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Intensified Downstream Processing in Propylene to Epichlorohydrin Process

TU Delft

Intensified Downstream Processing in Propylene to Epichlorohydrin Process

By

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This thesis is confidential and cannot be made public until April 25, 2023.

Preface

This thesis marks the beginning of the end of my journey at TU Delft. Almost two years I have spent here taught me more than I could have imagined, not only scientifically but also personally. No words can express my gratefulness for all knowledge and experience I have gained during these years. However, I believe that this dissertation is not my last contribution to the chemical industry research since process engineering has always been close to my heart. I have grown up in a city where a similar chemical plant was operating, and I remember how significantly my hometown has benefited from the presence of the plant and then severely suffered after it was shut down. This experience helped me realise how crucial research is in the engineering world, where adapting state-of-the-art technologies may prevent a situation like this from happening. I believed that industry could make people's lives easier and better throughout my whole life, and I would like to contribute to this goal as an engineer in the future.

Finally, I would like to thank my supervisor Prof.dr.ir.Tony Kiss for his remarkable support with his knowledge and experience and the time devoted to improving my work. Undoubtedly, his engagement enabled me to develop both as an engineer and a person.

Ł. Madej
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List of abbreviations

ACH- Allyl chloride
CDP-1-chloropropane-2,3-diol
CMP-1-chloro-3-methoxypropan-2-ol
DCP- Dichloropropene
DCPOL- Dichloropropanols
ECH- Epichlorohydrin
ELECNRTL- Elecrolyte NRTL property method
GTE- Glycerol to Epichlorohydrin
HE-Heavy Ends
HETP-Height Equal Theoretical Plate
HPPO- Hydrogen Peroxide to Propylene Oxide
LLE- Liquid-Liquid Equlibrium
MeOH- Methanol
NRTL-Non Random Two Liquids property model
LE-light ends
HP-Hydrogen Peroxide
TCP- Trichloropropane
TS-1- Titanium Silicate
PDH- Pitzer-Debye-Huckel fromula
UNIFAC- Universal Quasichemical Functional Group Activity Coefficients
VLE- Vapour-Liquid Equilibrium
B- Bottoms flowrate
D- Distillate flowrate
E- Reaction Activation Energy
F- Feed flowarte
G- Gibss Free Energy
H-Column Height
L-Liquid Flowrate
N-Number of stages
S- Sidestream
Q- Enthalpy of reaction
V- Vapour Flowrate
T- Temperature
a- NRTL binary parameter
b- NRTL binary parameter
c-concentration
k- reaction rate constant
r- recovery of component
p- pressure
q- mole fraction of liquid in the feed
x- component molar fraction in liquid phase
y- component molar fraction in vapour phase
z- molar fraction of component in feed
α- relative volatility
β- recovery of medium boiling component in distillate
γ- activity coefficient
ρ-density
µ- dynamic viscosity
τ- residence time

Abstract

The modern chemical industry faces many challenges, such as energy transition. However, energy transition alone will not provide enough improvements to the industry to maintain profitability and increase sustainability. To achieve these goals, chemical processes have to be appropriately optimised, and only the synergy of these two factors can improve existing processes.

Epichlorohydrin production is an important industrial process, but it suffers from several drawbacks such as high energy consumption, significant wastewater production, and low atom efficiency. This is caused by chlorohydrin-based technology, which requires operations in very diluted solutions. In this thesis, a novel chlorohydrin-free technology for ECH production was investigated. This approach could allow operation in more concentrated solutions, but this route is in the early development stage. One of the most crucial design parameters for this process is proper solvent selection. On the one hand methanol appears to be the most suitable compound for this purpose. On the other hand, some papers reported the separation system for this case to be infeasible due to several azeotropes present in the post-rection mixture. However, with proper constraints and understanding of components' azeotropic behaviour, a separation system, which enables obtaining high purity ECH, was created and applied to the production process.

To perform a comparison between HP route and chlorohydrin process an Aspen Plus simulation of both processes were created. For the hydrogen peroxide route with methanol as solvent a novel separation system which enables high purities of ECH were created. Furthermore, possibilities to optimise distillation in the given process were investigated because this unit operation requires significant expenses in terms of CAPEX and OPEX. A review of advanced distillation techniques concludes that Dividing Wall Column distillation is the most suitable technique for this purpose. This technology was then applied to replace two columns, which purifies the intermediate Allyl Chloride (ACH) from the process. Aspen Plus simulations of both processes with and without applied DWC distillation were created to evaluate the influence of these improvements. Moreover, to establish the impact of DWC distillation, an Aspen Plus model of this apparatus was created.

Simulation results indicate that this novel epoxidation reaction produces 98% less wastewater than the traditional process. Additionally, the novel approach offers a 10% higher yield and a smaller amount of by-products than the chlorohydrin process. Energy consumption per unit of ECH is also lower for the novel route. Application of DWC distillation led to 3.5% decrease in OPEX, while the CAPEX was smaller by almost 5%. These results indicate that applying a novel epoxidation route and DWC may benefit a given plant. However, more research needs to be performed to implement a novel process in the industry.

1. Introduction

1.1. Challenges of modern industry

One of the main challenges of global industry is shifting from old traditional processes towards new, more effective ones. These changes are not only imposed by laws such as the EU CO_2 emission quota but also by global market trends. Since prices of natural gas and other fossil fuels have recently achieved all-time high values, need for novel solutions for the industry has emerged. As the chemical industry consumes a significant amount of energy, it is essential to provide it with proper solutions to lower the emission of carbon dioxide and other by-products and improve the profitability and operability of chemical plants. Since chemical industry is very cautious when applying new processes and technologies and prefers using well-studied technologies, the difficulty of shifting processes towards better, novel solutions is even higher.

1.2. Epichlorohydrin as an important commodity

One of the most energy-hungry processes is epichlorohydrin production. This compound is used to produce many essential products such as foams, paints and rubbers. Furthermore, epoxy resins play an essential role in the industry due to their high resistance to corrosion [1]. The chemical structure of epichlorohydrin is shown on figure 1.

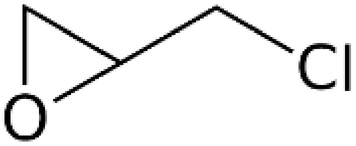


Figure 1. Chemical structure of ECH [2]

High energy consumption is not the only disadvantage of epichlorohydrin production. Besides this, the process suffers from several factors which have a massive impact on the economy and the overall profitability of manufacturing. One of them is high CO_2 emission, which is even more significant nowadays, when the cost of carbon dioxide emission in the European Union is at all-time high. It is predicted that the emission price will rise steadily in the future. Another drawback of epichlorohydrin manufacturing is the production of significant amounts of wastewater. It is estimated that, around 30-40 tonnes of wastewater is produced for every tonne of ECH. This waste stream is hard to treat, because it contains very diluted solution of inorganic salt [3] and residual amounts of highly reactive organic components such as ECH.

Figure 2. Changes in carbon dioxide prices in the EU in Eur/tonnes[4]

To tackle the disadvantages mentioned above, novel routes to produce ECH has been established, such as the GTE (Glycerol-to-epichlorohydrin) process [5], which did not significantly improve the process, because the amount of formed sewage has not decreased to the desired amount. Additionally, little effort has been put into optimising existing plants and investigating chlorohydrin-free processes, which can provide significant savings in wastewater production. Therefore a novel chlorohydrin-free process based on epoxidation with hydrogen peroxide was investigated to establish a novel route with significantly reduced wastewater production. Moreover, the epichlorohydrin production process includes a high number of distillation steps. Considering that distillation has very low energy efficiency and columns have high investment costs, it may be beneficial to optimise this part of the plant. The battery limits of the ECH plant are shown below.

