These sheets can be set parallel to each other with varying inclinations of the corrugations or so that the adjacent sheets are perpendicular to each other. Different packing types of distillation columns can be seen in Figure 14.

When random packings are used, there is always inhomogeneity in the column. This inhomogeneity may cause the maldistribution of the liquid, which further decreases the mass transfer efficiency of the column. In many cases, the structured packings can provide better homogeneity than random packings, and thus they are better choice. Other important requirements, which packings should fulfill are a high surface area and a low pressure drop. [25]

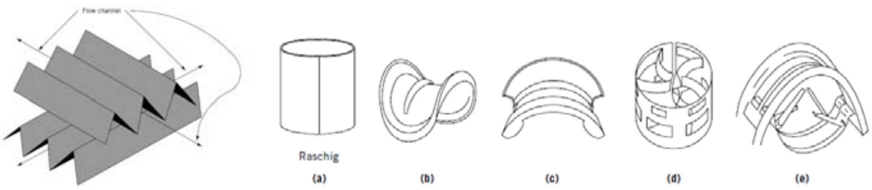

Figure 14. Typical packing types of packed distillation columns. Corrugated metal sheets, rings and saddles [14].

4 ENERGY EFFICIENCY OF DISTILLATION

Distillation is still the most commonly used separation method, although it is one of the most energy consuming processes in the chemical industry. According to Emtir [5], distillation is both an energy intensive and inefficient process, which accounts for about 3 % of world's energy consumption. The rising costs of energy and raw materials have driven the industry to search for potential energy savings. This has also led to improving the energy efficiency of distillation, which has become a significant target of research over the few last years. The third factor, which has also had an influence, is an awareness of the environment, which has increased during the last decades. The savings in energy consumption also results in lower CO_2 emissions. [4]

4.1 Energy conservation methods in distillation systems

Emtir [5] introduces potential ways to achieve energy savings in distillation and some of these ways are described in Figure 15. The first of these is to replace distillation completely with other separation methods or prevent distillation at all. This is not always possible, but in some processes this may be a potential way. Adsorption, membrane processes, absorption or crystallization are examples of other unit operations which can replace distillation in some cases. In some concentration processes it is also possible to prevent distillation and therefore, trying to sell dilute, crude solutions which are not concentrated. Using this method, it is possible to achieve the largest savings.

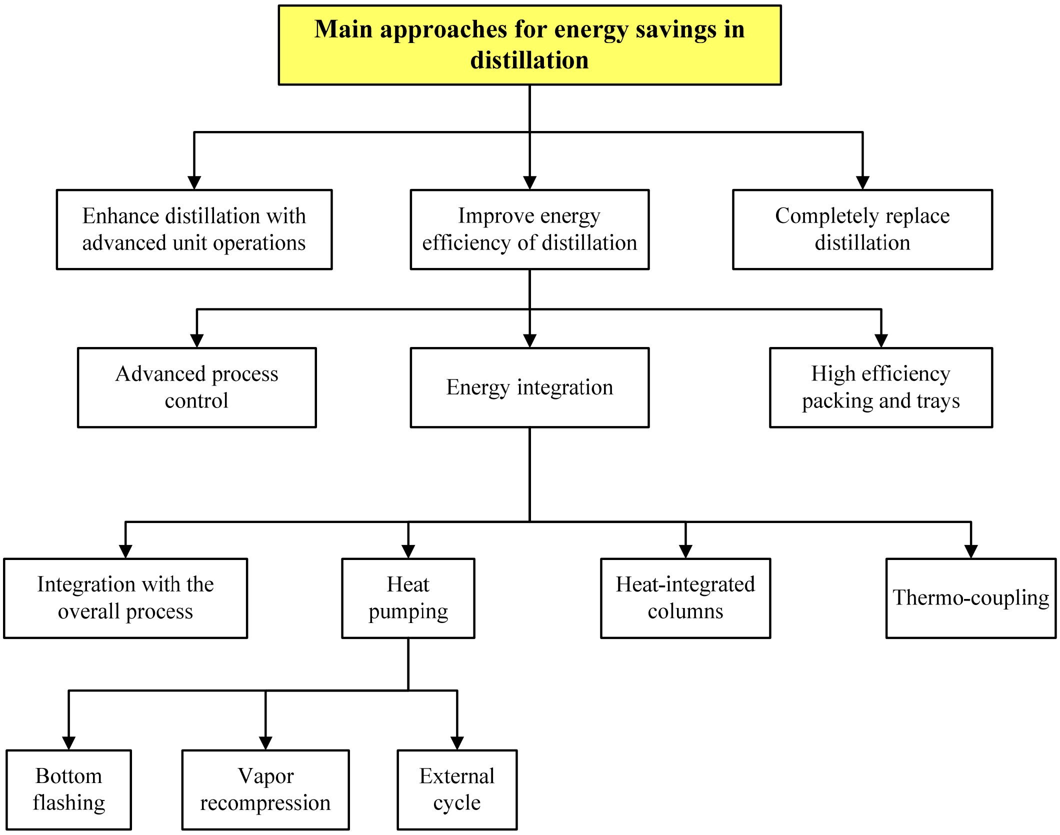

Figure 15. Potential ways to improve the energy efficiency of distillation [5].

The second way is to enhance conventional distillation with an advanced unit operation. Another separation process can be combined with a distillation unit so that the distillation product is refined by this process. In this way, distillation can be operated so that the product purity is not very high. In addition, the reflux flow and the vaporizer duty of the column can be kept low and this further leads to further reductions in energy use. At the same time, the capacity of the column increases.

The third and the most common way to achieve energy savings in distillation is to improve the energy efficiency of the distillation itself. Energy integration, advanced process control and equipment improvements are common ways to carry out improvements that produce savings in energy consumption.

4.2 Energy requirements and losses of distillation

According to Emtir [5] distillation is thermodynamically removal of entropy of mixing. It is a process, which requires work (energy) for separation and this work requirement W can be evaluated as follows:

$$W = -RT\sum x_{Fi}\ln(\gamma_i x_{Fi}) \tag{13}$$

where	W	minimum work consumption per mole of feed
	T	temperature
	R	gas constant
	x_{Fi}	mole fraction of component i in the feed
	γ_i	activity coefficient of component i in the feed

In many separation processes the energy for separation is not supplied by mechanical work W. Instead, the energy is usually supplied in the form of heat Q. The ability of heat energy to be converted into work is called exergy E. [5, 24]

$$E = Q\frac{T_h - T_0}{T_h} \tag{14}$$

where	T_h	heat temperature (abs.)
	T_0	ambient temperature (abs.)

Feed and product streams of distillation contain also energy, which is possible to convert to work. In these cases, exergy can be formulated as follows: [30]

$$E \equiv H - T_a S \tag{15}$$

where	H	enthalpy flow
	T_a	reference temperature
	S	entropy flow

According to Ognisty [30], the principle of Carnot heat engine is a useful way to evaluate the theoretical maximum energy efficiency of an ideal reversible distillation. The Carnot heat engine extracts heat from a high temperature source and discharges it at a low temperature. Between this operation, the heat engine works and power is produced [31]. A simple distillation process, which consists of a distillation column, a vaporizer, and a condenser, can be regarded as a heat engine. The analogy between these processes can be seen in Figure 16. Heat is supplied at the bottom of the column in the vaporizer and removed at the top in the condenser. In the vaporizer the heat is added at a high level of temperature and in the condenser removed at a low level. The decline in heat provides the effort needed to separate or concentrate the feed solution into the bottom and the overhead products. [30]

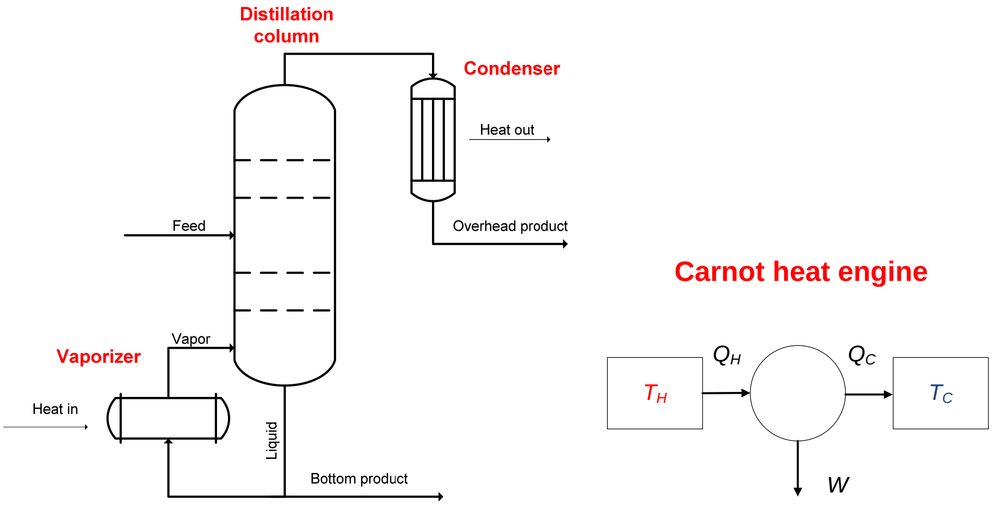

Figure 16. The analogy between a simple distillation column and a Carnot heat engine.

When a distillation is regarded as a heat engine, the theoretical minimum work required for the distillation W_{heat} can be evaluated by an exergy difference between a heat input $T_{\text{vaporizer}}$ and an output $T_{\text{condenser}}$. This exergy difference provides the work, which is performed during distillation as follows:

$$W_{heat} = Q_H \frac{T_{Vaporizer} - T_0}{T_{Vaporizer}} - Q_C \frac{T_{Condenser} - T_0}{T_{Condenser}} \tag{16}$$

where	Q_H	heat flow supplied
	Q_C	heat flow removed
	$T_{Vaporizer}$	temperature at vaporizer
	$T_{Condenser}$	temperature at condenser

The exergy difference between the product and feed streams (E_{product} - E_{feed}) are equal to the required heat for distillation. However, in a real distillation column thermodynamic inefficiencies always occur, and these consume the heat work needed to overcome pressure, temperature, and composition of the driving forces. Momentum is lost due to a pressure drop in the column. Heat is lost due to temperature difference and mixing due to composition differences. When these inefficiencies W_{lost} are included, the exergy difference balance for distillation is achieved: [30]

$$E_{product} - E_{feed} = W_{heat} - W_{lost} \tag{17}$$

When the inefficiencies of distillation increase, the loads of the vaporizer and condenser W_{heat} have to be increased at the same time, in order to keep the exergy difference balance. In turn, when the loads of the vaporizer and condenser are increased, the lost work term W_{lost} must also be increased. As a result of this, the higher energy efficiency of distillation can be achieved when the lost work of the distillation, and the loads of the vaporizer and the condenser, are optimized. The energy efficiency of a distillation system can be studied by a McCabe-Thiele diagram, shown in Figure 8. The closer the operating lines pass the equilibrium curve the more energy efficient the distillation is. [30]

4.3 Energy integration

Energy integration is an important way to improve the energy efficiency of distillation. It is a method that optimizes energy and heat recovery in the distillation process by utilizing waste energy in those parts of the process where it is needed. When the energy is in the form of heat, energy integration is called heat integration. It reduces the heat losses of the process and makes it possible to decrease external heat utility loads. [30, 32] Emtir [5] divides the energy integration of distillation into four parts: overall process integration, heat pumping, heat integrated columns and thermo-coupling. This distribution was shown in Figure 15.

4.3.1 Pinch analysis

Pinch analysis is a systematic technique, which can be applied to plan heat integration of a chemical process, such as distillation. It is based on analyzing the heat flows of the process by fundamental thermodynamics. The second law of thermodynamics: heat flows from a hot source to cold one, is a basic concept of the analysis. Pinch analysis is described in Figure 17 by the hot and the cold composite curves of the heat flows of a process. By these composite curves, the amount of heat, which can be recovered by heat integration, can be determined. In addition, the composite curves reveal how much heat has to be supplied or removed by external utilities, such as steam or cooling water. [33]

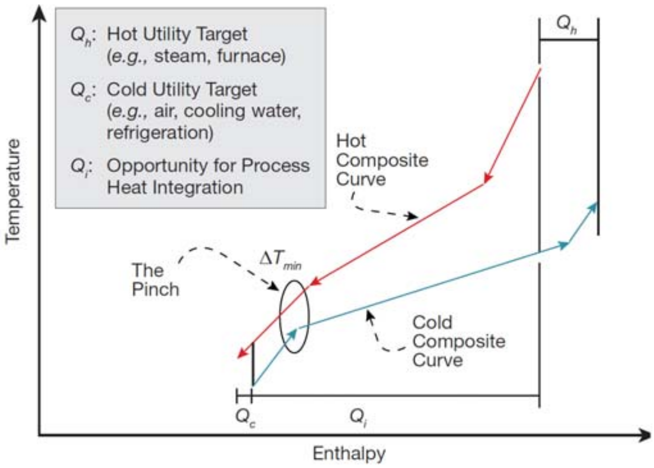

Figure 17. Pinch analysis of a chemical process. Hot and cold composite curves are formed by hot and cold heat flows in the process. These curves are used to determine the heat recovery and the need of the external utilities of the process [33].

In Figure 17, the composite curves are placed together on a single temperature-enthalpy plot. The hot and the cold composite curves represent the sum of all the heat flows in the process. The hot composite curve is the sum of all the hot streams and the cold is the sum of all the cold streams. Hot streams are also called heat sources and cold streams heat sinks. Heat can be recovered in the area where the hot composite curve passes above the cold composite curve. At this point, heat can be transferred from the hot sources (high temperature part) to the cold ones (cold temperature part). The external heat utilities are needed when hot and cold composite curves are not on top of each other. The need of the hot utility Q_h can be read from the right hand side of the hot composite curve. Consequently, the need of the cold utility Q_c can be read from the left hand side of the cold composite curve. The vertical distance of the composite curves is defined by a minimum allowable temperature difference ΔT_{min}. This temperature difference is selectable and it embodies how much heat can be recovered by the process itself. When the temperature difference is decreased, more heat is recovered by the process itself. Then the number and the size of the heat exchangers increase together with the capital costs. Subsequently, when this difference is increased, the need of the external hot and the cold utilities increase. The capital costs then decrease, but the utility costs are higher. In most cases the temperature difference has to be larger or equal to a defined minimum allowable temperature, in order to keep the capital costs reasonable. [33, 34]

4.3.2 Heat integration

In distillation heat integration can be applied by two ways. Heat can be integrated inside the distillation process itself or it can be integrated between an overall process and the distillation. These heat integration ways can also be overlapped. However, the integration of conventional distillation process into an overall process is often problematic due to practical limitations. The distance between the distillation and the overall process may be such long that the heat integration is not feasible, for example. Often this has led to develop the heat integration of the distillation process itself. [5]

Inside the distillation process heat integration can be used to reduce the cooling water requirements and the size of the overhead condensers. It is also a useful method to decrease the heat losses of the distillation or to decrease the load of the vaporizer. [30] In many cases, the heat load of the vaporizer is about the same magnitude as the cooling load in the condensers. In these cases the available heat load of the condensers may be utilized for heating another process stream.

A common heat integration solution is also to preheat a cold feed stream with the hot products [25]. From the energy balance equation (12) it can be seen that one way to decrease reboiler duty Q_{Vap} is to increase the enthalpy of the feed stream $H_{\text{Feed.}}$ The feed enthalpy can be increased in two ways. The first of these is to preheat the feed with external heat and another way is to preheat the feed stream with the bottom product. [25, 35]

Stichlmair and Fair [25] state that one way to use heat integration in distillation is to convert the high pressure steam to a low pressure during distillation. This is possible if high pressure steam net is available and if it can be utilized in the distillation. The high pressure steam can then be used in the vaporizer where it is converted to low pressure steam. The low pressure steam can be further used for other targets. Only exergy is consumed, i.e. no steam and no energy.

According to Ognisty [30], the heat integration of distillation can be carried out by a pump around system. This is widely used in atmospheric and vacuum distillation columns to remove heat at selected stages. An example of a pump around system can be seen in Figure 18. Hot liquid is taken out of the intermediate product stage of the distillation column and pumped to another process in which the heat of the hot liquid is utilized. After this, the cooled liquid is pumped back to the column at a higher level. The sub-cooled liquid is used to cool the rising vapor in the column and it further reduces heat and cooling water losses.

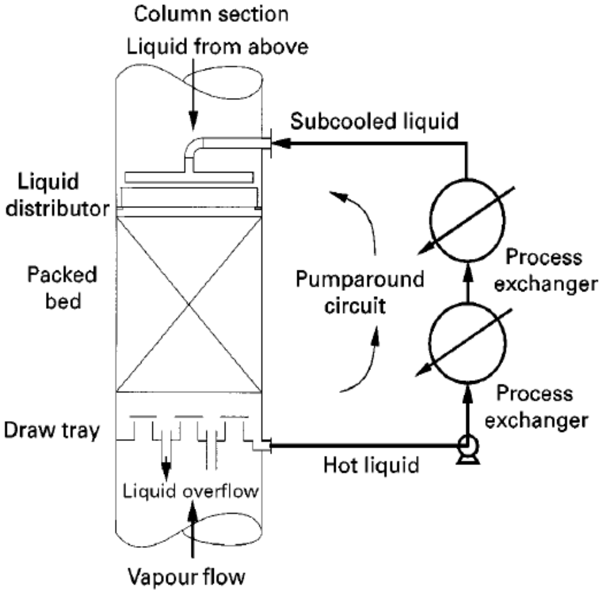

Figure 18. Heat integration by a pump around system in a packed distillation column [30].

Ognisty [30] states that a significant amount of energy is saved in crude oil distillation units by pump around systems. The major capital costs of the system are not very high. They include the necessary pumps, heat exchangers, and pipelines. The system is feasible if the intermediate product flow is high enough and suitable heat sinks are available.

4.4 Heat pumping

A heat pump is a device which works inversely compared to a Carnot heat engine (Figure 16). The heat pump requires work or energy to remove heat from a low temperature source and to convert it to a high temperature level. The working principle of the heat pump is shown in Figure 19. A low pressure liquid is fed into an evaporator in which the liquid boils at a low temperature. At the same time, low pressure vapor is produced. This low pressure vapor is further compressed to a higher pressure by a compressor, which requires energy. The high pressure vapor produced flows to a condenser where the vapor is condensed and the latent heat of the vapor is released. [31]

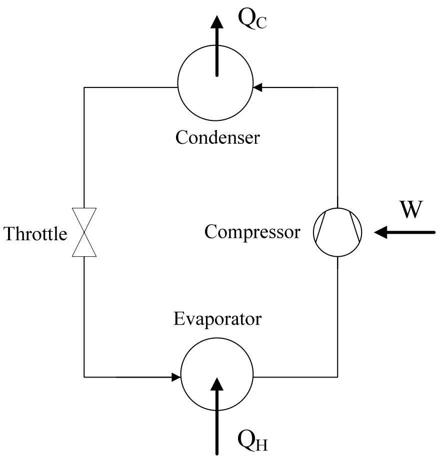

Figure 19. Working principle of a conventional mechanical heat pump [31].

4.4.1 Vapor compression and mechanical vapor recompression

The heat pump cycle can be combined with a distillation column in one or two ways. According to Enweremadu [36], the simplest way is to replace the steam and cooling water in the distillation with an appropriate heat exchange agent, which flows in a closed system. In this system, which can be seen in Figure 20, heat is exchanged between the distillation column and the heat pump cycle by heat exchangers. This system is called vapor compression (VC) and it is equipped with a vapor compressor, which works like a conventional heat pump. The advantages of this kind of system are the high steam savings, which can be achieved in the vaporizer of the distillation column. Additional steam is not needed due to the utilization of the overhead vapor. The disadvantages are the high investment and operating costs. In addition, adequate heat transfer fluid is often difficult to find due to stringent operational and safety requirements. [37]

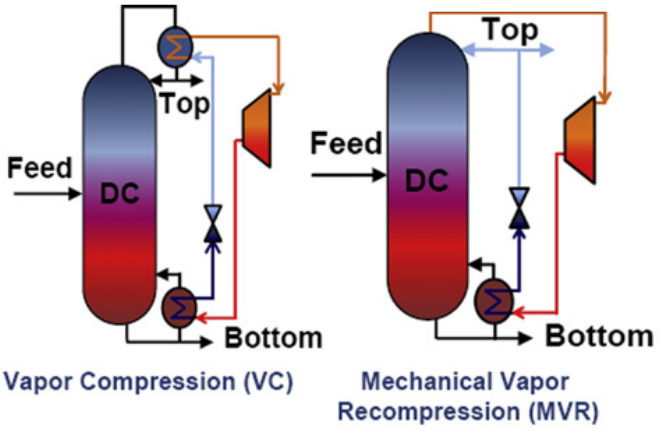

Figure 20. Heat pump assisted distillation systems. Vapor compression and mechanical vapor recompression [37].

The other ways which, connect the heat pump cycle to a distillation column, utilize either the overhead or the bottom product of the distillation as a heat exchange medium. One of these is a mechanical vapor recompression (MVR), which is also shown in Figure 20. [25, 36] As with the vapor compression system, the vapor recompression system is also equipped with a compressor, which raises the energy level of the overhead vapor by increasing pressure and temperature. The pressurized vapor is further fed into the reboiler where the vapor is condensed by the exchange of heat from the bottom liquid of the distillation column. This kind of heat pumping system may be feasible if the boiling points of the overhead and the bottom products are near to each other. In such cases the top and the bottom temperatures of the column are not significantly different and the overhead vapor can be utilized in the reboiler. The vapor recompression system usually has a slightly higher efficiency and lower investment costs than vapor compression. However, the investment costs of the system are usually high enough for the investment to have long payback time. [30, 37]

4.4.2 Thermal vapor recompression

A common way to create vacuum conditions in a distillation column is to use a steam ejector. An ejector is a kind of vacuum pump, which can work in a single or several stages depending on the strength of the vacuum [26]. The vacuum is created by high velocity steam (motive fluid), which is fed through a steam nozzle. Steam flows further through a converging-diverging diffuser in which the vacuum is formed. At the same time, the vacuum creates suction in a suction chamber that is connected to a vessel or pipeline. As a result of this, fluid in a vessel or pipeline is sucked up into the chamber. The fluid sucked up, such as vapor and motive steam, are mixed through the diffuser and after that discharged. A basic construction picture of a steam jet ejector is shown in Figure 21. [38]

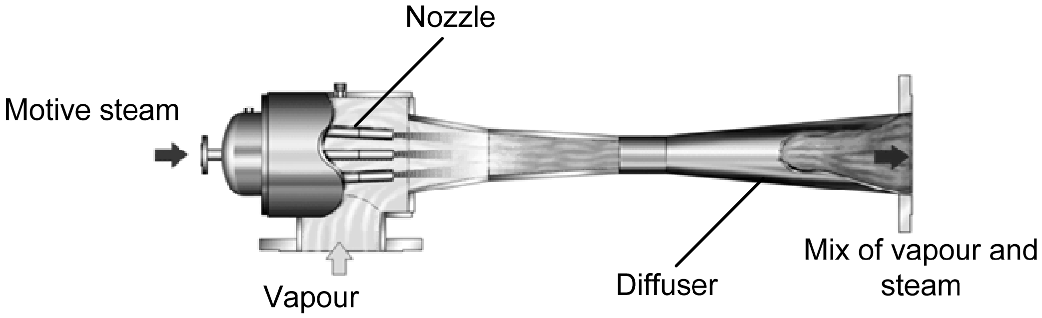

Figure 21. A basic construction of a steam ejector [39].

In addition to the pressure control of distillation, steam ejectors can be used in energy efficient applications of distillation. An example of these is a modification of a heat pump. In this application, steam is produced for a reboiler of a distillation column by utilizing a steam ejector. The steam ejector is driven by motive steam, which compresses a part of the overhead vapors into the pressure, which is required to boil the bottom liquid of the distillation column. The vapor mixture is condensed and the condensate is discharged or used as reflux in the distillation column. This kind of application is called thermal vapor recompression (TVR) and it is shown in Figure 22. [37]

An advantage of this kind of heat pump system is utilizing of the overhead vapor, which contains considerable heat energy to reuse. This system may be feasible if a close boiling mixture is distilled. The top and the bottom temperatures of the distillation column are not quite different and the overhead vapor can then be utilized in the reboiler. [30, 37] The capital costs are smaller compared to the system that uses a conventional heat pump, because steam ejectors are cheaper than mechanical heat pumps. In addition, steam ejectors do not include moving parts and thus the need for maintenance is negligible. A disadvantage is the steam consumption according to the motive steam of the ejector. In addition, the vacuum system of the distillation column should be equipped with an additional ejector or a vacuum pump system, which would create the vacuum into the distillation column. The creation of the vacuum is not feasible with the steam ejector of the thermal vapor recompression system. [26, 40]

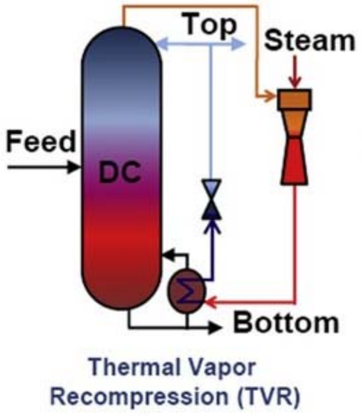

Figure 22. A steam ejector assisted heat pump system of distillation column [37].

The cooling water and the steam requirements of the distillation can be decreased considerably by heat pumping. However, Benkö and Fonyo [31] state that heat integration is often a more economical way to save energy than heat pumping. That is why they recommend that all heat integration possibilities should be studied before heat pumping is applied. The vapor compressor increases the investment costs of the heat pump assisted distillation systems. Moreover, the operating costs are increased due to electricity consumption. [30, 31]

4.5 Intermediate heat exchange

Steam and cooling water consumption of the reboiler and the condenser can also be reduced by intermediate heat exchangers. The heat duty of the actual reboiler is reduced when an additional reboiler is added to a distillation column. The temperature level of this inter-reboiler is lower than the actual one. If extra heat from other process streams is available, it is possible to utilize this heat in the additional reboiler. Significant savings in steam consumption of the distillation can then be achieved. Similarly, the cooling water consumption of the actual condenser can be reduced by an intermediate condenser. In this case, the heat of the overhead vapor is partially removed by an inter-condenser before the actual one. [30, 31]

The effect of adding an inter-reboiler into a distillation column is shown in Figure 23 in which the column energy efficiency is considered by a McCabe-Thiele diagram. When an additional reboiler is added, the stripping section operation line passes the equilibrium curve closer and this leads to the better energy efficiency of the column. However, a disadvantage is the number of higher stage requirements in the distillation column; more equilibrium stages are needed in order to carry out the required separation. [30]

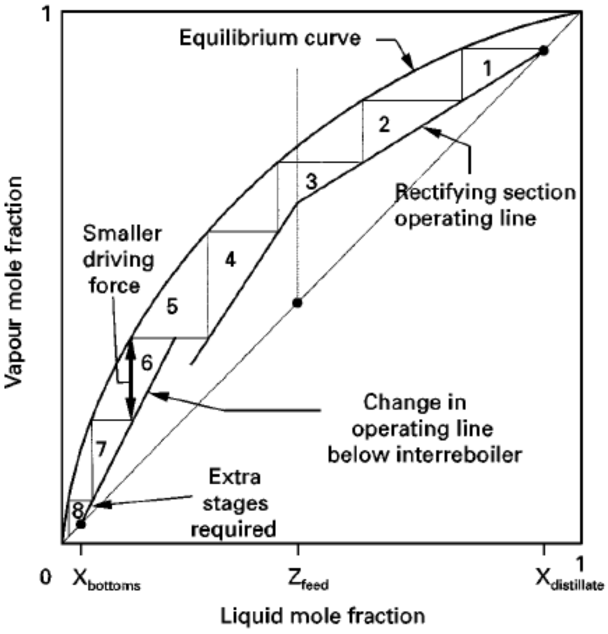

Figure 23. The effect of adding an inter-reboiler in a distillation column shown in using a McCabe-Thiele diagram [30].

4.6 Energy efficient process control

An energy efficient process control is an important part of distillation. Its aim is to produce distillation products, which reach the necessary quality with minimum use of energy. However, distillation always requires a certain safety margin or specification limits for the product specifications in order that the required product quality is always obtained. According to Gross [41], the energy requirement of distillation increases exponentially with increasing product purities. Because of this, too high specification limits may cause high energy costs. Thus, the most energy efficient method would be to distill products for their quality, which should be as close to the desired purity as possible. In addition to the product specifications, there are also other controllable factors which affect the energy efficiency of distillation. Reflux flow, boiling power (reboiler duty) and distillation pressure are examples of these.

4.6.1 Reflux flow

The operating reflux flow or ratio affects the energy costs of the distillation system. The reflux is usually used to adjust the quality of the overhead product or distillate. High reflux flow increases the purity of the overhead product, but at the same time it increases the reboiler duty, which leads to higher energy consumption. Thus, when an energy efficient distillation is sought, the optimum value for the reflux should be determined. The aim is to find the value which is as small as possible but at the same time produces the required purity for the overhead product or distillate. [14]

The relationship between the reflux and the energy consumption of distillation can be seen in the McCabe-Thiele diagram (Figure 8) and in Equation (10). The reflux ratio determines the slope of the operating line of the rectifying section. When the ratio is minimized, the slope is small and the operating lines pass the equilibrium curve closely. The energy efficiency of the system is then high. When the slope of the operating line is large, the reflux flow is high and the operating line is far from the equilibrium curve. This distance leads to low energy efficiency.

The dependence between the reflux ratio, the operating, the capital, and total costs of distillation is shown in Figure 24. When the reflux ratio increases, the operating costs (especially energy costs for vaporizing) increase almost linearly at the same time. Therefore, an optimum reflux ratio should be chosen and controlled in order that energy costs are optimized. [14]

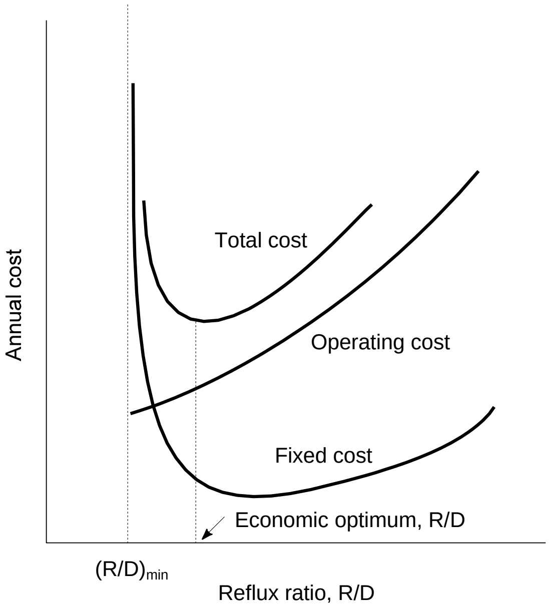

Figure 24. The effect of reflux ratio on the operating, fixed, and total costs of the distillation [14].

4.6.2 Boiling power

The boiling power of the vaporizer (reboiler duty) is a key variable which is controlled to achieve the required bottom product purity or quality. Usually, the high boiling power consumes considerable energy but provides a better quality of distillation products. The low boiling power takes less energy but the quality of the products is low. Thus, the optimizing of the reboiler duty is important. [29]

Harju et al. [29] studied the energy consumption of distillation of pentane-hexane mixture in a multistage rectification column. They stated that the purity of the overhead product (pentane) can be increased by increasing the boiling power of the reboiler. In addition, they stated that when the boiling power was increased, the number of required equilibrium stages for achieving a specific separation was decreased. They concluded that the 40 % increase in equilibrium stages can be compensated by the 11 % increase in energy use.

4.6.3 Distillation pressure

Distillation pressure is also an important variable, which affects the energy consumption of distillation. High pressure leads to a high boiling temperature and vice versa. This further affects the boiling power and the energy consumption. According to Harju et al. [29] the distillation pressure of pentane-hexane mixture affects significantly the required boiling power. The required boiling power increases when the distillation pressure increases. As a result of this the increasing operating pressure increases the energy consumption of distillation.

4.7 Feed system

The feed system is an important part of distillation. The location, thermal state, and splitting of the feed stream are factors which affect the energy consumption. Stichlmair and Fair [25] states that the thermal state of the feed stream has an effect on the heat requirement of distillation. The liquid feed requires more heat than a vapor feed. However, if the liquid feed is prevaporized, then the total energy requirement is higher than with a liquid feed.

Faagau [42] has studied the effect of the feed stream location on the energy efficiency of distillation. He states that the entrance part of the distillation column work inefficiently if the feed stream is introduced at the wrong place in the column. In this case, the distillation column requires more energy to achieve the required separation. The feed location usually depends on the feed composition and final product specifications. If the feed composition of distillation is greatly changed, it is especially important to recheck if the feed is introduced on an optimum feed plate. This can be done by process simulation, for example. When a multistage rectification column is designed, the optimum feed plate can be determined by the McCabe-Thiele method, which was introduced in Figure 8. The optimum feed plate is located on the intersection point of the stripping and the rectification operating lines.

It is also possible to influence the energy consumption of the distillation by feed splitting. Feliu and Soave [35] studied the energy consumption by theoretical and simulation means. They split the feed stream of propane-benzene mixture into two streams one of which was preheated and fed into middle part of the column. Another stream was fed as cold stream into an upper section of the column. The simulation results showed that it is possible to decrease the energy demand of the condenser and the reboiler duty with this kind of feed splitting.

4.8 Energy efficient equipment systems

The energy efficiency of distillation can be improved by proper equipment. The column internals, column insulation, measurements, heat exchangers, pumps and different vacuum, and reboiling systems are examples of equipment that can be considered when an energy efficient distillation is developed. It is important to design, operate, and maintain these devices properly in order that the energy efficiency can be achieved.

4.8.1 Column internals

Ognisty [30] states that the column internals have a significant impact on the pressure drop of the column. When plates are used, a part of the vapor energy is consumed as the pressure drops to form liquid droplets. The rising vapor has to then overcome the liquid level on each tray, which causes exergy losses. When packings are used, liquid is distributed over the packings and the vapor is allowed to flow counter currently through the pores of the packings. The packings resist the vapor flow and cause pressure drop but this is lower than the pressure drop of the plate columns.

According to Jödecke et al. [43], a common retrofit of existing distillation columns is to change old plates or packings to energy efficient and low pressure alternatives. When the low pressure drop internals are used, the exergy losses according to momentum and temperature difference are reduced. This further leads to savings in energy consumption. Sulzer, Koch, Raschig and Montz are well-known manufactures of trays and packings. They have designed high performance structured packings, which can replace the conventional packings by allowing a significant capacity and performance increase. These manufacturers offer high performance packings for various industrial applications. Koch-Glitsch HC, Montz M, Raschig Super-Ring and Sulzer MellapakPlus series are some examples of these high performance solutions. Photographs of some of these packings can be seen in Figure 25.