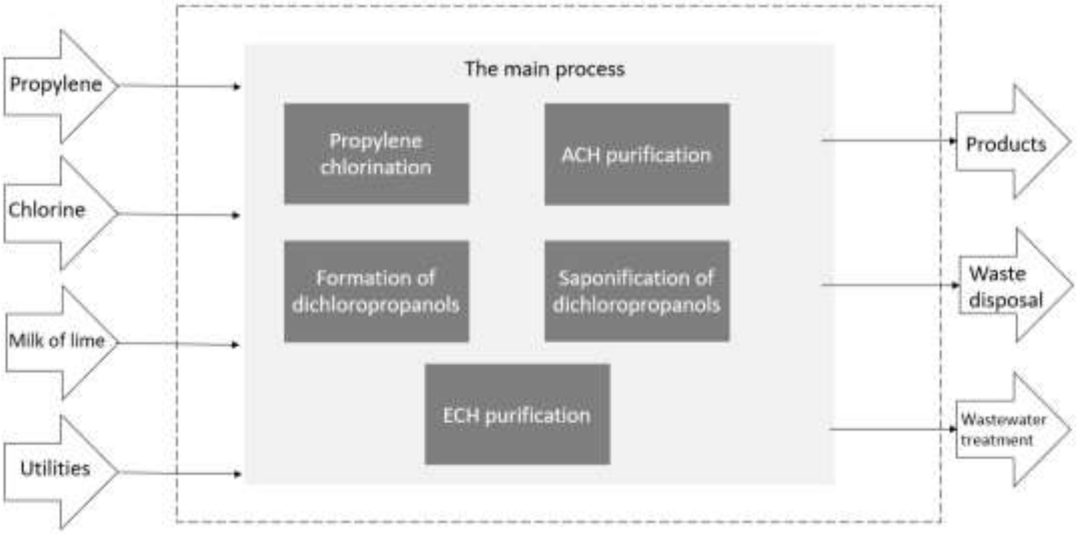


Figure 3. Battery limits for the ECH production

As shown on figure 3, optimisation of the existing plant has been conducted within the displayed boundaries.

After literature review, following research gaps were identified for ECH manufacturing:

- ECH manufacturing process produces significant amounts of wastewater, which is hard to treat. Currently used technologies (Glycerol-to-epichlorohydrin process and chlorohydrin process) do not offer significant field form improvement, but hydrogen peroxide route is believed to improve this process. Although several papers propose HP route as more efficient, sustainable and cheaper process to produce ECH, no direct comparison between HP process and chlorohydrin process has been reported
- Methanol is considered as suitable solvent for epoxidation reaction but separation of this component form post-reaction mixture is believed to be infeasible
- High energy consumption and high investment cost were reported in the section of plant used for ACH manufacturing, but no solution have been suggested

. This thesis aims to achieve following goals:

- Establish proper separation system for HP process with methanol as solvent
- Create comparison between the chlorohydrin and HP route of ECH to establish which method offers better parameters
- Apply most suitable advanced distillation technique to reduce a number of columns by at least one and reduce the energy demand and investment expenses of ECH plant by 5%.

In this report, a separation system for the HP process with methanol as solvent was created. Additionally, to optimise distillation in ACH section variety of advanced distillation techniques such as cyclic distillation, dividing wall column, Heat Integrated Distillation column and heat pump assisted distillation were studied to investigate the most suitable tool for process improvement. From the technologies mentioned above, only DWC could provide simultaneous savings in capital and operational expenses [6]. Therefore this technology was applied to the processes considered in this project. To establish the technological parameters of the process, an Aspen Plus simulation of both classic ECH process and HP process were made. Subsequently, DWC distillation was applied to both plants to investigate the usefulness of this technique to given processes. Results obtained indicate that HP based process is characterised by 98% lower wastewater production and 10% higher process yield in terms of propylene. DWC distillation allowed less than 5% savings in CAPEX for both cases, and OPEX was reduced by 3.5%. Finally, despite higher overall energy requirements for the HP process, the unit cost (cost of manufacturing 1 kg of ECH) was lower for this case, due to the higher yield of the process. Additionally, the unit profit (profit per 1 kg of ECH) was higher for the chlorohydrin-free route process, indicating that the novel route may replace the current process. Additionally, the novel technology can be partly retrofitted to the existing plants, by replacing the part of the plant responsible for ECH synthesis, while maintain the ACH unit from the old, chlorohydrin process.

2. Literature review

2.1. Technologies for ECH production

2.1.1. Traditional propylene-to-epichlorohydrin process

The first process for epichlorohydrin manufacturing was developed in 1947 by Shell [1]. It uses propylene and chlorine as raw materials. According to this approach, propylene is chlorinated in high temperatures (around 500 ºC) under relatively low pressures (1-2 bar) [1]. Under these conditions, chlorination equilibrium is shifted towards allyl chloride (ACH). However, side reactions also occur. It is essential to perform this reaction with excess propylene to prevent chlorine from entering the separation steps. All of the reactions are characterised by a free-radical mechanism [7]. Main occurring reactions are listed below [8].

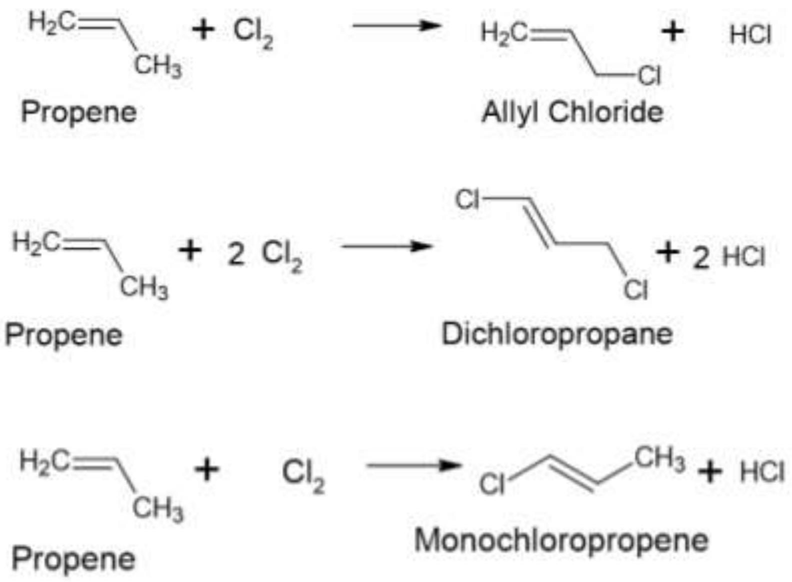


Figure 4. Main reactions occurring during propylene chlorination

Achieving a well-mixed mixture of chlorine and propylene is crucial to obtain satisfying yields of ACH since the areas with a high local chlorine concentration can lead to the production of more chlorinated compounds, such as dichloropropene [9]. The post-reaction mixture is then cooled and HCl is separated in the distillation column [10]. This process requires obtaining HCl as liquid distillate to prevent chlorination of propylene to chloropropane, which can occur in steel pipes catalysed by iron chloride [10]. Separated hydrogen chloride is subsequently absorbed in the water to produce hydrochloric acid, sold at concentrations dependent on the customer’s demands. In the next step, propylene is separated from the chlorinated hydrocarbons [11]. This separation occurs in a distillation column, with propylene as vapour distillate [12]. Pressure in this column is usually equal to 6 bars to increase the boiling point of components, which enables to use more cost-effective cooling medium, such as cooling water [13]. Once propylene is separated, raw ACH is removed from low and high boiling chlorinated hydrocarbons [12]. In the first column, the low boiling fractions are separated as distillate opposite to allyl chloride and high boiling components, which become the bottom stream. In the second distillation column, allyl chloride is obtained as distillate, while the high boiling fractions are obtained as a bottom stream [12]. PFD of ACH production is shown on Figure 5.