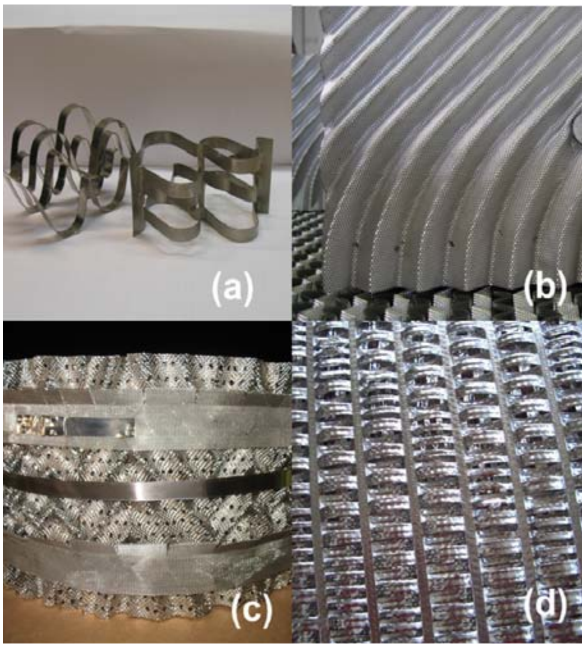

Figure 25. High performance random and structured packings (a) Raschig Super-Ring, (b) Montz-pak B1M, (c) MellapakPlus, (d) Raschig Super Packing [43].

4.8.2 Column insulation

Distillation columns usually operate above an ambient temperature, which causes heat losses along the column and especially at the vaporizer. According to Enweremadu [36] these heat losses increase condensation and reduce evaporation. Because of this, the vapor flow decreases in the upper part of the column and the amount of overhead product decreases at the same time. The lost heat could be utilized in some other process stream. In some cases, these heat losses can be decreased by insulation of the distillation column. However, this is not always possible. When heat sensitive chemicals especially are distilled, the temperature in the column may rise too high if the column is insulated. This may further cause the decomposition of the chemicals.

4.8.3 Pumps

Distillation units always contain pumps, which are used to move fluids from lower pressures to higher ones. Principally, they are used to transfer liquid from one place to another. Feed liquids are pumped into the distillation column, and product liquids from the distillation column to the receiving tanks. The cooling water for heat exchangers is circulated through the coolers by cooling water pumps, for example. However, all pumps need energy to work. Often this energy is electric energy and its consumption has to be taken into account when the energy efficiency of distillation is evaluated. Energy efficient pumping is part of energy efficient distillation.

According to the guide of Motiva [44], the energy efficiency of pumping can be improved by adjusting the pumping in a proper way. The main adjusting methods are: throttling control, on-off control, bypass flow control and speed control of which the speed control is the most energy efficient adjusting method. The rotation speed control can be carried out by variable speed drives (VSDs) or by hydraulic switches, from which the VSDs are the most used application nowadays. The VSD changes the frequency of the electricity which is used in the pump. It is then possible to affect the rotation speed of the electric motor of the pump and supplement the actual rotation speed of the pump. The VSD makes it possible to adjust the pumping such that the load of the pump is taken into account.

4.8.4 Pressure control by vacuum pumps

Vacuum conditions can also be formed in a distillation column by a vacuum pump instead of a steam ejector [25]. Rotary positive displacement pumps are common vacuum pumps, and a liquid ring pump is much used in distillation columns. The liquid ring pump contains a rotor, which is mounted eccentrically within a stationary housing. This housing is filled with a working fluid, such as water. The rotational motion of the rotor produces a rotating liquid ring at the edges of the housing. The rotor causes oscillation of the liquid ring within the cells of the rotor. These oscillations cause further compression of the gas from the suction to the discharge opening. The working fluid has to be added to at times to compensate the losses. [45] A simple construction of a vacuum pump can be seen in Figure 26.

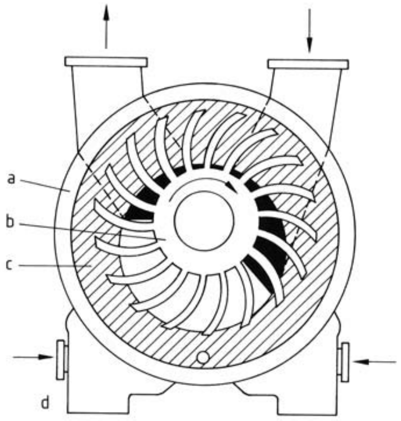

Figure 26. Liquid ring vacuum pump. a) stator, b) rotor, c) liquid ring, d) liquid inlet [45].

Compared to the steam ejector, the vacuum pump does not consume steam at all. Thus, it may provide some energy savings if the price of electrical energy is competitive with the price of the steam. However, vacuum pumps often need more maintenance. A simple distillation system in which a vacuum pump is used was shown in Figure 4. [46]

4.9 Energy efficient distillation columns

Energy efficient distillation columns have been widely studied over the last few years. Column coupling, divided-wall columns (DWC), and internally heat integrated columns (HIDiC) are distillation solutions which many researchers are now focusing on. In addition to these, there are some commercial distillation solutions on the market, which are designed for energy efficiently. One of these kinds of distillation systems is Sulzer distillation technology. This technology is reviewed more precisely in the process development study part of this thesis.

4.9.1 Column coupling

Column coupling may be a way to save energy in processes where several distillation columns are used. Usually, it is applied if more than two components are separated. The column coupling can be divided into two categories. One of these is direct and the other indirect such as thermal column coupling. In direct column coupling, the product streams of a distillation column are coupled with another distillation column. When these two columns are combined into a single column, where the middle part is divided into two parts by a vertical wall, a more efficient distillation system is constructed. This column is called a divided-wall column. Indirect column coupling utilizes waste heat from one column and transfers it to a second column. It is an effective way to reduce heat requirements, and it is more frequently used method than direct column coupling. A disadvantage of indirect column coupling is the increased capital costs due to additional pumps and compressors. The column arrangements of direct and indirect column coupling are shown in Figure 27. [25]

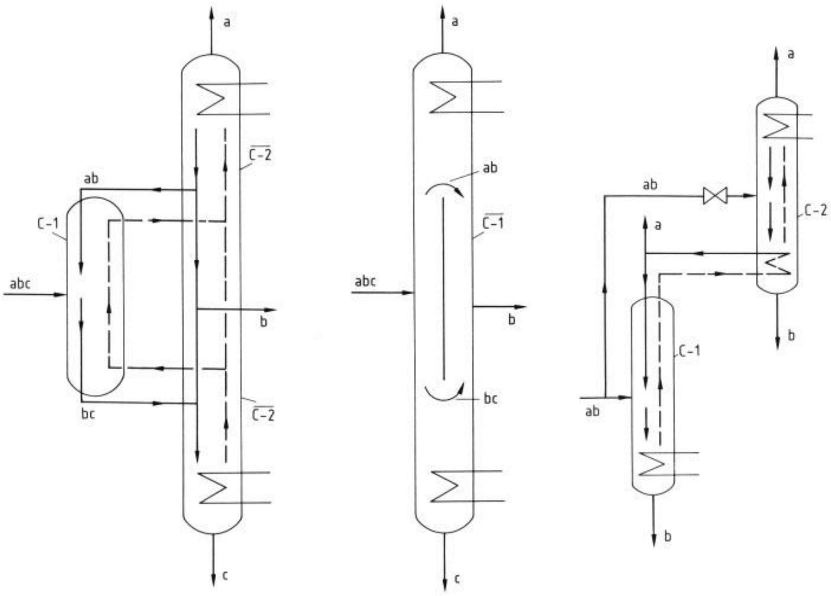

Figure 27. Separation of a ternary mixture abc with direct column coupling and a divided wall column. Indirect column coupling is applied to the separation of a binary mixture ab [25].

4.9.2 Internally heat integrated columns

Internally heat integrated columns are distillation columns where heat is integrated into the whole rectifying and the whole stripping sections [47]. The working principle can be seen in Figure 28. Vapor from the stripping section is compressed into the rectifying section. The rectifying section operates at a higher pressure and temperature, which further allows the internal heat transfer from the rectifying to the stripping section. According to Bruinsma et al. [48], HIDiCs improve the heat reversibility of distillation and they may achieve even 30 – 50 % more energy savings compared to the conventional vapor recompression.

Akiya et al. [47] state that economically feasible HIDiC solutions can be achieved for the separation of binary close boiling mixtures. However, a disadvantage of HIDiCs is the need of compression work, which increases the energy consumption and operating costs. Currently, commercial HIDiCs are under development and there is only a pre-commercial column, the capacity of which is 15 000 t/year, in Japan [48].

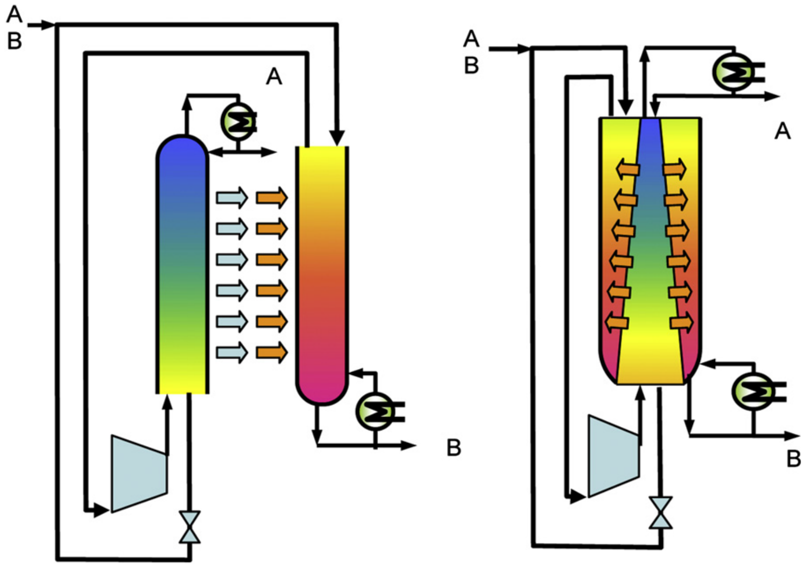

Figure 28. Working principle of an internally heat integrated distillation column [4].

PROCESS DEVELOPMENT STUDY PART

5 SOLVAY VOIKKAA PLANT VOIKKAA

The Solvay Voikkaa Plant is a hydrogen peroxide plant, which manufactures hydrogen peroxide and peracetic acid for domestic and foreign markets. Hydrogen peroxide is manufactured in the anthraquinone auto-oxidation process in which crude hydrogen peroxide (~ 40 wt%) solution is formed through hydrogenation, oxidation, and extraction stages. Hydrogen for the hydrogenation reaction is produced in a hydrogen plant, which is a part of the factory. From the AO-process some of the crude hydrogen peroxide is concentrated by distillation, and the other part is sold as a crude solution. [49] The concentrated hydrogen peroxide solutions account for about 50 % of the annual capacity of the factory [13]. A simple block diagram of the manufacturing process of hydrogen peroxide at the Solvay Voikkaa Plant is shown in Figure 29.

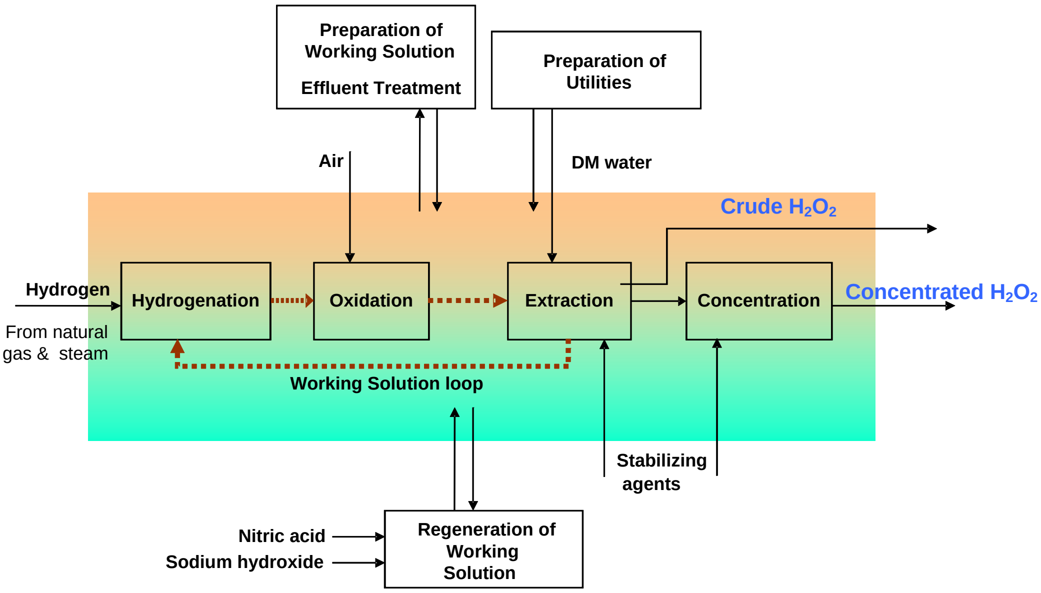

Figure 29. Manufacturing process of hydrogen peroxide at the Solvay Voikkaa Plant [49].

5.1 Utility and energy consumption

The hydrogen plant includes a steam boiler that produces steam for the needs of the hydrogen production. Usually, there is also excess steam, which is consumed all over the factory, such as in distillation. In distillation, steam is used to heat the vaporizer and as motive fluid in the steam ejector system. In the AO-process, steam is used as a heat exchange medium and as a stripping agent. If the need for steam is higher than produced by the hydrogen plant, steam is also produced by an external boiler, which works with natural gas that is bought from an external supplier. [50]

The factory uses demineralized water (dmw) as process water for the unit operations. Demineralized water is produced by purifying chemically treated water from impurities and mineral ions, which may cause the decomposition of hydrogen peroxide. It is supplied from the nearby pulp plant Kymi. In distillation, demineralized water is used as reflux. [50]

Other utilities and forms of energy, which are consumed in the factory, are river water, instrument air, and electrical energy. River water is used as cooling water in the heat exchangers of the factory and it is pumped from the River Kymi, which is located next to the factory. The warmed, pure, cooling water is then returned to the river. Electrical energy is bought from an external electricity supplier and it is used over the entire factory. The main consumers of electrical energy are pumps and compressors. Instrument air is used to control automatic valves, for instance, and it is produced by compressors. [50]

6 CONCENTRATION OF HYDROGEN PEROXIDE AT SOLVAY CHEMICALS FINLAND

At the Solvay Voikkaa Plant, crude hydrogen peroxide is concentrated to 50 and 60 wt% solutions by vacuum distillation. Moreover, 35 and 50 wt% distillates are manufactured for special uses due to their higher purity compared to the concentrated products. The content of total organic carbon (TOC) in distillates is lower than in the concentrated solutions, and therefore they can be used in specific applications.

Distillation is carried out in a packed distillation column (100/2) to which a vacuum is created by a two-stage steam ejector system (105). The bottom product of the distillation is concentrated hydrogen peroxide solution (purge) and the overhead product is water vapor that contains small amounts of hydrogen peroxide. [12] The flow sheet of the concentration of hydrogen peroxide at the Solvay Voikkaa Plant is shown in Figure 30.

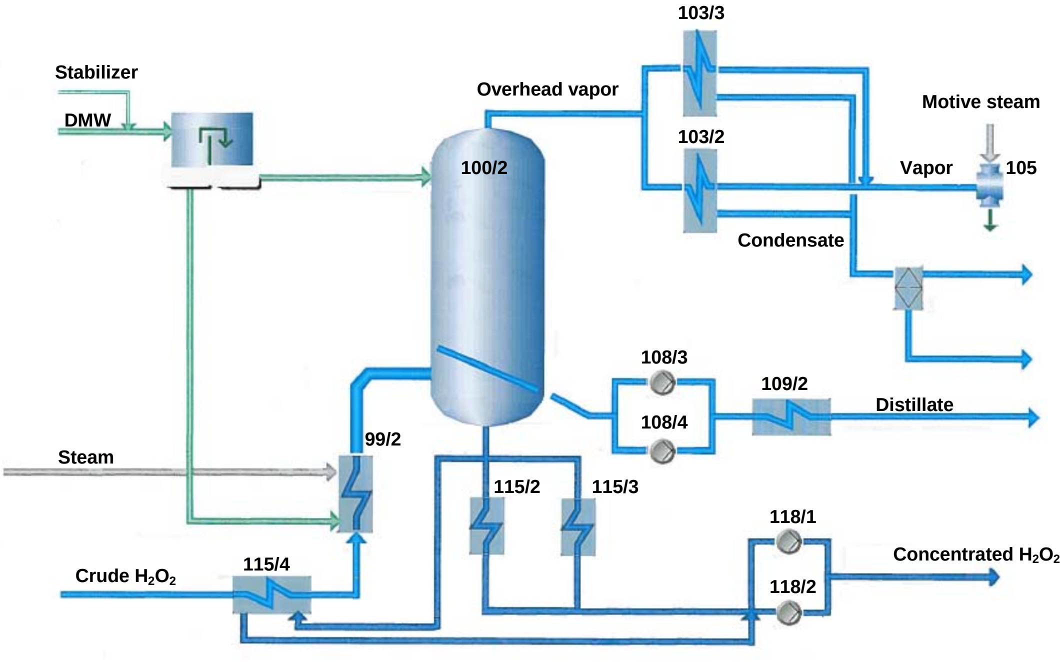

Figure 30. Concentration of hydrogen peroxide produced by distillation at the Solvay Voikkaa Plant. The main equipment of the concentration unit: packed distillation column (100/2), preheater of the feed (115/4), vaporizer of the feed (99/2), condensers of the overhead vapor (103/2-3), steam ejector system (105), pumps of the distillate (108/3-4), pumps of the bottom product (118/1-2), coolers of the bottom product (115/2-3). The feed pump of the crude hydrogen peroxide (114/3) is not shown in the flow sheet [52].

The distillation column can be operated in two modes: in concentration (cc) or in distillation (ds) mode. In the concentration mode, only concentrated solution (either 50 wt% or 60 wt%) is manufactured. In the distillation mode, both the concentrated solution and the distillate are manufactured at the same time. 35 wt% distillate can be manufactured with the 50 wt% purge and 50 wt% distillate with 60 wt% purge. Product concentrations of the distillates and concentrated solutions are shown more precisely in Table IV. [12, 53]

Table IV The product concentrations of the hydrogen peroxide solutions at the Solvay Voikkaa Plant. ST-40 is a crude hydrogen peroxide solution. ST-50 and ST-60 are concentrated products. AG-Bath-35 and CG-50 are distillates [54].

Product name	Concentration, wt%
ST-40	38.5 – 41.0
ST-50	40.0 – 49.9
ST-60	59.0 – 59.9
AG-Bath-35	35.0 – 35.7
CG-50	49.0 – 49.9

6.1 Process description of concentration

The crude hydrogen peroxide solution, from the AO-process, is fed into a storage tank, from which it is pumped to the concentration unit by the feed pump (114/3). The crude solution is warmed in a preheater (115/4) where the heat of the bottom product is utilized to heat the crude solution. From the preheater the crude solution is fed into a vaporizer (99/2) in which it is partially vaporized by low-pressure steam. The pure steam condensate, which is formed in the vaporizer, is circulated to a receiving tank from which it can be reused as boiler water, for example. The mixture of vapor and liquid from the vaporizer is directed to the bottom of the distillation column where the actual concentration is carried out. The concentrated hydrogen peroxide solution is formed at the bottom of the column and its strength is controlled by the steam flow of the vaporizer. [12, 53]

The vapor, released from the feed solution, flows towards the top of the column as a counter current with the pure demineralized water, which is fed into the distillation column as reflux. The most significant function of the reflux is to purify the hydrogen peroxide residues in the overhead water vapor so that the hydrogen peroxide content is as small as possible. Normally, the hydrogen peroxide content in the overhead vapor is in the magnitude of parts per million (ppm). [12] However, Dadabhoy et al. [11] have recommended that the H_2O_2 content in the overheads should be under 500 ppm. Another function of the reflux is to adjust the concentration of the distillate [12].

The distillate is formed in the collection plate under the packed bed, from which it can be pumped to a storage tank through a cooler (109/2). When the distillate is not recovered, it is allowed to overflow through the collection plate to the bottom of the column among the concentrated hydrogen peroxide. The concentrated hydrogen peroxide is further directed through the preheater and product coolers (115/2-3) to a storage tank. If the heat exchange duty of the preheater is high enough, the product coolers are not used at all. [12, 53]

The overhead vapor is condensed in the overhead condensers (103/2-3), which work with cooling water. In winter time the cooling water, which leaves the condensers, is utilized to heat the chemically purified water coming into the factory. The vapor condensate from the condensers is directed partly to the regeneration step of the AO-process where it works as washing water. The other part of the condensate is fed into the waste water treatment of the factory. The non-condensable vapor is sucked into the two-stage ejector system, which creates the vacuum conditions in the distillation column. Steam is fed into each stage of the ejector from which it is directed into the condensers of the ejector system. The condensates are further directed into a receiving tank, from which they are discharged to the river. [12, 53]

6.2 Safety aspects

As was previously mentioned, safety aspects strongly control the distillation of hydrogen peroxide. These aspects take into consideration the decomposition of hydrogen peroxide and the formation of the explosive mixture between hydrogen peroxide and organic compounds.

The stability of hydrogen peroxide is decreased at high temperatures and this may further cause the extensive decomposition of hydrogen peroxide. In distillation, temperatures are high and this may lead to excess decomposition during the distillation. In order that the decomposition can be minimized, the stability of the crude hydrogen peroxide should be high enough before it is fed into the distillation. In addition of this, the stability of the crude solution has to be improved in the distillation column by adding an extra dose of stabilizer into the column. This is performed by adding the stabilizer into the flow of the reflux.

Proper temperature control of the distillation column also prevents decomposition. The distillation must be carried out at such a low temperature that the decomposition is minimal. The crude hydrogen peroxide solution (~ 40 wt%) boils at 110 °C under atmospheric pressure, which would cause its decomposition. The boiling of the crude hydrogen peroxide solution is achieved at a lower temperature when the distillation is carried out under a vacuum. It is recommended that 75 °C is the maximum allowable temperature in distillation. In emergencies, it is possible to feed cooling water (dmw) into the vaporizer if temperatures seem to rise too high. [12, 55]

The concentrated hydrogen peroxide forms explosive mixtures with organic compounds as was shown in Figure 1. This is the safety aspect, which should be taken account when hydrogen peroxide is distilled. The crude hydrogen peroxide solution always contains small residues of organic impurities, which come from the AO-process and this causes the explosion hazard in the distillation. As a result of this, the carbon content of the crude hydrogen peroxide is not allowed to be over 1000 ppm. The residues of the organic compounds in the crude solution can be minimized by a long delay of the crude solution in the feed tank of the concentration. The delay allows the decantation and further separation of the organic matter and hydrogen peroxide due to density differences. In addition, the level of the feed tank is kept high enough (> 60 %) in order that it is not possible for the decanted organic matter to spread to the distillation column. [12]

Organic matter may also cause an explosion hazard in the distillation if the concentration of the crude solution is too low. Then, the organic matter is strongly concentrated at the same time with the dilute crude solution. To prevent this concentration of the feed crude solution is recommended to be over 30 wt%. [12]

RESULTS AND EXAMINATION

7 CURRENT ENERGY EFFICIENCY OF CONCENTRATION

The energy efficiency of the concentration unit of the Solvay Voikkaa Plant is being improved continuously. The plate distillation column has been changed to a packed one and high energy efficiency structured packing has started to utilize

[64]. The pure condensate of the vaporizer is reused as boiler water and some of the overhead condensate is utilized as washing water in the regeneration stage of the AO-process. Moreover, the warm cooling water, which comes from the overhead condensers, can be used to preheat the cold chemically purified water, which inflow into the factory.

The structured packing of Montz was changed to high performance packing of Sulzer in 2011. At the same time, the height of the packing was broadened from 4 m to 6 m, which made even better energy efficiency possible. At that time, the heat at the bottom product of the distillation column was also started to be utilized by the preheater of the feed (115/4). Moreover, the modern plate type heat exchanger (109/2) was introduced, to cool the distillates. A concurrent modification was that the pump at the bottom product (118/2) was equipped with a variable speed drive (VSD), which decreased the consumption of the electrical energy [65]. Furthermore, the flow measurements of the feed, bottom product, and distillate were renewed to a more accurate Micro Motion (MiMo) type flow and density measurements. These measurements made possible increasingly accurate and energy efficient process control. In the past, before the MiMo-measurements, the products were concentrated to close or even over the upper limit of the strength specifications, in order that the product specifications were achieved. After the modification, the products were diluted to the desired strength by dmw if necessary. This kind of over concentration consumed much more energy compared to the concentration which is applied nowadays. At present, the products are directly concentrated to concentrations in the middle range of the product specifications. This kind of concentration is energy efficient as was discussed in the literature section.

The latest improvement of the energy efficiency has been performed in 2013. This improvement was that the cooling water pump G1401/A was equipped with a VSD. This improves the energy efficiency of the entire factory but it also gives advantages to the energy efficiency of the concentration unit. Due to VSD, the pump G1401A uses only about 60 % of the maximum electric power in winter time.

7.1 Energy and utility consumptions

The energy and utility consumptions with the old Montz concentration unit of the Solvay Voikkaa Plant are shown in Table V. The consumptions are calculated only for the concentration operation modes. The distillation modes are excluded due to the low quality of measurement data. The energy and utility consumptions are calculated by the mass balances of the concentration unit. The calculations are based on the measurements of the process, approximations, and theoretical estimations. The process data of the concentration unit was saved in databases from which it has been utilized. The average values of the process measurements for a period of several hours were used in the calculations. In this case, three time periods were used to evaluate the average consumptions. The results were presented per pure hydrogen peroxide ton in order for them to be comparable with each other.

Table V Average energy and utility consumptions of the old Montz concentration unit of the Solvay Voikkaa Plant. Three time periods were used to evaluate the consumptions.

	Mode of the distillation column	
	50 % cc	60 % cc
Steam, kg/t H_2O_2	728	1422
Demineralized water, m^3/t H_2O_2	0.08	0.3
Cooling water, m^3/t H_2O_2	26.2	39.8
Heat, MWh/t H_2O_2	0.6	1.1
Electricity, kWh/t H_2O_2	5.7	9.3

The energy and utility consumptions of the new Sulzer concentration unit with the improvements of 2011-2013 can be seen in Table VI. The current energy and utility consumptions are calculated for all operation modes of the concentration.

Table VI Average energy and utility consumptions of the current concentration unit of the Solvay Voikkaa Plant. Three time periods were used to evaluate the consumptions.

	Mode of the distillation column			
	50 % cc	60 % cc	35 % ds	50 % ds
Steam, kg/t H_2O_2	731	1264	689	1258
Demineralized water, m^3/t H_2O_2	0.1	0.2	0.1	0.4
Cooling water, m^3/t H_2O_2	18.6	31.4	19.4	34.9
Heat, MWh/t H_2O_2	0.6	1.0	0.5	1.0
Electricity, kWh/t H_2O_2	3.8	6.0	4.0	7.0

The results show that the energy and the utility consumptions are higher at the 60 % cc-mode than at the 50 % cc-mode and this can be seen both in the old and the current consumptions. The most significant difference can be seen in the steam consumption, but the difference can be seen also in the consumption of the demineralized water, the cooling water, and the electricity.

At present, the steam consumption of the 50 % cc-mode is about 731 kg/t H_2O_2 whereas the consumption at the 60 % cc-mode is about 1264 kg/t H_2O_2. The consumption of DMW and cooling water at 50 % cc-mode are 0.1 m^3/t H_2O_2 and 18.6 m^3/t H_2O_2. The corresponding results for the 60 % cc-mode are 0.2 m^3/t H_2O_2 and 31.4 m^3/t H_2O_2. The consumption of electricity is about 3.8 kWh/t H_2O_2 at the 50 % cc-mode and 6.0 kWh/t H_2O_2 at the 60 % cc-mode. The steam consumptions of the old concentration unit have been 728 kg/t H_2O_2 at the 50 % cc-mode and 1422 kg/t H_2O_2 at the 60 % cc-mode. The consumption of DMW and cooling water at 50 % cc-mode have been 0.08 m^3/t H_2O_2 and 26.2 m^3/t H_2O_2. The corresponding values for the 60 % cc-mode are 0.3 m^3/t H_2O_2 and 39.8 m^3/t H_2O_2. The consumption of electricity has been about 5.7 kWh/t H_2O_2 at the 50 % cc-mode and 9.3 kWh/t H_2O_2 at the 60 % cc-mode.

At the distillation modes the energy and the utility consumptions are nearly equal to the corresponding concentration modes. The specific steam consumption is slightly lower in the distillation modes but the consumption of cooling water, demineralized water, and the electricity are slightly higher, in turn. The increased cooling water and the electricity consumptions are caused by the pumping and the cooling of the distillates. Moreover, the controlling of the strength of the distillate may increase the consumption of the demineralized water.

The results show that the steam consumption at the 60 % cc-mode has been decreased by almost 13 % after the renovation of the concentration unit. However, the corresponding difference in the steam consumption cannot be seen at the 50 % cc-mode with the old and the current concentration units; here the steam consumptions are almost equal. More time periods should be included in the calculations in order that more accurate levels of the steam consumption could be achieved. This would further show more accurate results and the difference between the steam consumptions of the old and the current concentration units at the 50 % cc-modes.

However, favorable development of the energy and the utility consumptions can be seen in the results. The improvements of the concentration unit, which were implemented in 2011-2013, have also affected this development. The new distillation column with high performance structured packing, preheater, VSD pumps, and advanced process control are parts of the favorable development. Due to the VSD pumps, the electricity consumption is decreased from 5.7 kWh/t H_2O_2 to 3.8 kWh/t H_2O_2 at the 50 % cc-mode. The same trend can be seen at the 60 % cc-mode in which the electricity consumption is decreased from 9.3 kWh/t H_2O_2 to 6.0 kWh/t H_2O_2. The cooling water consumption is decreased due to the preheater, which is used to cool the bottom product instead of the bottom product coolers.

The energy efficiency of the concentration unit is also enhanced by the concentration procedure and more accurate flow measurements. At present, the concentrated products are no longer concentrated over the product specifications, as with the old distillation column. This has significantly decreased the steam and utility consumptions.

7.2 Energy and utility costs

The energy and utility consumptions are used to estimate the costs of the concentration of hydrogen peroxide. The prices of natural gas, electricity, dmw, and cooling water, which are used in the calculations of the costs, can be seen in Table VII. The price of natural gas includes the current energy and transfer prices. The price of cooling water is estimated by using the electricity consumption of the cooling water pump G1401/A. The price of the demineralized water is based on the energy analysis of LCA [50]. The energy and the utility costs are calculated to both old and the current concentration units and they are shown in Tables VIII and IX. As previously, the costs of the old distillation modes are excluded.

Table VII Costs of energy sources and utilities at the Solvay Voikkaa Plant [13, 50].

Energy source / utility	
Natural gas	32 €/MWh
Electricity	60 €/MWh
Demineralized water	0.039 €/m^3
Cooling water	0.008 €/m^3

Table VIII Energy and utility costs of the old Montz concentration unit of the Solvay Voikkaa Plant.

	Mode of the distillation column	
	50 % cc	60 % cc
Heat, €/t H_2O_2	17.7	34.7
Demineralized water, €/t H_2O_2	0.003	0.01
Electricity, €/t H_2O_2	0.34	0.56
Total, €/t H_2O_2	18.1	35.2

Table IX Energy and utility costs of the current concentration unit of the Solvay Voikkaa Plant.

	Mode of the distillation column			
	50 % cc	60 % cc	35 % ds	50 % ds
Heat, €/t H_2O_2	17.8	30.8	16.8	30.7
Demineralized water, €/t H_2O_2	0.004	0.009	0.004	0.01
Electricity, €/t H_2O_2	0.22	0.36	0.24	0.42
Total, €/t H_2O_2	18.0	31.1	17.0	31.1

The costs of the concentration of hydrogen peroxide are directly proportional to the energy and the utility consumptions and thus, the same trend as in the consumptions can be seen in the costs. Presently, the concentration of hydrogen peroxide to the 50 wt% and the 60 wt% solution costs about 18 €/t H_2O_2 and 31 €/t H_2O_2. Before the renovation of the concentration unit, the concentration cost about 18 €/t H_2O_2 at the 50 % cc-mode and 35 €/t H_2O_2 at the 60 % cc-mode. The costs of the 60 % cc-mode have been decreased by 4 €/t H_2O_2 but the costs of the 50 % cc-mode have stayed nearly equal. The costs of the distillation modes are in the same magnitude with the corresponding concentration modes. In general, the results show that the most significant part of the costs is the steam (heat), which covers over 98 % of the total costs in the all operation modes.

8 IMPROVING ENERGY EFFICIENCY OF CONCENTRATION

The potential ways to improve the energy and cost efficiency of distillation were introduced in the literature part in chapter 4. There, it was concluded that the largest savings in energy consumption can be achieved if distillation is reduced or completely avoided. At the Solvay Voikkaa Plant, distillation cannot be totally avoided. The transporting and storing costs can be kept lower with the concentrated hydrogen peroxide solutions. In addition, some of the customers favor concentrated hydrogen peroxide solutions in their processes. However, distillation can be reduced if more and more hydrogen peroxide is sold as 40 wt% crude solution, which comes directly from the AO-process and bypasses the distillation. In addition, the promoting of the sale of the 50 wt% hydrogen peroxide would decrease the costs of the concentration.

Until now, the concentration of hydrogen peroxide has only been carried out by distillation on an industrial scale. Thus, the distillation cannot be replaced with other unit operations. The utilization of advanced unit operations to enhance distillation is also challenging, and it is not presently feasible at the Solvay Voikkaa Plant. Currently, the potential savings can be achieved by improving the energy efficiency of the distillation itself. Heat integration, advanced process control, and equipment improvements are the ways to improve the energy efficiency of distillation at the Solvay Voikkaa Plant.

8.1 Advanced process control

The process control of the concentration unit of the Solvay Voikkaa Plant can be improved. The potential ways to improve the process control of the concentration unit are to optimize the temperatures of the overhead condensers and the flow of the reflux. In this study, experiments were done in order that the optimum conditions and process controls of the concentration would be achieved. The experiments were carried out only in the concentration modes.

8.1.1 Optimization of temperatures of overhead condensers

The vacuum of the distillation column is created by the steam ejector system and fine-tuned by the temperatures of the overhead condensers. When the temperatures of the condensers are high, the cooling water volume flow rate into the condensers is low. The vapor pressure of the distillation column is then higher than with the low temperatures of the condensers. At this time, the pressure of the column is also higher. In turn, if the temperatures of the condensers are adjusted to low values, the cooling water flow into the condensers is high. Further, this should result in lower vapor pressure and lower column pressure, which should lead to better vacuum conditions and lower reboiler duty. The steam consumption should be decreased and the duty of the cooling water pump should be increased, which further results in higher electricity consumption.

Until now, the temperatures of the overhead condensers have not been adjusted very accurately at the Solvay Voikkaa Plant. Therefore, the most energy efficient and economic temperatures of the overhead condensers were studied. The temperatures were determined by experiments, which were carried out using the distillation column of the Solvay Voikkaa Plant.