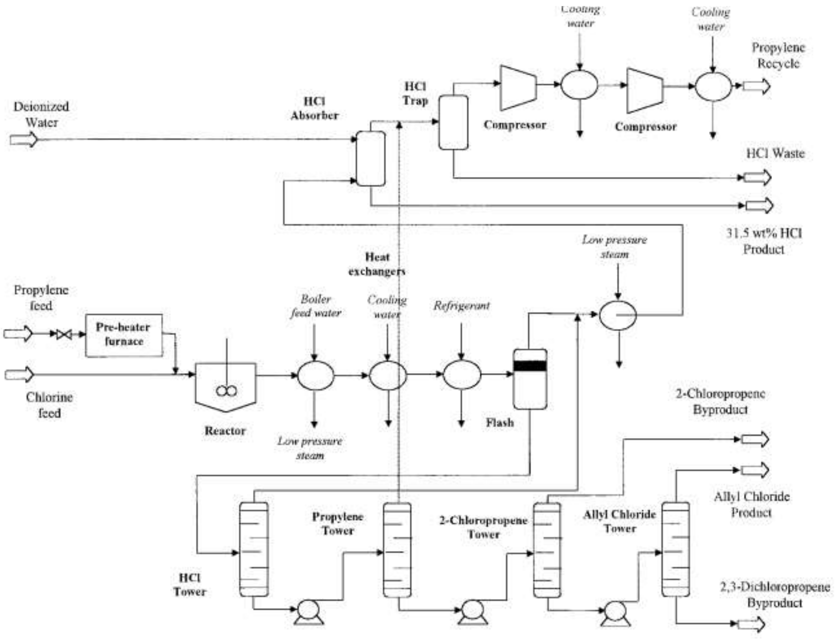


Figure 5. Process flow diagram of ACH plant [14]

In the next step, pure allyl chloride is then fed into a hydrochlorination reactor. ACH reacts with hypochlorous acid produced by stripping chlorine gas through the water inside this reactor. As a result of this reaction, two main products are formed: 1,2-dichloropropanol and 1,3-dichloropropanol with a ratio of 70:30, respectively [15]. The main by-product of this step is trichloropropane (TCP). TCP is highly undesired in the final product, as epichlorohydrin contaminated with TCP, which leads to a change of colour when mixed with sodium hydroxide, cannot be used for resins production [16]. Additionally, this reaction has to be performed in a very diluted system as dichloropropanols solubility in water does not exceed 4% [15]. Reactions occurring in the hydrochlorination reactor are shown below.

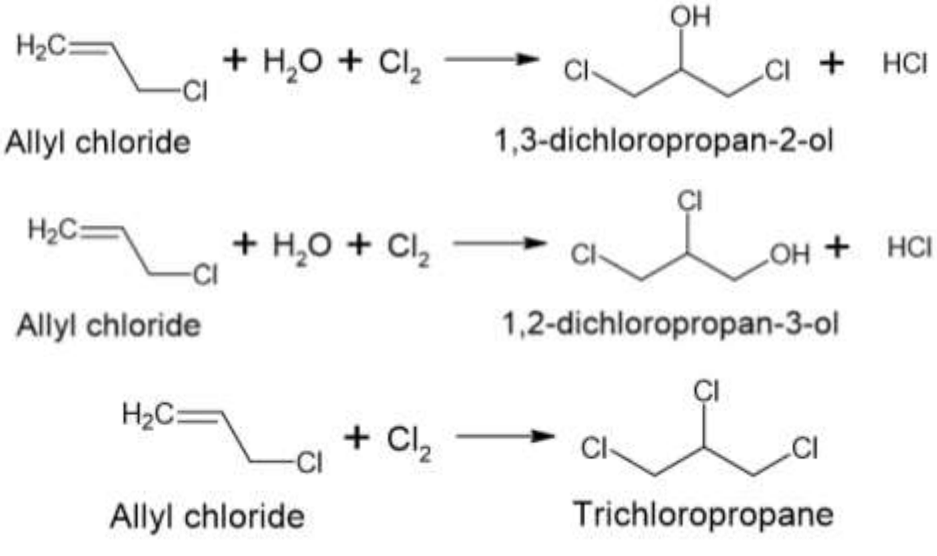


Figure 6. Reactions occurring in hydrochlorination reactor

This stream is then mixed with a slightly alkaline solution to remove residual chlorine [17]. An aqueous solution of dichloropropanols is then fed to a saponification reactor, modelled as PFR. Solution of dichloropropanols is saponified using either milk of lime or sodium hydroxide. However, the use of NaOH leads to slightly smaller production of wastewater, but is more challenging in terms of process control [18]. The yield of epichlorohydrin with respect to DCPOLs equals about 30% at the reactor outlet [18]. This mixture is then fed to the reactive stripping column, where medium pressure steam is provided to the bottom of the column [19]. Part of the saponification reaction is performed in the stripping column to remove epichlorohydrin from the aqueous environment to prevent side reactions [15]. The distillate from this column is obtained as a vapour stream, which is then condensed in the heat exchanger and subsequently, fed to the decanter where, phase splitting occurs. For the given mixture water phase is lighter than the organic phase and therefore separates as top layer [18]. The organic phase, which consists mainly of epichlorohydrin, is then sent for the further purification. The aqueous phase is fed to the stripping column as reflux [18]. Main reactions, as well as side reactions, are shown below.

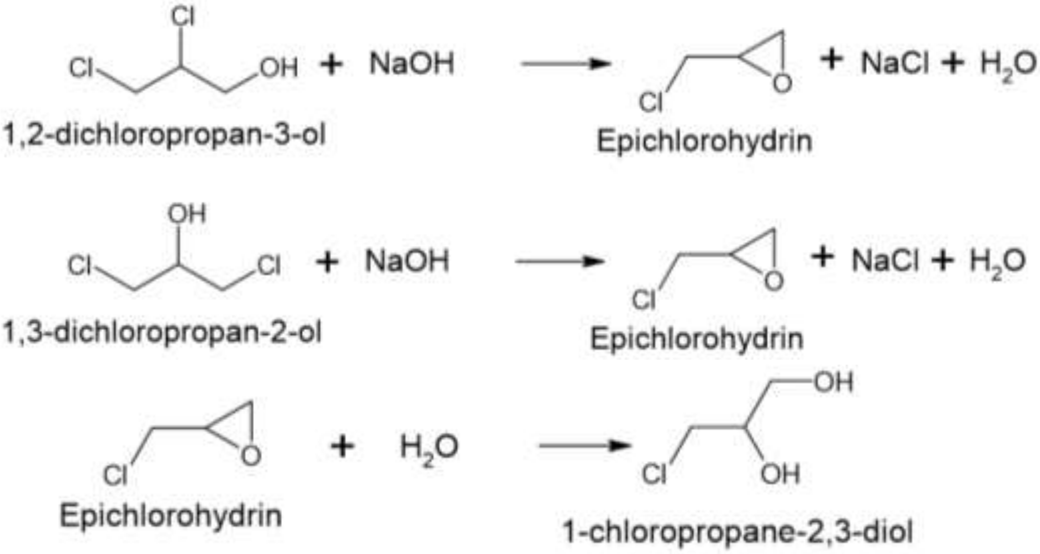
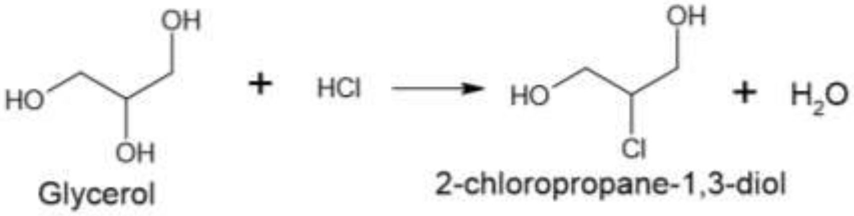


Figure 7. Reactions occurring saponification of dichloropropanols

Further purification of epichlorohydrin is performed in a system consisting of four distillation columns, where two of them are columns with vapour distillate condensed in the heat exchanger and then separated in a decanter [15]. Again, aqueous phase is reverted to the column as reflux while the other one is further purified. The final purity of ECH is 99,9% mass [19]. The most significant drawbacks of this technology are high energy consumption and a large amount of produced wastewater. Furthermore, sewage stream is hard to treat, because it is very diluted. Additionally, as this stream may contain residuals of organic components, it presents a possible threat to the wastewater treatment plant, due to the possibility of negative influence on microorganisms used for wastewater treatment [3]. Also, this process suffers from very low atom efficiency in terms of chlorine, because all the chlorine used to produce DCPs after saponification, reacts to form wastewater. Additionally, the stripping column consumes a significant amount of steam (about 16 tonnes/hour) [18].

2.1.2. Glycerol to epichlorohydrin process

This process was created by Solvay in 2011 [20] as reverse a to the traditional process of glycerol production. When glycerol prices have significantly dropped, as a result of mass biodiesel production, it became profitable to produce epichlorohydrin from glycerol [21]. In this technology, dichloropropanols are formed from glycerol and hydrogen chloride instead of propylene and chlorine. The first stage of this process consists of glycerol purification, because glycerol from biodiesel production is often contaminated with methanol and water. Distillation has to be performed under vacuum due to the high boiling point of glycerol [5]. The next step consists of glycerol chlorination using gaseous hydrogen chloride, this step requires a catalyst in the form of high boiling organic acid [22]. The reactions occurring during glycerol chlorination are listed below in figure 8.