The experiments were performed at 50 % and 60 % cc-modes. The temperatures of the overhead condensers of the distillation column were changed and the effects of the changes were simultaneously studied. The overhead condensers were set to five different temperatures: 25 °C, 30 °C, 34 °C, 38 °C and 39.5 °C in which the vacuum conditions (column pressure), the steam consumption, and the cooling water consumption of the overhead condensers were studied. The column pressure and the steam consumption were measured by the process measurements but the cooling water consumption was approximated by calculations. The calculations were based on the mass flow of the overhead vapor and the cooling water temperatures of the overhead condensers, which were measured. The conditions of the concentration unit were kept constant for each temperature for many hours in order that the conditions were stabilized. Moreover, in this way, a long measurement period was achieved and the average values of the process measurements of this long period could be used. The results of the experiments can be seen in Tables X and XI. The results were further used to determine the most optimum temperatures of the overhead condensers and the total costs of the concentration process with the different temperatures.

Table X The results of the optimization of the overhead condensers of the distillation column at the Solvay Voikkaa Plant. Column pressure, steam and cooling water consumption were considered along with the steam, cooling water and total costs. A 50 % cc-mode was applied with five different temperatures of the overhead condensers.

	Temperature of the overhead condensers				
	25 °C	30 °C	34 °C	38 °C	39.5 °C
Column pressure, mbar	80	87	98	108	112
Steam, kg/t H_2O_2	667	681	708	720	741
Cooling water to condensers, dm^3/s	34	28	27	23	22
Steam costs, €/t H_2O_2	16.25	16.61	17.25	17.56	18.06
Cooling water costs, €/t H_2O_2	0.17	0.15	0.14	0.12	0.12
Total costs, €/t H_2O_2	16.50	16.84	17.47	17.77	18.27

Table XI The results of the optimization of the overhead condensers of the distillation column at the Solvay Voikkaa Plant. Column pressure, steam and cooling water consumption were considered along with the steam, cooling water and total costs. A 60 % cc-mode was applied with five different temperatures of the overhead condensers.

	Temperature of the overhead condensers				
	25 °C	30 °C	34 °C	38 °C	39.5 °C
Column pressure, mbar	91	98	105	114	118
Steam, kg/t H_2O_2	1253	1254	1268	1275	1278
Cooling water to condensers, dm^3/s	41	35	32	27	26
Steam costs, €/t H_2O_2	30.54	30.55	30.91	31.06	31.14
Cooling water costs, €/t H_2O_2	0.31	0.26	0.25	0.21	0.19
Total costs, €/t H_2O_2	30.97	30.93	31.27	31.39	31.46

The vacuum conditions of the distillation column improved when the temperatures of the overhead condensers decreased. The results show that the column pressure decreased from 112 mbar to 80 mbar when the temperatures of the overhead condensers were varied from 39.5 °C to 25 °C at the 50 % cc-mode. The same phenomenon can also be seen in the 60 % cc-mode. There, the column pressure decreased from 118 mbar to 91 mbar with the same temperature changes.

The stronger vacuum conditions led to lower reboiler duty and this can be seen in the steam consumptions, which were low at a low column pressures. The steam consumption at the 50 % cc-mode varied from 667 kg/t H_2O_2 to 741 kg/t H_2O_2 with the range of the column pressure 80 - 112 mbar. The same variation at the 60 % cc-mode was from 1253 kg/t H_2O_2 to 1278 kg/t H_2O_2 with the pressure range 91 - 118 mbar. The costs of steam are directly proportional to the consumptions. The costs vary from 18.1 €/t H_2O_2 to 16.3 €/t H_2O_2 at the 50 % cc-mode when the temperatures of the overhead condensers are changed from 39.5 °C to 25 °C. At the 60 % cc-mode, the costs of steam vary from 31.1 €/t H_2O_2 to 30.5 €/t H_2O_2.

The cooling water consumption of the overhead condensers increased when the temperatures of the condensers decreased. The cooling water flow changed from 22 dm^3/s to 34 dm^3/s when the temperatures of the overhead condensers were decreased from 39.5 °C to 25 °C in the 50 % cc-mode. The same trend can be seen in the 60 % cc-mode; where the cooling water consumption increased from 26 dm^3/s to 41 dm^3/s with the previous temperature changes. The consumptions of the cooling water were approximated with calculations, which may cause inaccuracy in the consumptions to some extent. The costs of cooling water vary with the cooling water consumptions. At the 50 % cc-mode the cooling water costs vary within a range of 0.12 – 0.17 €/t H_2O_2 when the temperatures of the overhead condensers were changed from 39.5 °C to 25 °C. In the 60 % cc-mode, the cooling water costs vary in the range 0.19 – 0.31 €/t H_2O_2 with the same temperature range.

The total costs of the concentration unit include steam, cooling water, dmw and electricity costs. The results of both concentration modes show that the total costs are low when the temperatures of the overhead condensers are also low. The total costs are 16.50 €/t H_2O_2 at the 50 % cc-mode when the temperatures of the overhead condensers are 25 °C and 18.27 €/t H_2O_2 when the temperatures of the overhead condensers are 39.5 °C. The same costs are 30.97 €/t H_2O_2 and 31.46 €/t H_2O_2 at the 60 % cc-mode. However, the total costs are minimized at the 60 % cc-mode, when the temperatures of the overhead condensers are 30 °C (30.93 €/t H_2O_2). The costs of steam dominate the total costs and the cooling water costs are only 1 % of the total costs.

In general, the results show that the most energy and cost efficient method is to operate the concentration unit with low temperatures of the overhead condensers during the winter time. The most optimum temperature at the 50 % cc-mode is 25 °C and at the 60 % cc-mode it is 30 °C.

8.1.2 Optimization of reflux flow

In the concentration of hydrogen peroxide, the main function of the reflux is to purify the overhead water vapor so that the content of hydrogen peroxide would be as small as possible. In this way, valuable hydrogen peroxide losses are minimized [13].

Referring to Dadabhoy's et al. seminar presentation [11], the reflux flow should be sufficiently high that the content of hydrogen peroxide in the overhead vapor does not exceed a specific limit. This limit at Solvay has been 500 ppm. However, at the Solvay Voikkaa Plant the concentration unit is operated with a much lower overhead of H_2O_2 residue (3 ppm), which has led to high reflux flow. A too high reflux flow causes higher reboiler duty and increases the consumption of demineralized water, which further lead to the higher costs. In addition, high reflux flow may cause flooding and poor separation of the column in some cases. A too low reflux flow may cause the starvation of the column, which has, among other things, an effect on the temperature profile of the column. The temperatures may increase in the upper part of the column, for example. This kind of temperature profile further refers to the spread and the enrichment of the high boiling component (hydrogen peroxide) to the upper part of the column. Based on this discussion, the optimization of the reflux flow is an important factor, which enhances the energy efficiency of the distillation of hydrogen peroxide.

As previously mentioned, the reflux flow of the distillation at the Solvay Voikkaa Plant has been optimized to 3 ppm overhead H_2O_2 residue at present. The reflux flow to the distillation column is controlled by the strength of the bottom product and the steam flow of the vaporizer. However, the temperature profile of the column has not been taken account in the process controls. At times, the temperatures of the column diverge from each other considerably, which refers to the inadequate hydration conditions. Engineer supervisor Timo Orava has performed experiments in order to optimize the reflux flow. These experiments have been done for both 50 % and 60 % concentration modes in 2011 and 2013. However, the precise analysis of the results has not been done. In this work, extra measurements were made to complement the older results. Both the older and the newer results were reviewed closely and the optimized reflux flows of the concentration modes estimated with these experiments. The reflux flows were determined for 3 and 25 ppm H_2O_2 content in the overhead and the costs between these reflux flows further evaluated. In addition, at proper temperature profile of the column has been proposed. The 25 ppm H_2O_2 content was chosen to be an upper limit of the hydrogen peroxide concentration since the concentration was observed to increase suddenly after this concentration.

The experiments were carried out in the distillation column of the Solvay Voikkaa Plant. In the experiments, the reflux flow of the column was changed and the effects of the change were studied at the same time. The reflux flow was decreased by small steps (0.1 - 0.01 m^3/h) and other adjustable variables were kept constant. The hydrogen peroxide content in the overhead condensate and temperatures of the column were measured in the each step of the reflux flow. The hydrogen peroxide content was measured manually with specific test strips and the temperatures of the column were measured by process measurements. The conditions of the concentration unit were kept fixed for each reflux flow for hours (1-2 h). The experiments were performed with four different hydrogen peroxide feed flows. These flows for 50 % concentration mode were 8.0, 10.0, 12.0 and 14.0 m^3/h. The feed flows for 60 % concentration mode were 7.0, 7.5, 9.0 and 10.0 m^3/h. The results of the all experiments are shown in Tables XXI-XXVIII, in Appendix III. The dependence between the hydrogen peroxide content in the overhead condensate and the reflux flow for the both concentration modes can be seen in Figures 31 and 32.

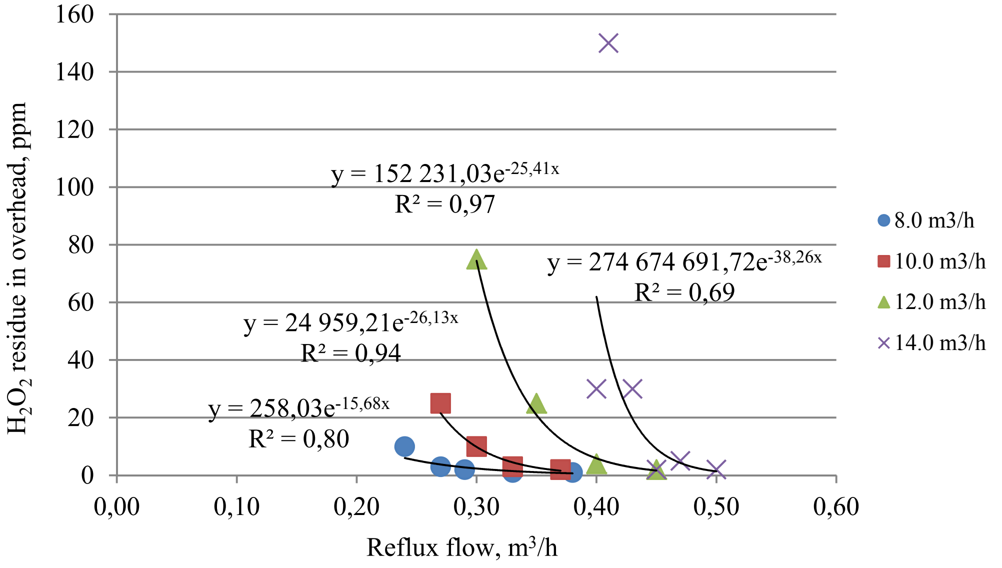

Figure 31. Reflux flow of the distillation column affects the amount of hydrogen peroxide residue in the overhead condensate. The amount of hydrogen peroxide residue in the overhead condensate was measured at several reflux flows at the Solvay Voikkaa Plant. 50 % cc-mode was applied with four different feed flows.

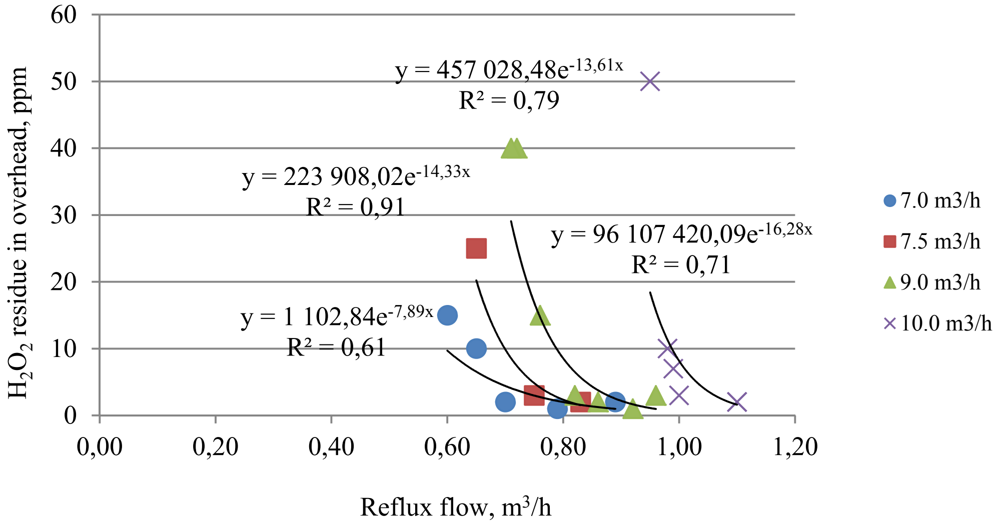

Figure 32. Reflux flow of the distillation column affects the amount of hydrogen peroxide residue in the overhead condensate. The amount of hydrogen peroxide residue in the overhead condensate was measured with several reflux flows at the Solvay Voikkaa Plant. 60 % cc-mode was applied with four different feed flows.

The figures show that the amount of hydrogen peroxide in the overhead vapor increases exponentially when the reflux flow is decreased. Thus, exponential curves were fitted to the measurements. These curves form models, which were used to approximate the reflux flows for 3 and 25 ppm H_2O_2 content in the overhead. R^2-values were calculated to show, how accurate the models are. The reflux flows with 3 and 25 ppm H_2O_2 content in the overhead are shown in Tables XII and XIII. The results of the experiments of 7.0 m^3/h feed flow at the 60 % cc-mode were excluded since the results were not reliable enough (R^2-values = 0.61 < 0.7).

Table XII The reflux flows of the distillation column of the Solvay Voikkaa Plant for four different feed flows with 3 and 25 ppm H_2O_2 content in the overhead condensate. The distillation column was operated at the 50 % cc-mode.

Feed flow, m^3/h	8	10	12	14
Reflux flow (3 ppm), m^3/h	0.28	0.35	0.43	0.48
Reflux flow (25 ppm), m^3/h	0.15	0.26	0.34	0.42

Table XIII The reflux flows of the distillation column of the Solvay Voikkaa Plant for four different feed flows with 3 and 25 ppm H_2O_2 content in the overhead condensate. The distillation column was operated at the 60 % cc-mode.

Feed flow, m^3/h	7.5	9.0	10.0
Reflux flow (3 ppm), m^3/h	0.78	0.88	1.06
Reflux flow (25 ppm), m^3/h	0.64	0.72	0.93

The results show that the required reflux flow is increased with the feed flow of the distillation column. Moreover, the 60 % cc-mode requires higher reflux flow compared to the 50 % cc-mode. In addition, the low hydrogen peroxide content in the overhead condensate is caused with higher reflux flow. These results can be seen more obviously in Figure 33 where the required reflux flows at the 50 % and 60 % cc-modes are presented as a function of feed flow of the distillation column. The reflux flow increases linearly with the feed flow of the distillation column.

However, the 50 % cc-modes (0.99) provide better correlation compared to the 60 % cc-modes (0.91, 0.88).

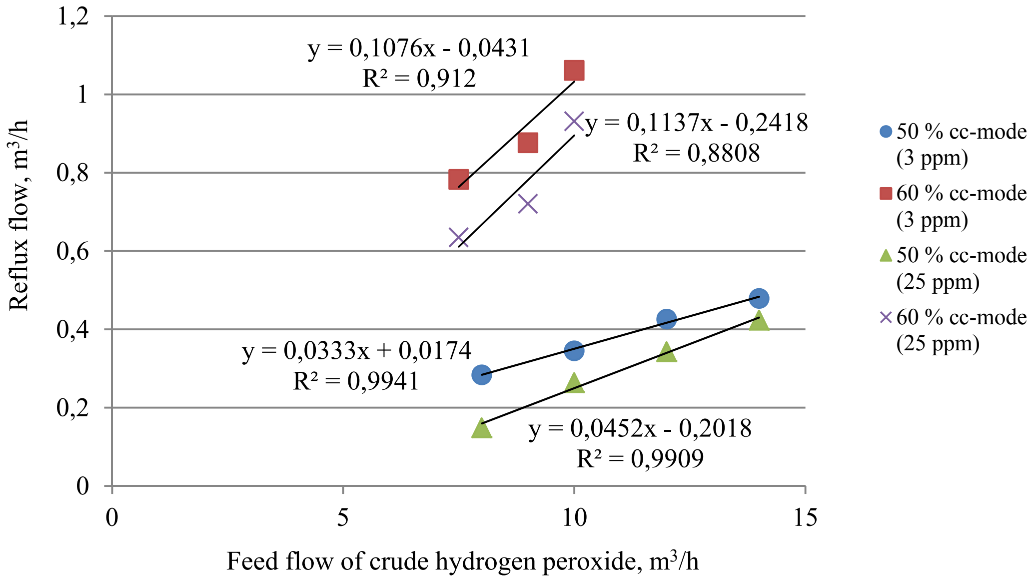

Figure 33. Reflux flows of the distillation column of the Solvay Voikkaa Plant with 3 and 25 ppm H_2O_2 content in the overhead condensate. Reflux flow increases linearly with the feed flow of the distillation column at 50 % and 60 % cc-modes.

The experiments showed also that the reflux flow affects the temperature profile of the column. When the reflux flow of the column was decreased, temperatures of the column began to rise. At first, the bottom temperature started to rise, then the middle temperature and after that, the top temperature. The hydrogen peroxide content in the overhead condensate was observed to stay low as long as the middle temperature started to rise. At this point, the hydrogen peroxide residue increased suddenly to high levels. Based on these results, the dependence between the temperature difference of the lower part of the column and the reflux flow was formed. This dependence for the previously presented feed flows can be seen in Figures 34 and 35.

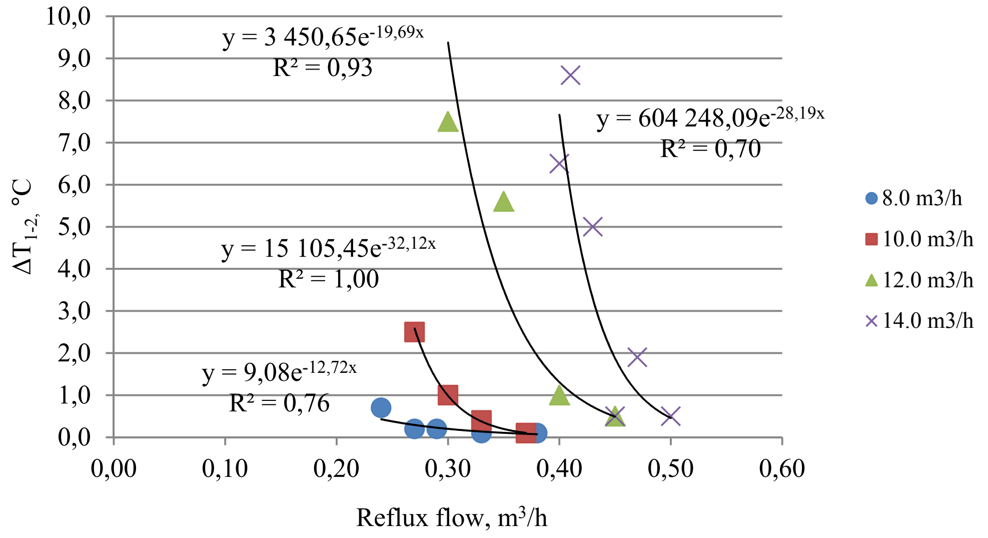

Figure 34. Reflux flow of the distillation column affects the temperature profile of the column. The temperature difference of the lower part of the column was measured with several reflux flows at the Solvay Voikkaa Plant. 50 % cc-mode was applied with four different feed flows.

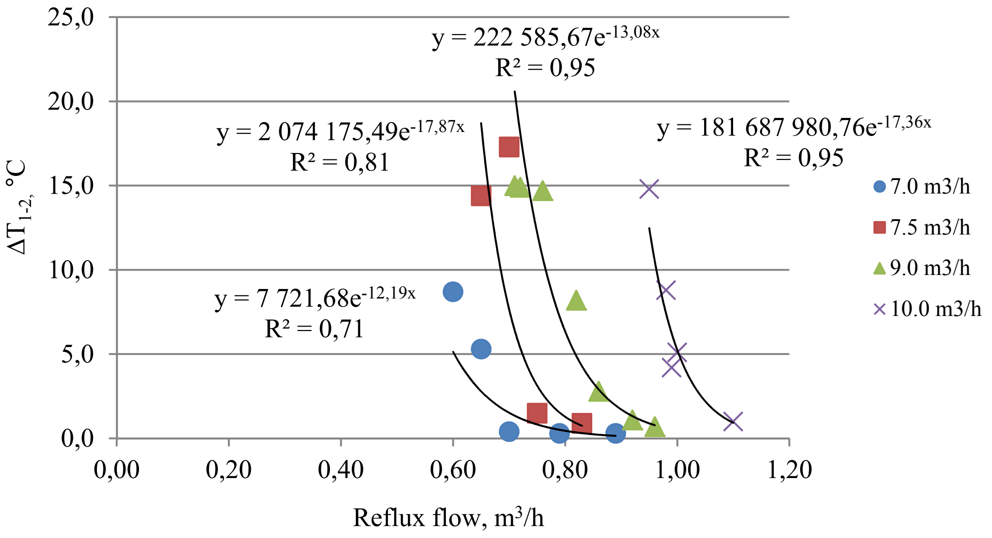

Figure 35. Reflux flow of the distillation column affects the temperature profile of the column. The temperature difference of the lower part of the column was measured with several reflux flows at the Solvay Voikkaa Plant. 60 % cc-mode was applied with four different feed flows.

The figures show that the temperature difference increases exponentially when the reflux flow is decreased as the H_2O_2 content in the overhead condensate.

Exponential curves were fitted to the measurements and these curves forms models, which were used to approximate the temperature differences for the previously determined reflux flows. R^2-values were calculated to show the accuracy of the models. The temperature differences of the lower part of the distillation column for the reflux flows with 3 and 25 ppm H_2O_2 content in the overhead condensate are shown in Tables XIV and XV. The results of the experiments of 7.0 m^3/h feed flow at 60 % cc-mode were excluded since the previously introduced results of the optimum reflux flow were not reliable enough (R^2-value = 0.61 < 0.7).

Table XIV Temperature differences of the lower part of the distillation column of the Solvay Voikkaa Plant with 3 and 25 ppm H_2O_2 content in the overhead condensate. The H_2O_2 content was controlled by the reflux flow of the distillation column and four different feed flows were applied at the 50 % cc-mode.

Feed flow, m^3/h	8	10	12	14
Reflux flow (3 ppm), m^3/h	0.28	0.35	0.43	0.48
ΔT_{1-2}(3 ppm),°C	0.2	0.2	0.8	0.8
Reflux flow (25 ppm), m^3/h	0.15	0.26	0.34	0.42
ΔT_{1-2} (25 ppm),°C	1.4	3.1	4.0	3.9

Table XV Temperature differences of the lower part of the distillation column of the Solvay Voikkaa Plant with 3 and 25 ppm H_2O_2 content in the overhead condensate. The H_2O_2 content was controlled by the reflux flow of the distillation column and four different feed flows were applied at the 60 % cc-mode.

Feed flow, m^3/h	7.5	9.0	10.0
Reflux flow (3 ppm), m^3/h	0.78	0.88	1.06
ΔT_{1-2} (3 ppm), °C	1.7	2.3	1.8
Reflux flow (25 ppm), m^3/h	0.64	0.72	0.93
ΔT_{1-2} (25 ppm), °C	24.5	17.8	17.3

The temperature differences of the lower part of the distillation column for the reflux flows with 3 and 25 ppm H_2O_2 content in the overhead condensate were used to form the dependence between the temperature difference and the feed hydrogen peroxide flow. This dependence can be seen in Figures 36 and 37.

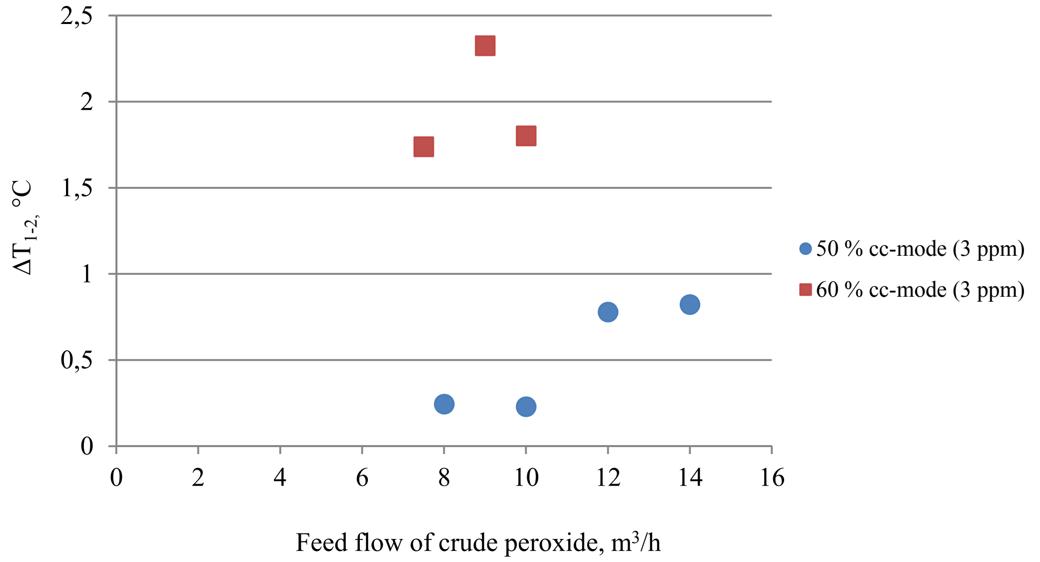

Figure 36. Temperature differences of the lower part of the distillation column of the Solvay Voikkaa Plant with 3 ppm H_2O_2 content in the overhead condensate. The temperature differences were determined with different feed flows at the 50 % and the 60 % cc-modes.

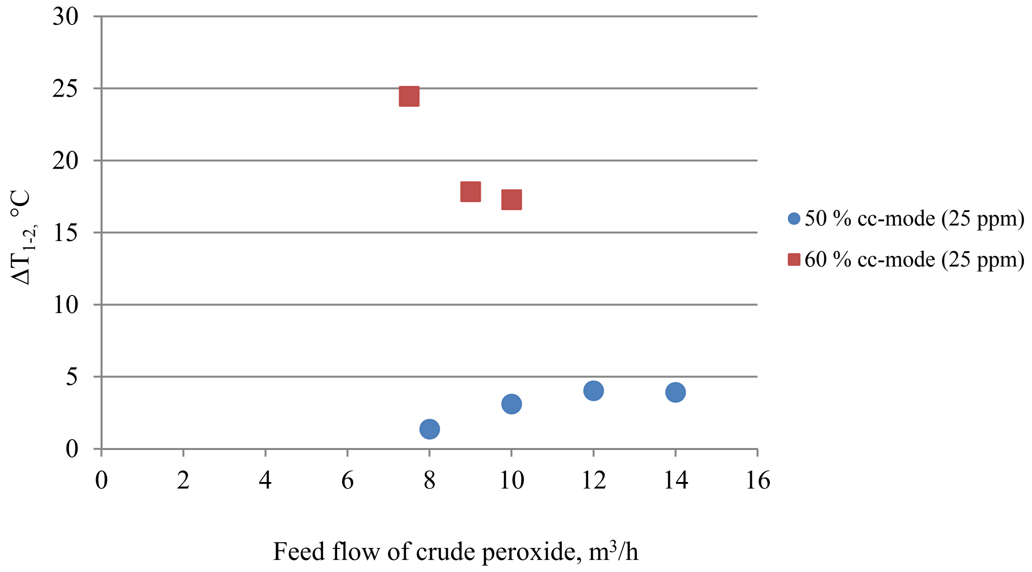

Figure 37. Temperature differences of the lower part of the distillation column of the Solvay Voikkaa Plant with 25 ppm H_2O_2 content in the overhead condensate. The temperature differences were determined with different feed flows at the 50 % and the 60 % cc-modes.

Figures 48 and 49 show that the temperature difference of the lower part of the distillation column does not increase linearly with the feed hydrogen peroxide flow. Figure 48 shows the temperature differences of the lower part of the distillation column with 3 ppm H_2O_2 content in the overhead condensate. In the 50 % cc-mode the temperature difference varies in the range of 0.2 - 0.8 °C with an average of 0.5 °C. In the 60 % cc-mode the temperature difference varies in the range of 1.7 - 2.3 °C with an average of 2.0 °C. Figure 49 shows the temperature differences of the lower part of the distillation column with 25 ppm H_2O_2 content in the overhead condensate. It shows that the temperature difference in the 50 % cc-mode varies between 1.4 – 4.0 °C with an average of 3.1 °C. In the 60 % cc-mode the variation is between 17.3 – 24.5 °C with an average of 19.9 °C.

These values were utilized to construct a controller for the process control system, which fine tunes the reflux flow by the temperature difference of the lower part of the distillation column. That controller was further used to control the H_2O_2 content in the overhead condensate. Experiments were carried out to confirm the proper function of the controller. At the same time, the experiments were used to evaluate the energy and the utility consumptions of the concentration with 3 and 25 ppm H_2O_2 content. These consumptions were further used to evaluate and to compare the costs of the concentration with 3 and 25 ppm H_2O_2 content.

In the experiments, the temperature difference of the lower part of the distillation column was changed by the controller and the effects of the changes were studied at the same time. Only one feed flow of the column was applied at each concentration mode. The feed flow was 11.2 m^3/h in the 50 % cc-mode and 7.5 m^3/h in the 60 % cc-mode. The temperature difference was set to near the average values, which achieved 3 and 25 ppm H_2O_2 content in the overhead condensate. The measured temperature differences in the 50 % cc-mode were 0.6 °C, 1.0 °C and 2.0 °C. The corresponding values at the 60 cc-mode were 0.8 °C, 0.9 °C, 2.0 °C, 2.2°C, 2.5 °C, 9.3 °C and 10 °C. The conditions of the column were kept fixed for several hours with each temperature difference. After that, the H_2O_2 content in the overhead condensate was manually measured with the test strips in order to ensure the proper function of the controller. The results of the experiments can be seen in Figure 38.

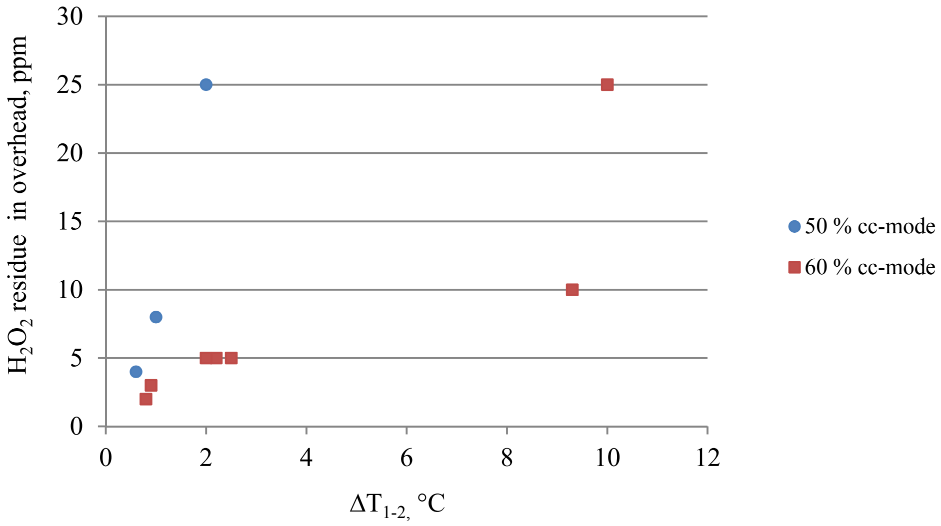

Figure 38. The temperature difference of the lower part of the distillation column, which is adjusted by the reflux flow of the column, has an effect on the H_2O_2 content in the overhead condensate. The experiments were carried out with one feed flow of the distillation column of the Solvay Voikkaa Plant. The feed flow of 11.2 m^3/h was applied in 50 % cc-mode and 7.5 m^3/h in the 60 % cc-mode.

The results imply the same phenomenon, which was seen in the experiments previously carried out. The temperature difference of the lower part of the distillation column, which is adjusted by the reflux flow of the column, has an effect on the hydrogen peroxide content in the overhead. The hydrogen peroxide content is increased when the temperature difference is increased by the decreased reflux flow. This can be seen clearly in the 50 % cc-mode in which the H_2O_2 content in the overhead was increased from 3 ppm to 25 ppm when the temperature difference was changed from 0.6 °C to 2.0 °C. These results are almost equal to the results, which were achieved with the empirical models. The results of the empirical models were shown in Figures 49 and 50. They estimate that the 3 and 25 ppm hydrogen peroxide content in the overhead would be achieved with the temperature differences of 0.5 °C and 2.0 °C on average.

The hydrogen peroxide content in the overhead is also increased in the 60 % cc-mode when the temperature difference of the lower part of the column is increased. The H_2O_2 content was 3 ppm with the temperature difference of 0.9 °C and 25 ppm with the temperature difference of 10 °C. However, the temperature difference of the 9.3 °C caused the 10 ppm hydrogen peroxide content, which does not agree with the other results. In general, the results of the 60 % cc-mode do not agree with the empirical models, as the results in the 50 % cc-mode do. The empirical models estimate that 3 ppm and 25 ppm hydrogen peroxide content in the overhead would be achieved with a temperature difference of 2.0 °C and 19.9 °C on average.

At the same time as the experiments, the steam consumption of the concentration unit and the H_2O_2 losses in the overhead were considered with the 3 and 25 ppm H_2O_2 content. These results were used to evaluate the costs of the concentration with the 3 and 25 ppm H_2O_2 content. These consumptions and costs are shown in Tables XVI and XVII.

Table XVI The results of the optimization of the H_2O_2 content in the overhead condensate of the distillation column at the Solvay Voikkaa Plant. The H_2O_2 content was adjusted by the temperature difference of the lower part of the distillation column, which further adjusted the reflux flow. Steam consumption, hydrogen peroxide losses in the overhead and the total costs of the concentration were considered at in the 50 % cc-mode.

	H_2O_2 content in overhead, ppm	
	3	25
ΔT_{1-2}, °C	0.5	2.0
Reflux flow, m^3/t H_2O_2	0.1	0.09
Steam consumption, kg/t H_2O_2	674	662
H_2O_2 losses, kg/t H_2O_2	0.002	0.02
Steam costs €/t H_2O_2	16.4	16.1
H_2O_2 losses (savings), €/t H_2O_2	0.004	0.006
Total costs of concentration, €/t H_2O_2	16.7	16.4

Table XVII The results of the optimization of the H_2O_2 content in the overhead condensate of the distillation column at the Solvay Voikkaa Plant. The H_2O_2 content was adjusted by the temperature difference of the lower part of the distillation column, which further adjusted the reflux flow. Steam consumption, hydrogen peroxide losses in the overhead and the total costs of the concentration were considered in the 60 % cc-mode.