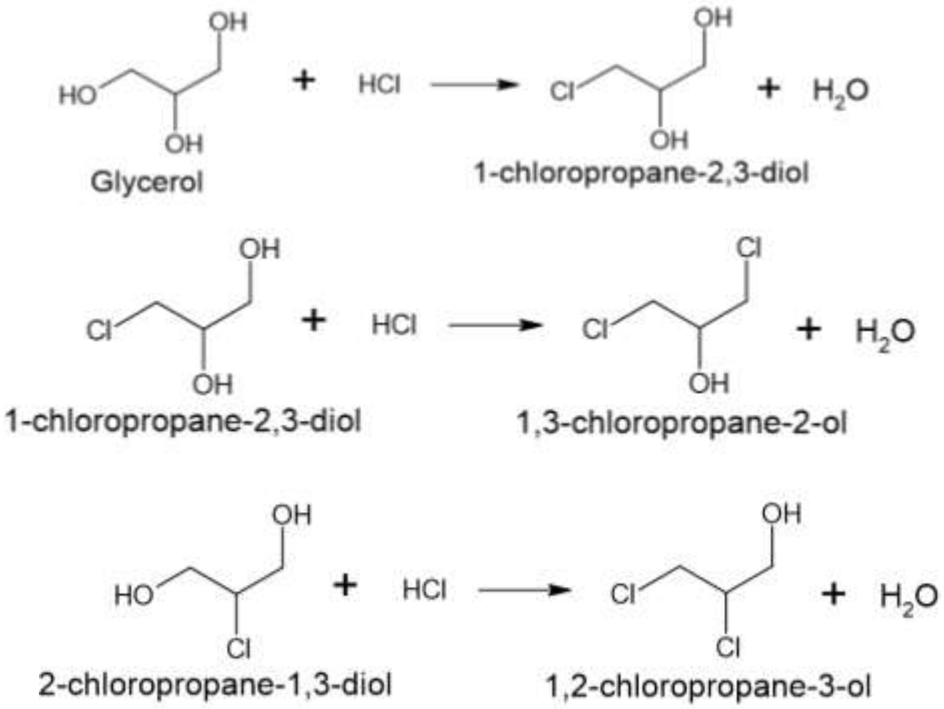


Figure 8. Reaction occurring during DCP formation in GTE process

These reactions yield a mixture of 1,3-dichlropropanol and 2,3-dichlorpropanol in a ratio of 30-50:1 [23], which is beneficial for the saponification reaction, because 1,3- isomer is more reactive [23]. On the other hand, the overall selectivity of chlorination reaction is low [22]. Furthermore, separation of dichloropropanols from monochlorohydrins and glycerol is challenging due to the high boiling points of components and these separations have to be performed under a vacuum [5]. The following steps are similar to the traditional ECH production process, where DCPs are saponified using sodium hydroxide or milk of lime.

Overall this technology exhibits several disadvantages similar to the previously described technology, such as high energy demand and a significant amount of sewage [1]. However, the main improvement is the replacement of propylene, with possibly cheaper and more renewable glycerol. On the other hand, increasing demand for edible fats significantly limits the amount of land used to obtain non-edible ones, which could limit the accessibility of bio-based glycerol [24]. Furthermore, the profitability of such plant strongly depends on glycerol prices, which are dependent on harvest efficiency. This parameter is limited by weather conditions, which become more unpredictable and potentially put the profitability of the plant at risk. As this approach did not solve the plant's most important issues, a new path for sustainable epichlorohydrin has been searched.

2.1.3. Hydrogen peroxide route

One of the most important, recent breakthroughs in olefin processing was the development of catalytic oxidation of the double carbon-carbon bond. This was first applied to the production of propylene oxide in the HPPO process [25]. This approach has several advantages over the traditional chlorohydrin route used to produce epoxides. Atom efficiency of this process can be significantly improved, as no intermediate chlorohydrin is required to make a final product [26]. The reaction is performed using solid titanium silicate (TS-1) as catalyst and hydrogen peroxide as oxidation agent [27]. Furthermore, the operating conditions of the epoxidation reactor are mild: temperature equals 60 ºC and pressure of 3 bar. Increased pressure is imposed for safety reasons, because hydrogen peroxide can decompose, forming oxygen that could form an explosive mixture with ACH or methanol [27]. The main drawback of this approach is the requirement of using solvent, which implies a need for recovery and recycling of solvent, which may be expensive. The possible solvents for this process are: methanol, ethanol, propanol, isopropanol and acetone. The reaction mechanism is relatively complex, as shown on Figure 9.

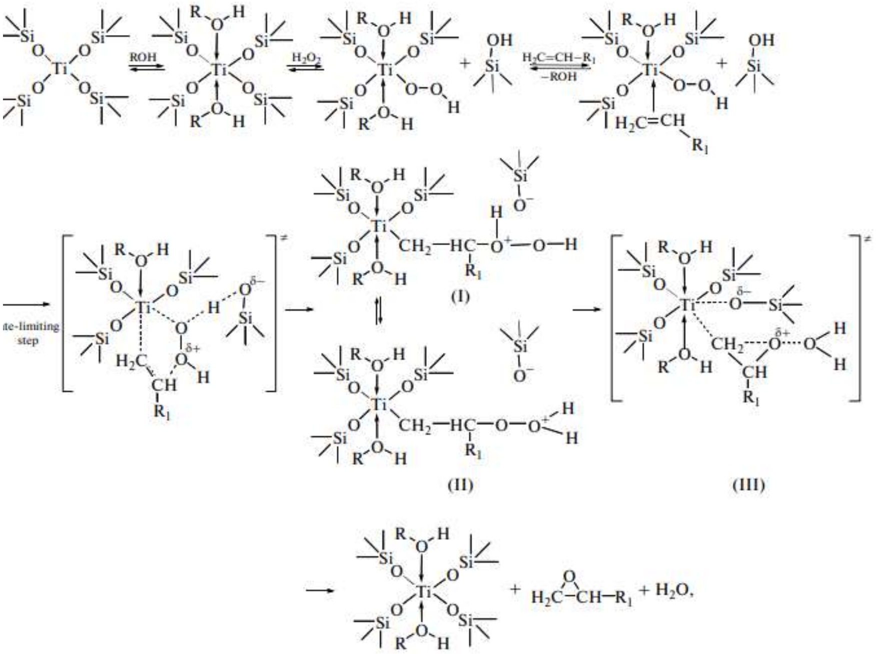
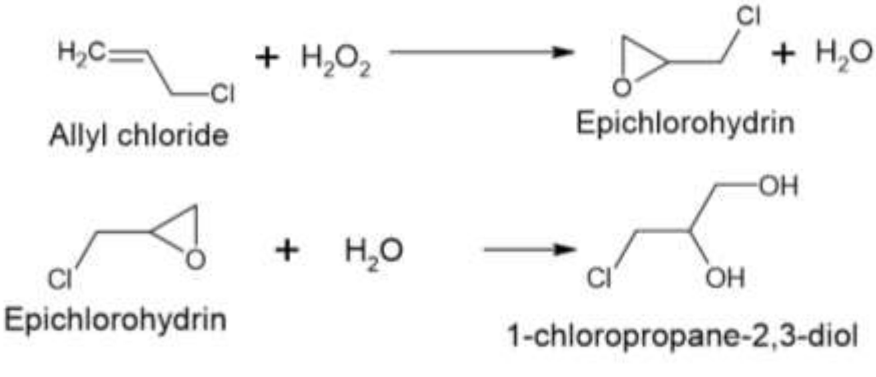


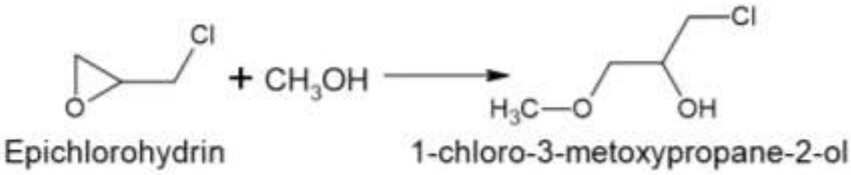
Figure 9. Mechanism of olefin epoxidation [28]

As shown on Figure 9, solvent not only homogenises the reaction mixture, because of low ACH solubility in water, but also takes part in the reaction mechanism, which implies that choice of the proper compound is highly influential on reaction yield and selectivity [27]. A longer carbon chain in alcohol molecules leads to a more difficult approach of allyl chloride molecules toward the catalyst site. Furthermore, the use of higher alcohols may lead to an increased rate of side reactions and therefore lower the overall yield of the process [27]. Some papers suggested that isopropanol may be a more suitable solvent due to its less complicated separation system and lower toxicity [29]. However, this statement is not relevant in the ECH process, because the most dangerous compound present in the plant is epichlorohydrin. Therefore, the safety measures will be limited by this compound’s toxicity and will not be influenced by less toxic solvent like methanol. Additionally, the separation system can be significantly simplified by using proper constraints, preventing remixing of separated components. Therefore methanol was chosen as the most suitable solvent for the process.

HP route consists of unit operations similar to the classical process, because it also uses ACH as an intermediate. After purification, this compound is mixed with methanol and hydrogen peroxide before entering the reactor. The ratio of allyl chloride to hydrogen peroxide should be equal to 2.77:1, while the amount of solvent should not exceed 65% mass [28].

The reactor model can be described as a fixed bed plug flow reactor. Reactions occurring on the catalyst surface are listed below [28].





$$2H_2O_2 \rightarrow 2H_2O + O_2.$$

Figure 10. Reactions occurring during ACH epoxidation with hydrogen peroxide

Epichlorohydrin is produced in first reaction on figure 10. and consumed in the second and third reaction. The primary by-products of these reactions are: 1-chloropropane-2,3-diol (CPD, reaction 2) and 1-chloro-3-methoxypropan-2-ol (CMP, reaction 3) [30], which are products of epichlorohydrin decomposition caused by water and methanol respectively. Hydrogen peroxides decompose to form water and oxygen (reaction 4). The expressions for reaction rate are shown below.

$$r_1 = \frac{k_1 b_{HP} C_{HP} C_{AC}}{1 + b_{HP} C_{HP} + b_{ECH} C_{ECH}} \tag{1}$$

$$r_2 = \frac{k_2 b_{ECH} C_{ECH} C_{W}}{1 + b_{HP} C_{HP} + b_{ECH} C_{ECH}} \tag{2}$$

$$r_3 = \frac{k_2 b_{ECH} C_{ECH} C_{M}}{1 + b_{HP} C_{HP} + b_{ECH} C_{ECH}} \tag{3}$$

$$r_4 = \frac{k_4 b_{HP} C_{HP}}{1 + b_{HP} C_{HP} + b_{ECH} C_{ECH}} \tag{4}$$

The reactions follow Langmuir-Hinshelwood [28] kinetics consistent with the mechanism shown on figure 9. Assumptions for the given scenario are following [28]:

1) The catalyst surface is uniform
2) The adsorption of initial olefin and water can be negligible
3) The target reaction takes place between hydrogen peroxide adsorbed on the catalyst surface and dissolved olefin
4) The rate-limiting step is the surface reaction
5) The side reactions occur on the catalyst surface.

As shown in equations 2 and 3, the reaction rates of side reactions 2 and 3 strongly depend on concentrations of water and methanol, which implies that a separation system should be constructed to remove these components first. Since the methanol concentration in the mixture is significantly higher than water, this compound should be removed first. However, compositions of the post-reaction mixture impose certain limitations on the separation system due to the presence of several azeotropes. All azeotropes present in the mixture are listed below, along with boiling points.

Tab. 1. Azeotropes present in post-reaction mixture and their properties [31]

Azeotrope	**Composition (wt%)**	**Boiling point [^oC]**	**Azeotrope type**
AC/MeOH	(87.7/12.3)	39.7	Homogenous
AC/W	(97.9/2.1)	43.4	Heterogenous
ECH/W	(72.0/28.0)	89.7	Heterogenous

The relatively low boiling point of AC/MeOH azeotrope and constraints mentioned above indicates that separation of allyl chloride and methanol should be performed as the first separation. This could increase the yield of epichlorohydrin and reduce the costs of further separation as the component with the biggest concentration will be removed first [32]. The remaining mixture consists of ECH, water, CDP and CMP and residual amount of methanol. Epichlorohydrin/water azeotrope is heterogeneous, meaning phase splitting will occur for given azeotropic composition as ECH solubility in water is limited [33]. This fact can be used to perform the purification of ECH. After phase splitting occurs, the aqueous phase can be sent to the stripper to remove and recycle remaining ECH, while the water obtained as the bottom stream can be sent for further treatment to the wastewater treatment plant. The organic phase, which consists mainly of epichlorohydrin, CDP and CMP is also sent to the stripping column to remove remaining moisture. The distillate from both columns is purely vapour and consists of ECH/W azeotrope. This stream is then condensed in the heat exchanger and sent back to the decanter. The bottom stream from the organics column is then sent to distillation column to separate ECH from CDP and CMP. Epichlorohydrin is obtained as distillate, while the high boiling organic components are obtained as a bottom stream. Performing this separation as the last step has several advantages: presence of CDP and CMP until the end of separation shifts the equilibrium of by-product formation towards substrates. Additionally, obtaining ECH as a top product from final column increases its quality. The layout of the separation system is shown below:

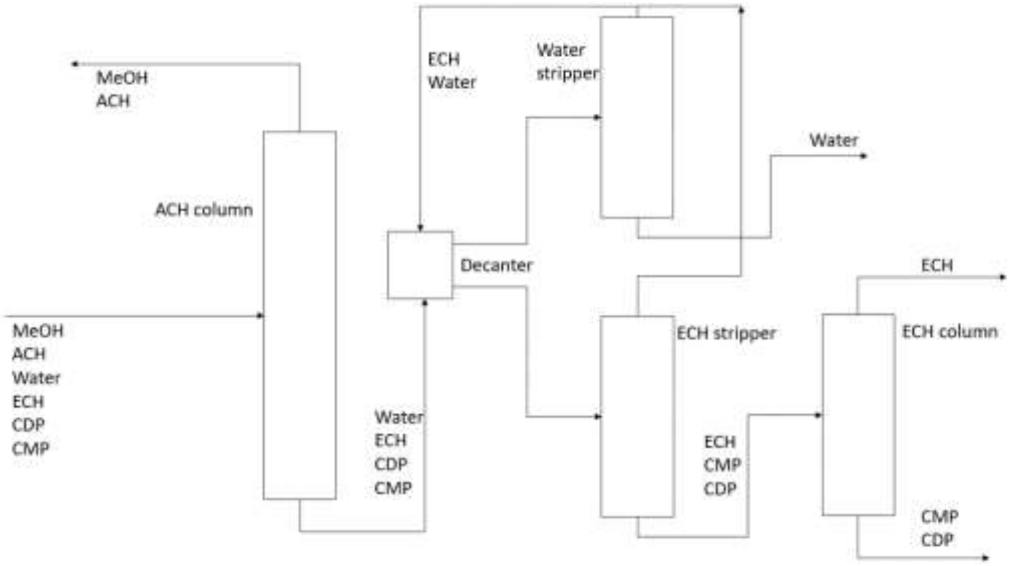


Figure 10. Layout of ECH separation system for HP route

Despite having several advantages over both GTE and traditional processes, it has not been applied in the industry. One of the reasons may be safety concerns. ACH and MeOH are reactive compound, which can violently decompose when exposed to oxygen [34]. As hydrogen peroxide undergo decomposition in this process, it creates molecules of oxygen which may cause an explosion. However, this difficulty can be overcome by introducing gaseous nitrogen to the top of allyl chloride column, where oxygen concentration can build up, but dilution by inert gas can prevent an explosive mixture from forming. Another possible reason for not introducing this process is high plant investment cost. Despite relatively cheap catalyst, the equipment cost for such a plant can be high, especially in the allyl chloride section, as some parts operate in high temperatures [1]. Furthermore, the purification of allyl chloride requires two distillation columns with significant height [12][35]. Therefore this process can benefit from implementing advanced distillation techniques to purify ACH, because application of a novel distillation technique can lead to decrease in both CAPEX and OPEX.

2.1.4. Comparison between technologies

A quantitative shortcut comparison was performed to compare the technologies described above. Results are listed in table 2.