	H_2O_2 content in overhead, ppm	
	3	25
ΔT_{1-2}, °C	0.9	10.0
Reflux flow, m^3/t H_2O_2	0.25	0.22
Steam consumption, kg/t H_2O_2	1237	1219
H_2O_2 losses, kg/t H_2O_2	0.003	0.03
Steam costs €/t H_2O_2	30.2	29.7
H_2O_2 losses (savings), €/t H_2O_2	0.004	0.01
Total costs of concentration, €/t H_2O_2	30.5	30.1

The results imply that the steam consumption is lower with the 25 ppm H_2O_2 content compared to the 3 ppm H_2O_2 content. In the 50 % cc-mode, the steam consumption is 662 kg/t H_2O_2 with 25 ppm H_2O_2 content and 674 kg/t H_2O_2 with 3 ppm H_2O_2 content. The corresponding values in the 60 % cc-mode are 1219 kg/t H_2O_2 and 1237 kg/t H_2O_2. The steam costs are directly proportional to the steam consumptions and they are 16.1 €/t H_2O_2 with 25 ppm H_2O_2 content and 16.4 €/t H_2O_2 with 3 ppm H_2O_2 content in the 50 % cc-mode. The steam costs in the 60 % cc-mode are 29.7 €/t H_2O_2 with 25 ppm H_2O_2 content and 30.2 €/t H_2O_2 with 3 ppm H_2O_2 content. The total costs of the concentration in 50 % cc-mode are 16.7 €/t H_2O_2 with 3 ppm H_2O_2 content and 16.4 €/t H_2O_2 with 25 ppm H_2O_2 content. The corresponding costs in the 60 % cc-mode are 30.5 €/t H_2O_2 and 30.1 €/t H_2O_2. According to these results, it is more energy and cost efficient to operate the concentration unit with 25 ppm H_2O_2 content than with 3 ppm H_2O_2 content. The savings, which would be achieved by minimizing the H_2O_2 losses are not of such significance compared to the savings of the steam costs.

If the distillation was operated 355 days per year, the annual savings would be thousands of euros with the 25 ppm H_2O_2 content in the overhead condensate compared to the 3 ppm H_2O_2 content. If the distillation was operated half of the year in the 50 % cc-mode and another half in the 60 % cc-mode, the annual savings would be 6 100 € in the 50 % cc-mode with the feed flow of 11.2 m^3/h crude hydrogen peroxide. In the 60 % cc-mode the savings would be 6 500 €/year with the feed flow of 7.5 m^3/h. The total savings would be 12 600 €/year. However, this calculation does not take into account the effect of the seasonal variations.

Based on the results of the experiments, the controller of the reflux flow controls the hydrogen peroxide content in the overhead condensate to some extent. Accurate concentrations are impossible to achieve, but the proper magnitudes of the concentrations of hydrogen peroxide in the overhead can be adjusted. However, the main function of the controller is to fine tune the reflux flow to the column and this function worked well.

8.2 Heat integration

Heat integration is already applied in the concentration unit of the Solvay Voikkaa Plant. The heated cooling water of the overhead condensers is used to preheat the chemically purified water if necessary. In addition, the condensate of the vaporizer is used as boiler feed water at the hydrogen plant. Moreover, the heat of the bottom product of the distillation column (purge) is used to preheat the feed (crude hydrogen peroxide). The heat is exchanged from the purge to the crude hydrogen peroxide by the preheater, the working principle of which was introduced previously. The performance of the preheater is evaluated in this chapter.

The heat integration system, such as the pump around systems and the intermediate heat exchangers, which were introduced in the literature part of the study, are not feasible solutions to enhance the energy efficiency of the concentration unit at the Solvay Voikkaa Plant. Both solutions need investments and the actual energy savings, which could be achieved, are minor. The volume flow of the distillate, which could be utilized in the pump around system, is such low that the amount of heat that could be made use of would be low. In addition, there are not many places, where the heat could be utilized, close to the concentration unit.

Although the heat integration is already applied in the concentration unit, it could be applied still better. There are many flows that include heat, which could be utilized, in the concentration unit. At present, the heat of the overhead condensates of the distillation column and the condensates of the steam ejectors are not utilized at all. In addition, the warmed cooling water of the distillate and the bottom product coolers is directed to the river. However, the heat content of these flows is sufficiently low that the utilization of this heat is not feasible with the direct heat integration. Heat pumps are needed to improve the heat content of these flows.

A local energy company (KSS-energy) provides a solution to this challenge. They are interested in heat integration with the Solvay Voikkaa Plant and they have provided Solvay with a possibility to join the district heat network of the town Kouvola, as heat supplier. This kind of co-operation would make use of both parties. Solvay has excess heat, which could be utilized to heat the district heat network and this would bring further income to Solvay. At the same time, KSS-energy would acquire a new heat supplier for the district heat network system. In this way, the excess steam, occasionally produced by the factory and the heat in the warmed cooling water could be utilized in an energy efficient way. This kind of system would require investments, which would consist of a heat pump system and a steam heat exchanger. [66] Neither of these investment costs nor possibility savings of the system are evaluated in this work. However, preliminary evaluations show that this kind of heat integration would be feasible.

8.2.1 Evaluation of the performance of preheater

At times, the preheater of the concentration unit may be fouled due to quinone residues as was discussed in the literature section. The fouling decreases the performance of the preheater and thus, it is important to check the performance of the preheater at times. The performance is checked in this work by comparing the temperature difference of the crude hydrogen peroxide solution across the preheater as a function of time. This comparison can be seen in Figure 39.

The preheater was installed in the concentration unit in autumn 2011, after which a 9 °C temperature difference was seen. Before this, the concentration unit did not contain a preheater at all, which is also demonstrated in Figure 39. The temperature difference has been zero or lower because the crude feed hydrogen peroxide solution has not been preheated at all before the vaporizer of the distillation column. Figure 39 shows that the preheater was fouled in spring 2012 and the low performance continued throughout the summer until the preheater was cleaned in autumn 2012. After that, the performance of the preheater has remained high and currently the preheater seems to work effectively due to the high temperature difference (9 °C). This temperature difference results, with the feed flow of 15 m^3/h, in the heat power of 150 kW, which is about 70 % of the heat capacity (212 kW) that is evaluated by the manufacturer.

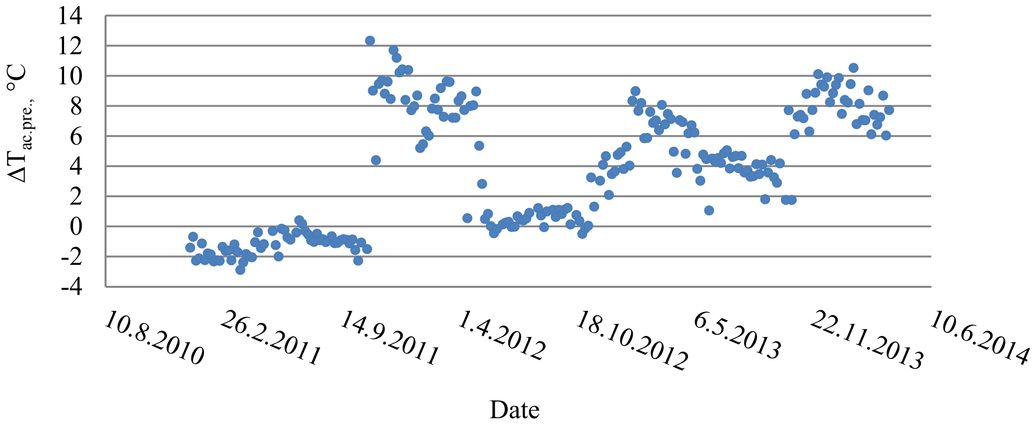

Figure 39. The performance of the preheater of the concentration unit at the Solvay Voikkaa Plant was evaluated by measuring the temperature difference across the preheater. The measurements were taken at five-day intervals and the outliners were excluded.

8.3 Equipment improvements

Currently, the energy efficiency of the equipment in the concentration unit at the Solvay Voikkaa Plant is high. The Solvay Voikkaa Plant uses the structured packing of Sulzer and according to Jödecke’s et al. study [43] the structured packing and the internals of the distillation column have high performance and more energy efficient solutions are not currently available. Moreover, the most widely used pumps are equipped with VSDs, which provide savings in the electricity consumption. The heat losses of the distillation column cannot be avoided since the column is not allowed to be insulated due to the decomposition feature of hydrogen peroxide. Although the current energy efficiency is high, some improvements according to the equipment of the concentration could be implemented. One of these is to replace the steam ejector system as the vacuum producer with a vacuum pump.

8.3.1 Vacuum system by a vacuum pump

The vacuum system of the concentration unit at the Solvay Voikkaa Plant could be constructed by a vacuum pump as in Figure 4. The steam ejector system could be replaced partly or totally with the vacuum pump system, which would consist of a pump, cooler and liquid tank. According to Myohanen [68] the steam ejector system is not necessary totally removed. It would make sense to keep the steam ejector with the vacuum pump since the creating of the vacuum with the vacuum pump takes many hours. With the steam ejector, the vacuum can be created much more rapidly, which also makes the start-ups of the concentration unit easier.

The expected costs and savings of the vacuum pump system are shown in Table XVIII. The utilization of the vacuum pump would decrease the steam consumption of the concentration unit due to the low operation of the steam ejector. The expected savings in the steam costs are 57 300 €/year, which consist of the steam costs of the ejector system. The excess steam, which would be formed due to low operation of the steam ejector, could be further dealt with by KSS-energy.

The expected investment costs of the vacuum pump system (30 000 €), which includes the costs of the pump, motor, cooler, liquid tank, pipelines, and installation, are low. The costs of the pump are based on an offer, which was request from a supplier. In addition, the costs of the installation, pipelines and liquid tank are evaluated with the investment costs of the same type of project at the Solvay Voikkaa Plant.

Table XVIII The expected costs and savings of installing a vacuum pump system of the distillation column at the Solvay Voikkaa Plant.

Investment costs, €	30 000
Operating costs, €/year	1500
Savings in steam costs, €/year	57 300
Total savings, €/year	55 800
Payback time, year	0.54

The operating costs are based on the evaluated electricity costs of the vacuum pump (3 kW) and they are also low (1500 €). The low investment costs and large total savings lead to a short payback time (0.54 year), which makes the vacuum pump system a feasible investment for the Solvay Voikkaa Plant.

8.4 Energy efficient distillation columns

The investment costs of totally new distillation column solutions are sufficiently high as not to be feasible at this time for the Solvay Voikkaa Plant. Moreover, internally heat integrated distillation columns (HiDCs) are such new technology and still under development that they are not potential solutions at present. In addition, only one distillation column is operated at the Solvay Voikkaa Plant and thus, it is not possible to apply column coupling in energy savings. However, Sulzer have conducted research into the concentration of hydrogen peroxide and they have proposed some improvements and modifications to the concentration.

8.4.1 Sulzer distillation technology

Sulzer have marketed distillation technology packages for many decades. Solvay engaged Sulzer (Meszaros) [67] to study and to improve the energy efficiency of the concentration unit of Solvay Chemicals USA Longview in 2007. The study is simulation based and it consists of equipment systems, which would enhance the energy efficiency of the concentration. According to the Meszaros' study [67] and the presentation of Solvay [69] Sulzer distillation has high energy efficiency due to three primary elements:

1. High performance structured packing
2. Energy recovery from overhead vapor
3. Use of stripping section in column

Sulzer has suggested that the using of the classical stripping section in the distillation column would enhance the energy efficiency of the distillation of hydrogen peroxide. Sulzer has even promised 45 % savings in the steam consumption with the use of the stripping section. However, the use of the stripping section would require large modifications to the concentration unit, which would cause further high investment costs. The structured packing would need to be changed in the construction, which consists of two parts. In addition, the conventional climbing film evaporator would need to be changed to a falling film evaporator due to the safety advantages. Due to high costs, these kinds of modifications are not feasible at the Solvay Voikkaa Plant at this moment. In addition, more research is needed to confirm how large the expected savings in the steam consumption would be at the Solvay Voikkaa Plant.

The feasibility and the advantages of the high performance structured packing and the energy recovery from the overhead vapor at the Solvay Voikkaa Plant are discussed in the following chapters.

8.5 Heat pumping

As was mentioned in the literature section, heat integration solutions should be exhausted before the heat pumping is applied. The reason for this is that the heat pumping is a more expensive way to utilize heat than the heat integration. However, if the long payback times for the heat pump systems are acceptable, large savings can be achieved by heat pumps. As previously mentioned, Meszaros [67] has studied the energy efficiency of equipment solutions, which are connected to the concentration of hydrogen peroxide. The energy efficiency of heat pump systems, such as mechanical vapor recompression and thermal vapor recompression were studied at the concentration of hydrogen peroxide. In this work Meszaros' study [67] was utilized to evaluate the feasibility of the heat pump systems in the concentration of hydrogen peroxide at the Solvay Voikkaa Plant.

8.5.1 Mechanical vapor recompression

A mechanical vapor recompression system, which is shown in Figure 40, is proposed for the distillation of hydrogen peroxide by Meszaros [67]. It includes a simple turbo blower or radial compressor (T-1), which is used to compress the overhead vapor of the distillation column to the temperature level which is high enough to evaporate the bottom product in the vaporizer (E-1). The compressor can be driven directly or via gears by an electric motor and the power of it is evaluated to be 1000 kW. In the vaporizer, the overhead vapor is condensed and directed to the receiving tank (V-1). Various types of vaporizers can be used depending on the product but Sulzer recommends a falling film evaporator for the distillation of hydrogen peroxide. A condenser (E-2) is used to adjust the energy balance of the system.

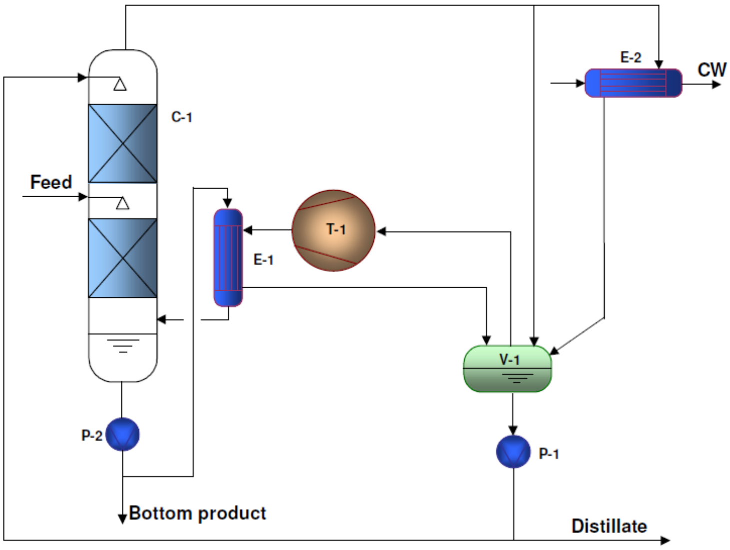

Figure 40. The energy of the overhead vapor of distillation column can be utilized by a mechanical recompression system. The system works like a heat pump, which compresses the overhead vapor to the temperature level, which evaporates the bottom of the distillation column. C-1 distillation column, E-1 vaporizer, E-2 overhead condenser, P-1 condensate pump, P-2 bottom product pump, T-1 compressor, V-1 condensate tank [67].

The expected investment and operating costs of a mechanical vapor recompression system are shown in Table XIX together with the savings, which could be achieved by the investment. The investment costs of the system are evaluated with Meszaros' study [67] and they do not include engineering and installation costs. The operating costs and the expected savings in steam costs are evaluated with the energy consumptions and the costs of the Solvay Voikkaa Plant. The total savings are further used to evaluate the payback time for the investment.

Table XIX The expected costs and the savings of a mechanical vapor recompression system in the distillation column at the Solvay Voikkaa Plant. The investment costs are evaluated by Meszaros' study [67], which was made for the concentration unit of Solvay Chemicals USA Longview. The investment costs do not include costs of engineering and installation. The operating costs consist only of electricity.

Investment costs, €	3 920 000
Operating costs, €/year	511 000
Savings in steam costs, €/year	887 000
Total savings, €/year	376 000
Payback time, year	10.4

A mechanical recompression system would offer high savings in the steam costs of 887 000 €/year. These costs include the steam, which would be produced for the conventional vaporizer and for the motive steam of the ejector system without the mechanical recompression system. The operating costs of the system consist of the electricity costs, which would be 511 000 €/year. The annual operating costs and the savings in the steam consumption would lead to the total annual savings, which are about 376 000 €/year. A drawback of the mechanical vapor recompression system is the very high investment costs 3 920 000 €, which would lead to a long 10.4 year payback time. Due to high investment costs and the long payback time, the mechanical vapor recompression system is not a feasible solution for improving energy efficiency of the concentration unit at the Solvay Voikkaa Plant.

8.5.2 Thermal vapor recompression

According to Meszaros' study [67], steam ejectors are the least expensive and the simplest heat pump solutions. Meszaros provides this kind of solution, shown in Figure 41, for the concentration of hydrogen peroxide. A steam ejector (T-1) is driven with motive steam (S) and it compresses a fraction of the overhead vapor to the necessary pressure and temperature level, which further heats the vaporizer (E-1) and boils the bottom of the distillation column. As in the case of the mechanical vapor recompression, the types of the vaporizer vary depending on the product. However, Meszaros recommend a falling film vaporizer for hydrogen peroxide. Additional condensers (E-2), (E-3) condense the remaining fraction of the overheads. The necessary vacuum for the distillation column is formed by a vacuum pump (VP-1).