Tab. 2. Quantitative comparison between technologies

	Traditional process	**GTE process**	**Oxidation by HP with methanol solvent**	**Oxidation by HP with isopropanol solvent**
Catalyst	None	Organic acid (i.e malonic acid)	TS-1	TS-1
Conversion (in terms of propylene)	73 %	~80%*	**Up to 83%**	Up to 83%
Selectivity	78%	Less than 60%*	**~82%**	~81%
By-products	Trichloropropane, dichloropropane, monochloropropane	Alpha-monochlorohydrin, Beta-monochlorochydrin, Ester of organic acids and monochlorohydrins	1-chloro-3-methoxypropan-2-ol (CMP), 1-chloropropane-2,3-diol (CPD)	Acetone, 1-chloropropane-2,3-diol (CPD)
Production of by-products [tonne per tonne of ECH]	0.370	~0.320	**0.231**	~0.240
By-products handling	Incineration	Incineration	Incineration	Incineration
Amount of wastewater in tones/tone of ECH	30-40	20-30	**1-5**	1-5
Solvent loss during reaction	N/A	N/A	**No**	Solvent reacts with HP and forms by-product
Energy demand [MW]	55-52	51-48	**42-50**	40-48

*conversion calculated with respect to glycerol

The table above shows that, most energy is consumed in the traditional process, which is the most widely used method to produce ECH worldwide. Additionally, it can be seen that the hydrogen peroxide process can offer savings in terms of energy usage and produced sewage. GTE process does not show a significant field for improvement, because distillation used in this technology is seriously constrained by high boiling points of used components. The hydrogen peroxide process with isopropanol as a solvent will not be considered in this report as it exhibits serious drawbacks such as losses of hydrogen peroxide and acetone production in the reaction mixture, because acetone can be oxidised to highly reactive organic peroxide, which could pose serious threat for safe plant operation. Therefore this report will focus on possible distillation optimisation for traditional process and HP process with methanol as solvent.

2.2. Distillation

Distillation is a separation technique, in which added and removed heat acts as a separation agent [32]. The separation is based on differences in components' volatilities, which can also be viewed as boiling points. In the industry, distillation plays a crucial role in many areas of chemical engineering. This process is applied to separate various mixtures such as crude oil, aromatics and alcohols [32]. Distillation enables high purities of separated components which is very important for the chemical industry since most pure components have a purity above 99% wt. As distillation consumes about 3% of the energy produced worldwide [36], the urge for energy optimisation in this field is significant. The need for distillation improvement leads to the creation of novel separation techniques that can improve specific parameters of the distillation process.

2.2.1. Identification of optimisation objectives

Purification of Intermediate ACH consists of many distillation steps, which consume significant amount of energy and require a high investment cost due to the considerable height of used columns. The sequence of distillation columns is used to obtain desired ACH purity. The first column is used to separate liquid hydrogen chloride from the hydrocarbons. This apparatus operates under very low temperatures to liquefy HCl to prevent by-product formation. This constraint can be overcome by selecting a column made of nickel instead of steel; however, this is not economically feasible because of the high cost of this metal [10]. The next column, used to separate unreacted propylene, operates under elevated pressure (about 6 bar) [12]. However, this column's dimensions are significantly smaller compared to the two remaining columns. The third column (Light end column) separates chlorinated components with lower boiling points from allyl chloride and high boiling chlorinated components. This column has a significant height (about 45 meters) [12]. The last column in this sequence is called heavy ends column, because it separates ACH from highly chlorinated components with higher boiling points. This column has a smaller height than LE columns but, it’s dimensions are still higher than propylene column. Therefore, LE and HE columns were chosen as most suitable for optimisation. Additionally they are not limited by technological constraints and are characterised by high investment costs. Columns selected for optimisation are displayed on the graph below

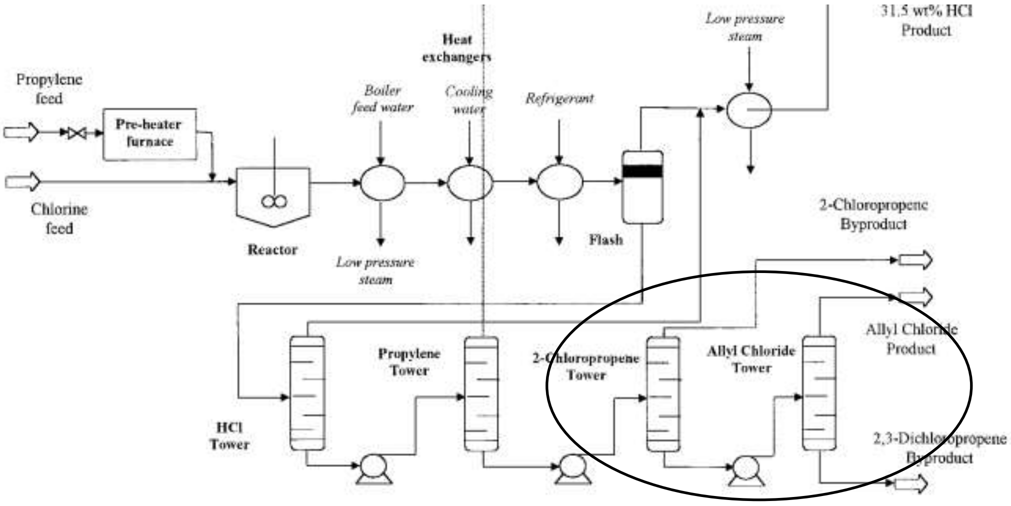


Figure 11.Columns chosen for the optimisation [14]

Columns used for the ECH purification were excluded from the considerations, due to the presence of heterogenous ECH/water azeotrope seriously limits the possibility of applying advanced distillation technologies. The optimisation goal is to simultaneously reduce the investment and operational cost of separation in given columns, while maintaining the purity of allyl chloride equal to 99.8% mass. Following advanced distillation techniques were investigated as possible tools for optimisation.

2.2.2. Advanced distillation techniques

2.2.2.1. Heat pump assisted distillation

In a classic distillation column, high-quality heat is provided to the reboiler of the distillation column, while in the condenser similar amount of heat is removed however, the energy quality significantly decreases [6]. To tackle this disadvantage, heat pump assisted distillation can be applied. This technology uses a similar working principle as heat pumps used for household heating. Heat pumps enable heat flow from areas with lower temperatures to regions characterised by higher temperatures. It may seem that this is against the second law of thermodynamics. However, closer investigation shows that this fundamental law has not been violated. In the distillation column, heat pump can be used for the low energy quality in the condenser to drive the column's reboiler [6]. Various techniques of vapour compression can be used to achieve this goal [37]. Following technologies can be considered for this task: vapour compression, mechanical vapour recompression and thermal vapour recompression [38].

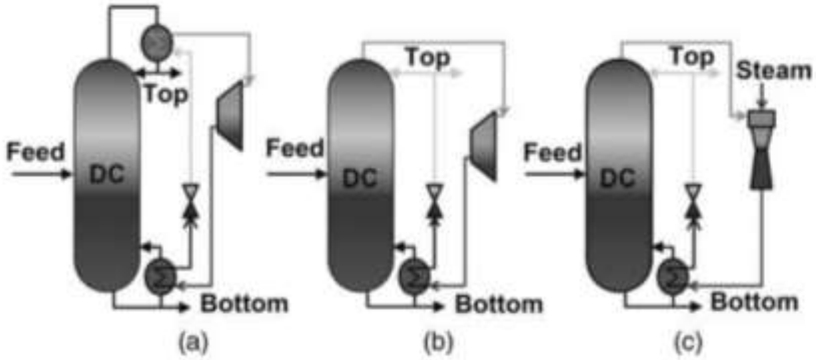


Figure 12. Different types of heat pump assisted distillation (a) vapour compression, (b) mechanical vapour recompression, (c) thermal vapour recompression [6]

First technique uses pressurisation and depressurisation of heat transfer medium, which flows in the closed loop. Fluid is evaporated in the condenser and then compressed to obtain a higher temperature. This high-temperature medium is then fed to a reboiler to perform evaporation. Next, the fluid is decompressed to decrease the temperature and liquefy the heat transfer medium. The vapour compression technique has been already proven on an industrial scale[6]. Mechanical vapour recompression and thermal recompression have similar working principles, but in this case, vapour distillate is used as heat transfer medium. In mechanical vapour recompression, compressor is used to increase the vapour temperature, while for thermal recompression technique, steam is used as the heating medium. After depressurisation, part of the liquid distillate is reverted to column as reflux, while the rest is obtained as distillate. These technologies can provide savings in terms of OPEX. However, this technology does not influence the amount of columns required for separations and their dimensions.

2.2.2.2. Heat integrated distillation column

Heat integrated distillation column is a most radical approach to heat pump assisted distillation, since instead of using a single heat source and heat sink, the whole stripping section is used as a heat source and rectifying section is considered as a heat sink [6]. This setup can offer significant savings in energy consumption and provide additional degrees of freedom, leading to the maximisation of energy savings. Additionally, internal heat integration can lead to a further increase in energy efficiency of the entire process [6].

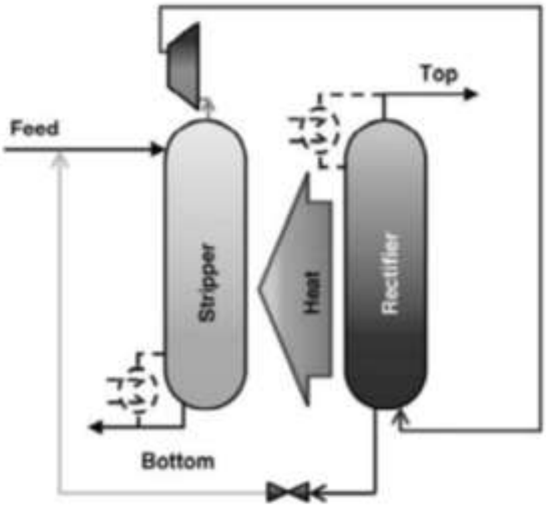


Figure 13. Scheme of heat integrated distillation column [6]

Despite offering significant improvements in energy consumption, this technique has not been implemented on industrial scale [38]. Moreover, this technique gives the best result when the difference in boiling points of components is within 25 ºC, which is not the case for the HE column. Additionally, this technology also does not provide a reduction in size and amount of distillation column used for the separation.

2.2.2.3. Cyclic distillation

Cyclic distillation is a novel technology, characterised by separation of vapour and liquid flow inside the distillation column. In a typical distillation process, vapour and liquid flow continuously throughout the column, with mass transfer occurring on trays or on packing. In this configuration, the value of Murphree tray efficiency is significantly lower than 100%, which indicates that higher number of trays have to be used compared to the ideal situation. To overcome this downside, vapour and liquid flow can be separated to increase the tray efficiency, leading to development of cyclic distillation. This technology can cause a reduction in column dimensions due to increased tray efficiency. As mentioned above operation of this column is periodical however, it can be considered quasi-continuous process. The operating scheme of cyclic distillation column is displayed below.

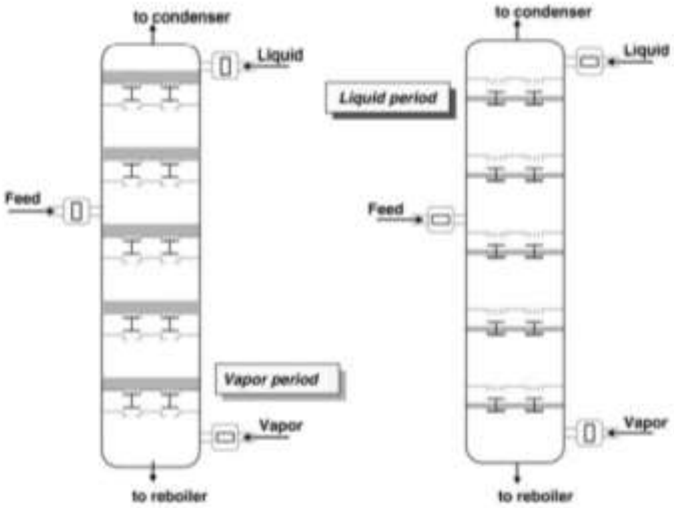


Figure 14. Vapour and liquid period in cyclic distillation [6]

The column’s periodic operation aims to maximise the driving force in a distillation column and minimise mixing liquids with different compositions [37]. Operation of this apparatus consists of two phases. In vapour flow phase, vapour flows through the column, while liquid remains stagnant on the trays, this phase usually takes up to 120 s, while the liquid period is generally shorter (about a few seconds). Due to maximised driving force, this enhanced distillation process can offer significant savings in column height. However, this technology alone cannot be applied to reduce the number of columns required for the separation.

2.2.2.4. Dividing wall column distillation

Separation of a ternary mixture is usually performed in a direct (lightest component is removed first) or indirect (heaviest component is removed first) system of two distillation columns [39]. Classical techniques have several disadvantages: very low energy efficiency due to remixing of components and high investment costs due to higher number of columns required for separation [40]. These difficulties can be overcome using thermally coupled distillation columns (Petlyuk column) or dividing wall column distillation columns. Petlyuk introduced a prefractionator to perform a split between the heaviest and lightest components where the medium boiling compound is distributed between the top and bottom product of the prefractionator. These streams are then fed to the main column. The top section of this column operates under specific conditions to separate the lightest and medium components. In contrast, the bottom of main column performs split between the heaviest and medium boiling components [41]. In this setup component with the lowest boiling point is obtained as distillate, compound with the highest boiling point is obtained as bottom stream and medium boiling component is obtained as side stream from main distillation column.
The direct and indirect sequence and Petlyuk arrangement are shown on figure 16.

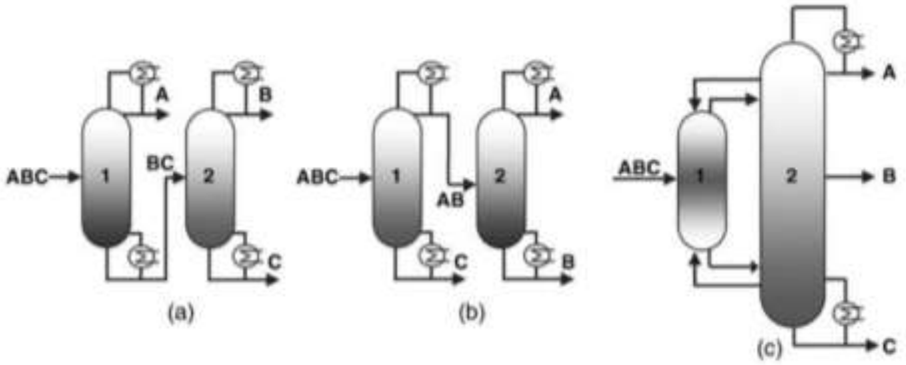


Figure 15. Direct (a), indirect sequence (b) and Petlyuk configuration(c) [6]

Since the prefractionator does not require any reboiler or condenser, because it is thermally coupled with the main column Petlyuk arrangement can offer significant energy savings. However, this approach also presents several disadvantages, such as difficulties to perform appropriate vapour and liquid splits between main column and prefractionator and bidirectional vapour flow [42]. These issues were partly solved by incorporating the prefractionator into the the main shell, which led to Dividing Wall Column distillation. In this scenario, higher side product purity can be obtained, which enables industrial application of DWC [43]. Structure of the DWC column is shown on figure 17.

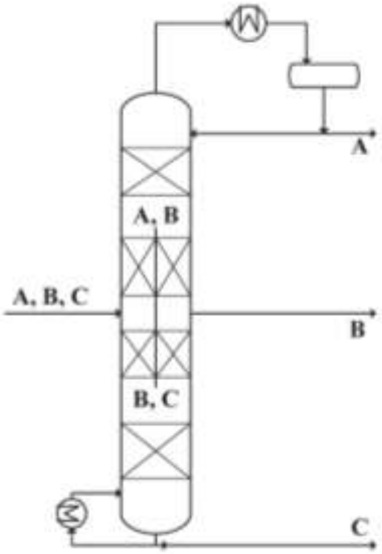


Figure 16. Dividing wall column [44]

First industrial DWC was applied by BASF, who remains the leader in this field as almost half of patents related to DWC were issued by BASF [45]. However, not every direct or indirect system can be converted to dividing wall column distillation. If the boiling points of components are too close, separation by DWC may not be efficient enough. Furthermore, operating pressure in both columns should be similar as it is impossible to achieve pressure difference between the prefractionator and the main column in the DWC setup.

Overall, DWC presents possibilities attractive to industrial applications and therefore becomes widely used in the industry. BASF was a pioneer in applying thermally coupled distillation columns. Thus, most of the currently operating DWC distillation columns operate at its site at Ludwigshafen, Germany; columns operating at this location have diameters varying from 0.4 to 4 m [46]. The biggest reported industrial DWC is located at Sasol's South African site, with a diameter of 5.2 m and height equal to 107 m [46].