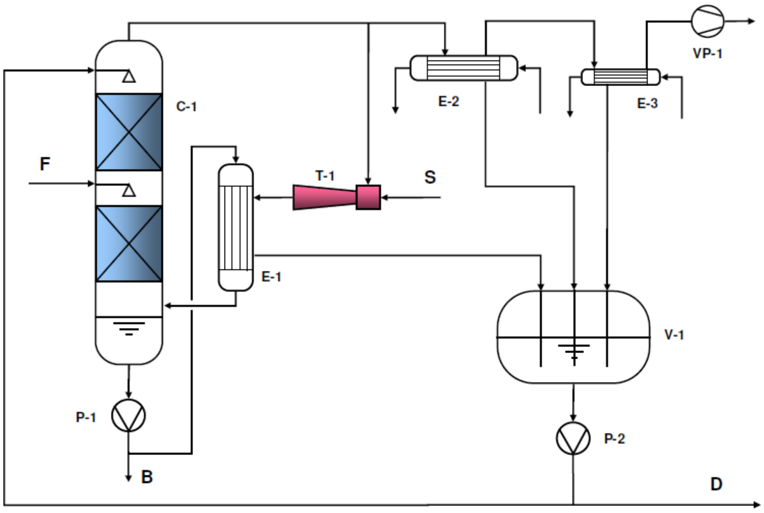

Figure 41. The energy from the overhead vapor of distillation column can be utilized by a thermal vapor recompression system. The system works like a heat pump, which compresses a part of the overhead vapor to the temperature and pressure level, which then evaporates the bottom of the distillation column. C-1 distillation column, E-1 vaporizer, E-2 overhead condenser, E-3 overhead condenser, T-1 steam ejector, VP-1 vacuum pump, V-1 condensate tank, P-1 bottom product pump, P-2 condensate pump [67].

The expected investment and the operating costs of the steam ejector system are shown in Table XX with the savings. The investment costs of the system are evaluated with the Meszaros' study [67] and, as in the case of the mechanical vapor recompression, they do not include engineering and installation costs. The operating costs and the expected savings in the steam costs are evaluated with the energy consumptions and the costs of the Solvay Voikkaa Plant. The total savings are further used to evaluate the payback time for the investment.

Table XX The expected costs and the savings of a thermal vapor recompression system of the distillation column at the Solvay Voikkaa Plant. The investment costs are evaluated using the Meszaros' study [67], which was made for the concentration unit of Solvay Chemicals USA Longview. The investment costs do not include costs of engineering and installation. The operating costs consist of steam, which is consumed in the ejector system, and electricity, which is consumed in the vacuum pump.

Investment costs, €	360 000
Operating costs, €/year	838 000
Savings in steam costs, €/year	887 000
Total savings, €/year	49 000
Payback time, year	7.3

The thermal vapor recompression system provides a high saving in the steam costs of 887 000 €/year. These costs include the steam, which would be produced for the conventional vaporizer and for the motive steam of the current steam ejector. The operating costs of the system (838 000 €/year) consist of the steam costs of the new ejector and the electricity costs of the vacuum pump. The annual operating costs and the savings in the steam consumption lead to the total annual savings, which would be about 49 000 €/year. The investment costs of the steam ejector system and the vacuum pump (360 000 €) are smaller than the costs in the case of the mechanical vapor recompression. However, the costs cause a long payback time (7.3 years) for the investment, which is the drawback of the system. Due to the high investment costs and long payback time, the steam ejector system is not a feasible solution to improve energy efficiency of the concentration unit at the Solvay Voikkaa Plant.

9 IMPROVEMENT PROPOSALS

Although the current energy efficiency of the concentration unit of the Solvay Voikkaa Plant is high, it can still be improved. One way to do this is to reduce the distillation. This could be carried out by promoting the sale of the crude hydrogen peroxide (~ 40 wt%). Furthermore, the promoting of the sale of the 50 wt% concentrated product would decrease the costs of the concentration. However, a more efficient way to improve the energy efficiency of the concentration unit of the Solvay Voikkaa Plant is to improve the energy efficiency of the concentration unit itself. The improvements can be divided into advanced process control, heat integration and energy efficient equipment solutions.

In this study, the temperatures of the overhead condensers and the reflux flow of the distillation column of the Solvay Voikkaa Plant were optimized. The results show that the temperatures of the condensers should be adjusted to low values. The optimized temperatures in the 50 % cc-mode are 25 °C and in the 60 % cc-mode 30 °C. The reflux flow should be adjusted by the temperature difference of the lower part of the column so that the hydrogen peroxide residue in the overhead condensate would be 25 ppm. The preliminary tests showed that the 25 ppm H_2O_2 residue in the overhead was achieved in the 50 % cc-mode when the temperature difference was about 2 °C. At that time, the reflux flow to the column was 0.09 m^3/t H_2O_2. The corresponding values in the 60 % cc-mode were 10 °C and 0.22 m^3/t H_2O_2.

The steam ejector of the concentration unit of the Solvay Voikkaa Plant can be partly replaced by a vacuum pump system. The annual savings, which this investment could provide, are significant (55 800 €). In addition, the payback time of the investment would be short (0.54) and therefore, this investment would be feasible at the Solvay Voikkaa Plant.

10 CONCLUSION

Distillation is a unit operation of process industry, which is usually used to separate chemical compounds from each other in the liquid phase. In some cases it can also be applied to concentrate liquid mixtures. A drawback of the distillation is that it is one of the most energy consuming unit operations of the process industry. An increase in energy and raw material prices has led to a search for ways to improve the energy efficiency of distillation. In this Master's Thesis these process modification options were studied in connection with the concentration of hydrogen peroxide at the Solvay Voikkaa Plant. The aim of the work was to improve the energy efficiency of the concentration unit.

The Solvay Voikkaa Plant is a hydrogen peroxide plant, which manufactures crude aqueous hydrogen peroxide (40 wt%) by the anthraquinone process. A part of the crude hydrogen peroxide is further concentrated to 50 wt% and 60 wt% hydrogen peroxide and this concentration is carried out by distillation. The main principles of distillation were introduced in the beginning of this work including an in depth review of hydrogen peroxide. The concentration unit and the antraquinone process of the Solvay Voikkaa Plant were presented in the process development study part of the work.

Energy analysis of the concentration unit of the Solvay Voikkaa Plant was carried out in this study. The analysis includes an evaluation of the current utility and energy consumptions of the concentration unit. In addition, the old concentration unit, which was renewed in 2011, was included in the analysis in order that the effects of the renovation could be seen. The results of the energy analysis were shown in Tables V and VI. The results implied that the energy and utility consumptions are higher in the 60 % cc-mode than in the 50 % cc-mode. The most significant difference can be seen in the steam consumption. At present, the steam consumption of the 50 % cc-mode is about 731 kg/t H_2O_2 whereas the consumption of the 60 % cc-mode is about 1264 kg/t H_2O_2. The corresponding values for the old concentration unit were 728 kg/t H_2O_2 in the 50 % cc-mode and 1422 kg/t H_2O_2 in the 60 % cc-mode.

The results showed that the distillation modes consume nearly equal amounts of energy and utilities as the corresponding concentration modes. Furthermore, the results revealed that the steam consumption in the 60 % cc-mode was decreased significantly after the renovation of the concentration unit. However, the corresponding decrease could not be seen in the steam consumption of the 50 % cc-mode. However, the favorable development of the energy efficiency of the concentration unit can be seen in the results.

The results of the energy analysis were further used to evaluate the costs of the concentration. These costs were presented in Tables VIII and IX. The costs were directly proportional to the energy and the utility consumptions and thus, the same trend as in the consumption results could be seen in the costs. Currently, the concentration of hydrogen peroxide to 50 wt% and 60 wt% solutions costs 18.0

€/t H_2O_2 and 31.1 €/t H_2O_2. The corresponding costs with the old concentration unit were 18.1 €/t H_2O_2 and 35.2 €/t H_2O_2. On the basis of the results, 4 € savings per tons of pure H_2O_2 were achieved in the 60 % cc-mode with the renovation of the concentration unit in 2011. The most significant factor of the costs is steam (heat), which covers over 98 % of the total costs. Thus, if the aspiration is to decrease significantly the costs of the concentration, it is essential to reduce the steam consumption.

The main approaches to achieve savings in distillation were introduced in the literature part of this work and their feasibility was evaluated in the process development study part. These approaches can be categorized into three main groups from which the first is to replace distillation with other separation methods or prevent it totally if possible. In this way, the largest savings can be achieved. At the Solvay Voikkaa Plant, distillation cannot be totally prevented since the storing and the transporting costs can be kept reasonable with the concentrated hydrogen peroxide solutions. However, distillation can be reduced if an increasing amount of hydrogen peroxide is sold as a crude 40 wt% solution. In addition, the costs of the concentration can be reduced by promoting the sale of the 50 wt% concentrated product. The second way to improve the energy efficiency of distillation is to enhance conventional distillation with advanced unit operations. An advanced separation process can be combined with a distillation column so that the product of the distillation is refined by this process. In this way, the distillation can be operated with lower energy consumption. This method is not possible with the concentration of hydrogen peroxide since this concentration can only be carried out by distillation.

The third and the most common way to achieve energy savings in distillation is to improve the energy efficiency of the distillation itself. At the Solvay Voikkaa Plant this method is also the most potential. Energy integration, advanced process control, and equipment improvements are the main ways to carry out these energy efficient improvements. Energy integration can be further divided into heat integration, heat pumping, and internal heat integrated distillation columns. The energy efficient equipment of distillation consists of energy efficient column internals, packings, plates, and pumps. Advanced process control covers the optimization of the process controls energy efficiently.

The process control of the concentration unit of the Solvay Voikkaa Plant was improved as a result of this work. The first improvement was the optimization of the temperatures of the overhead condensers of the distillation column through the experiments. The results of the experiments were shown in Tables X and XI. The experiments showed that the temperatures of the overhead condensers affect the cooling water consumption of the condensers and the pressure of the column. The column pressure further affects the steam consumption of the vaporizer. In the most optimal conditions, the temperatures of the overhead condensers were low and the cooling water consumption high. As a result of this, the pressure of the column was minimized together with the steam consumption. At the most optimal conditions of the 50 wt% cc-mode, the temperatures of the overhead condenser and the cooling water consumption were 25 °C and 34 dm^3/s. The column pressure was then 80 mbar and the steam consumption 667 kg/t H_2O_2. The total costs of the concentration in this case was 16.50 €/t H_2O_2. At the optimum conditions of the 60 % cc-mode, the temperatures of the overhead condensers and the cooling water consumption were 30 °C and 35 dm^3/s. The column pressure was 98 mbar and the steam consumption 1254 kg/t H_2O_2. The total costs of the concentration in this case were 30.93 €/t H_2O_2.

The energy efficiency of the process control of the concentration unit was also enhanced by the optimization of the reflux flow of the distillation column. The optimization was carried out with the experiments, which showed that the reflux flow affects exponentially the hydrogen peroxide content in the overhead condensate of the distillation column. The results of these experiments were shown in Figures 31 and 32. The decreasing of the reflux flow increased exponentially the hydrogen peroxide content in the overhead. During the experiments, it was also noted that the reflux flow affects the column temperatures as well. The temperatures started to rise when the reflux flow was decreased. The temperature difference of the lower part of the distillation column was increased exponentially when the reflux flow was decreased, which can be seen in Figures 34 and 35. As a result of this, a controller of the process control system was constructed to fine-tune the reflux flow into the distillation column by the temperature difference of the lower part of the column. The column was operated with 3 ppm and 25 ppm H_2O_2 content in the overhead with the controller, and, at the same time, the steam consumption, hydrogen peroxide losses and the reflux flow were considered.

The results of these operations can be seen in Tables XVI and XVII and they show that the steam consumption of the concentration unit is decreased when the reflux flow is decreased. The decreasing reflux flow increased the hydrogen peroxide content in the overhead. The steam consumption was 674 kg/t H_2O_2 in the 50 % cc-mode with the reflux flow of 0.1 m^3/t H_2O_2. At that time, the H_2O_2 content in the overhead was 3 ppm. The corresponding values with the reflux flow of 0.09 m^3/t H_2O_2 were 662 kg/t H_2O_2 and 25 ppm . The steam consumption in the 60 % cc-mode with the reflux flow of 0.25 m^3/t H_2O_2 was 1237 kg/t H_2O_2 and the H_2O_2 content was 3 ppm. The corresponding values with the reflux flow of 0.22 m^3/t H_2O_2 were 1219 kg/t H_2O_2 and 25 ppm.

Based on these results, the operation of the distillation column with 25 ppm H_2O_2 content is more energy and cost efficient than the operation with 3 ppm H_2O_2 content. With this kind of operation the annual savings can be thousands of euros. The preliminary tests showed that 25 ppm H_2O_2 residue in the overhead was achieved in the 50 % cc-mode when the temperature difference in the lower part of the column was set to 2 °C. At that time, the reflux flow to the column was 0.09 m^3/t H_2O_2. The corresponding values in the 60 % cc-mode were 10 °C and 0.22 m^3/t H_2O_2.

Energy efficient equipment can also be used to enhance the energy efficiency of the concentration unit at the Solvay Voikkaa Plant. The distillation column is already equipped with high performance structured packing and internals and the replacing these is not necessary. Instead, one method to improve the energy efficiency would be to replace the steam ejector system of the concentration by a vacuum pump system. The annual savings, which this investment could provide, are tens of thousands of euros. Moreover, the payback time of the investment would be short (0.54 year) and therefore, this investment would be feasible. The expected savings and the costs of this investment were shown in Table XVIII.

Heat pumping is also a method of increasing the energy efficiency of the concentration. This was discussed in more detail in Chapters 4.4 and 8.5. The feasibility of the heat pump systems at the concentration unit of the Solvay Voikkaa Plant was evaluated with Meszaros' study [67], which was produced for the concentration unit of Solvay Chemicals USA Longview. Based on these evaluations, mechanical vapor recompression and thermal vapor recompression are not feasible investments for the Solvay Voikkaa Plant due to the high investment costs and long pay back times.

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Optimization of the reflux flow of the distillation column

Table XXI Optimization of the reflux flow of the distillation column with the feed flow of 8 m^3/h in the 50 % cc-mode.

	Reflux flow to the distillation column, m^3/h				
	0.38	0.33	0.29	0.27	0.24
H_2O_2 residue, ppm	1	1	2	3	10
T_1, °C	43.9	44.2	44.0	44.2	44.6
T_2, °C	43.8	44.1	43.8	44.0	43.9
T_3, °C	43.5	43.8	43.6	43.6	43.6
ΔT_{1-2}, °C	0.1	0.1	0.2	0.2	0.7

Table XXII Optimization of the reflux flow of the distillation column with the feed flow of 10 m^3/h in the 50 % cc-mode.

	Reflux flow to the distillation column, m^3/h			
	0.37	0.33	0.30	0.27
H_2O_2 residue, ppm	2	3	10	25
T_1, °C	45.8	45.2	45.8	47.3
T_2, °C	45.7	44.8	44.8	44.8
T_3, °C	45.4	44.4	44.4	44.4
ΔT_{1-2}, °C	0.1	0.4	1.0	2.5

Table XXIII Optimization of the reflux flow of the distillation column with the feed flow of 12 m^3/h in the 50 % cc-mode.

	Reflux flow to the distillation column, m^3/h			
	0.45	0.40	0.35	0.30
H_2O_2 residue, ppm	2	4	25	75
T_1, °C	46.7	47.0	51.8	54.8
T_2, °C	46.2	46.0	46.2	47.3
T_3, °C	45.8	45.6	45.3	45.5
ΔT_{1-2}, °C	0.5	1.0	5.6	7.5

Table XXIV Optimization of the reflux flow of the distillation column with the feed flow of 14 m^3/h in the 50 % cc-mode.

	Reflux flow to the distillation column, m^3/h					
	0.5	0.47	0.45	0.43	0.41	0.40
H_2O_2 residue, ppm	2	5	2	30	150	30
T_1, °C	47.7	44.2	47.3	47.7	51.7	54.4
T_2, °C	47.2	42.3	46.8	42.7	43.1	47.9
T_3, °C	46.7	41.4	46.4	41.6	41.4	46.3
ΔT_{1-2}, °C	0.5	1.9	0.5	5.0	8.6	6.5

Table XXV Optimization of the reflux flow of the distillation column with the feed flow of 7 m^3/h in the 60 % cc-mode.

	Reflux flow to the distillation column, m^3/h				
	0.89	0.79	0.70	0.65	0.60
H_2O_2 residue, ppm	2	1	2	10	15
T_1, °C	47.3	47.1	46.9	51.8	55.7
T_2, °C	47.0	46.8	46.5	46.5	47.0
T_3, °C	46.5	46.4	46.1	45.8	45.8
ΔT_{1-2}, °C	0.3	0.3	0.4	5.3	8.7

Table XXVI Optimization of the reflux flow of the distillation column with the feed flow of 7.5 m^3/h in the 60 % cc-mode.

	Reflux flow to the distillation column, m^3/h			
Reflux flow, m^3/h	0.83	0.75	0.7	0.65
H_2O_2 residue, ppm	2	3	.-	25
T_1, °C	42.4	43.6	59.9	57.2
T_2, °C	41.5	42.1	42.6	42.8
T_3, °C	40.8	41.5	41.6	41.7
ΔT_{1-2}, °C	0.9	1.5	17.3	14.4

Table XXVII Optimization of the reflux flow of the distillation column with the feed flow of 9 m^3/h in the 60 % cc-mode.

	Reflux flow to the distillation column, m^3/h						
	0.96	0.92	0.86	0.82	0.76	0.72	0.71
H_2O_2 residue, ppm	3	1	2	3	15	40	40
T_1, °C	49.5	49.9	51.5	56.7	63.6	63.6	63.9
T_2, °C	48.8	48.8	48.7	48.5	63.0	48.7	48.9
T_3, °C	48.3	48.3	48.2	48.0	51.5	47.9	48.0
ΔT_{1-2}, °C	0.7	1.1	2.8	8.2	14.7	14.9	15.0

Table XXVIII Optimization of the reflux flow of the distillation column with the feed flow of 10 m^3/h in the 60 % cc-mode.

	Reflux flow to the distillation column, m^3/h				
	1.10	1.00	0.99	0.98	0.95
H_2O_2 residue, ppm	2	4	7	10	50
T_1, °C	48.0	52.1	51.1	55.7	61.9
T_2, °C	47.0	47.0	46.9	46.9	47.1
T_3, °C	46.3	46.2	46.2	46.2	46.4
ΔT_{1-2}, °C	1.0	5.1	4.2	8.8	14.8