2.3. Selection of the most suitable distillation technology

The comparison between possible benefits of each technology are shown in table 3.

Tab. 3. Comparison between improvements offered by each technique

	Energy requirements reduction	Column dimensions reduction	Reduction in number of columns
Heat pump assisted distillation	Yes	No	No
Heat Integrated Distillation column	Yes	No	No
Cyclic distillation	Yes	Yes	No
Dividing wall column	**Yes**	**Yes**	**Yes**

The optimisation objective is to reduce the number of columns, energy requirements and investment cost for the distillation process, which suggests that only DWC offers possibilities to accomplish these two goals simultaneously. Furthermore, this way of optimisation is also recommended by the algorithm described by Kiss [6]. Another factor, which promotes dividing wall column as the most suitable technology, is that differences between boiling points of components are higher than 20 ºC, making it possible to perform the separation in one column. Additionally, operating pressure in both LE and HE columns are similar (1.9 and 1.19 bar, respectively), favouring DWC as the most suitable technology. The design and simulation procedure for the DWC column is described in detail in the next chapter.

2.4. Dividing Wall Column design and simulation

The dividing wall column design is more complex than regular distillation due to additional degrees of freedom [6]. Besides degrees of freedom typical for every distillation column, such as distillate flowrate (D), bottoms flowrate (B), sidestream (S), boil-up ratio (V/B) and reflux ratio (R=L/D), the DWC column has an extra degree of freedom which arises from presence of wall inside the column: liquid split r_L. Vapour split is not usually considered as a control variable, because it is determined by the wall placement, which cannot be changed during column operation. This is caused by the fact that the usually dividing wall is welded to the column walls [47]. One of the best tools for dividing wall column design is the V_{min} diagram. This method enables fast estimation of possible energy savings and provides a valuable analysis of parameters for DWC simulation in simulation environments such as CHEMCAD and Aspen Plus. V_{min} graph plots vapour flow above the feed divided by feed flowrate (V/F) versus product flowrate divided by feed flowrate (D/F) [6]. These parameters can be obtained using simple simulations in Aspen Plus by simulating each split for the ternary mixture (A, B, C, where A is the lightest, C heaviest and B is medium boiling components). The vapour flowrate above the feed stage can be directly retrieved from Aspen Plus, as well as the distillate flowrate. An example of V_{min} diagram with marked characteristic points is shown on figure 18:

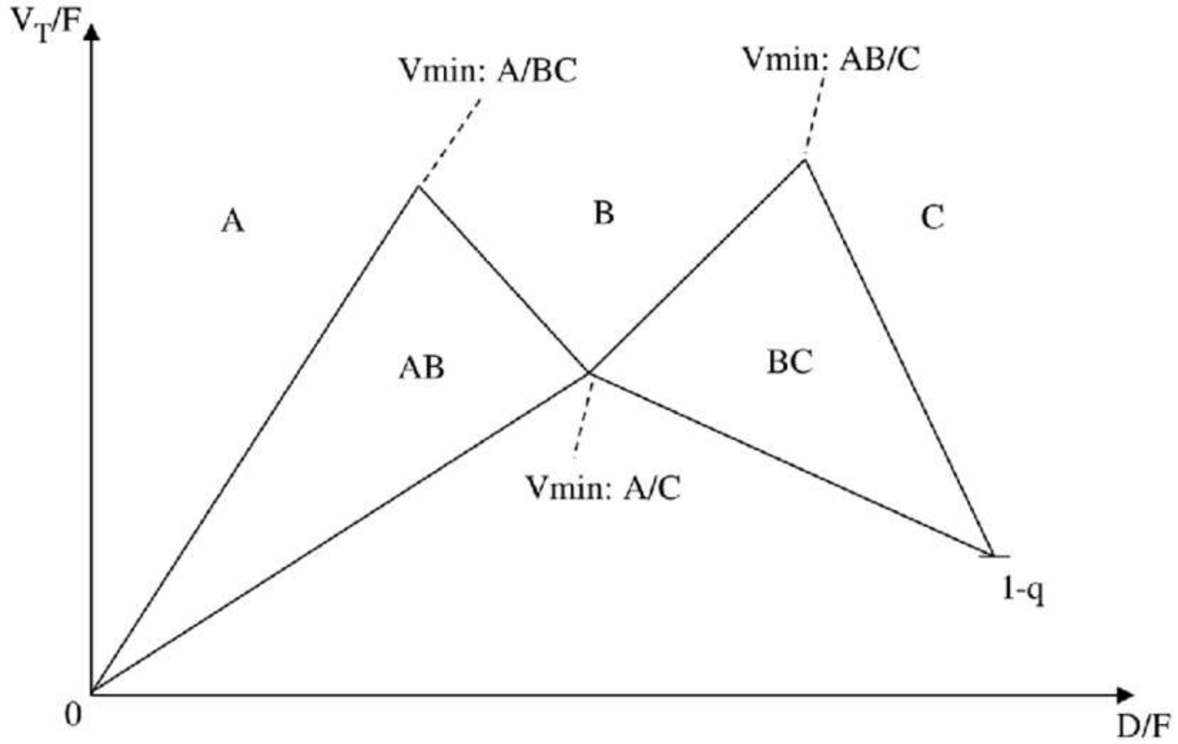


Figure 17. V_{min} diagram [48]

The total energy requirement for the DWC column is the amount of energy required to perform the most difficult separation [49]. The prefractionator of DWC column operates under conditions required to perform the easiest split (separation of heaviest and lightest component, P_{AC} split). The top of the column separates the lightest component from medium boiling one (P_{AB} split) and at the bottom of the column P_{BC} split is performed. As mentioned above, this graph is created for a situation represented by an infinite number of stages in case of every separation. However, the number of stages can be assumed as $N=4N_{min}$, where N_{min} is a number of stages calculated using the Fenske equation [50]. Another way to establish a V_{min} diagram is by solving the Underwood's equation for given splits. This method does not require simulation software, but since it is based on a constant relative volatility assumption, it is less accurate than a simulation-based one [51].

Despite becoming a useful industrial separation technique, commercial simulation software such as ChemCAD and Aspen Plus does not involve any, even simple DWC model. However, DWC can be simulated using 1 to 4 standard columns models [43]. For Aspen Plus, the most suitable rigorous column model for this task is a RadFrac model and for ChemCAD, it is a Tower model. As in this report, Aspen Plus was used to simulate the operation of Dividing Wall Column distillation, only use of RadFrac model will be discussed. The most suitable model that gives maximum flexibility and provides the best reflection of actual situation is a four-column model [44]. One column can act as one part of the DWC column, as shown on figure 19.

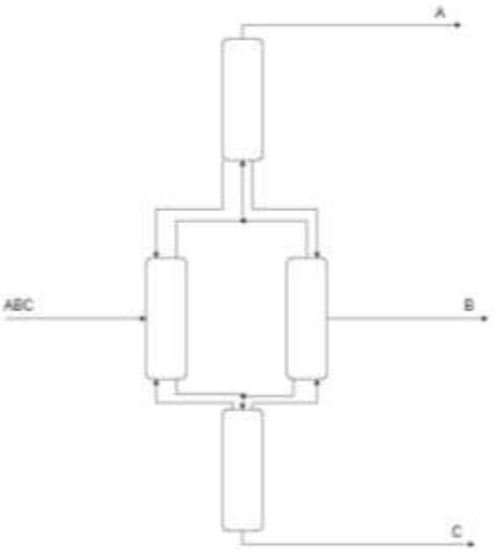


Figure 18. Four columns setup for DWC simulation [45]

To initialise this setup, every column has to be first run as a standalone unit using the internal flowrates calculated from the V_{min} diagram. The temperature of liquid streams has to be set to boiling point and vapour streams' temperature has to be set to dew point at given pressure [44]. The streams composition can be established by the V_{min} diagram method or other procedures such as the Triantafyllou&Smith methodology. This approach is based on the Fenske-Underwood-Gilliland-Kirkbride method, assuming constant molar flowrates and relative volatilities. This approach uses three columns instead of four and applies both shortcut (DSTWU model in Aspen) and rigorous (RADFRAC) distillation models available in commercial software, which do not require extensive iterative calculations[52]. Sotudeh&Shahraki also proposed a three-column model, but this approach is based only on Underwood's equation. In the first step, the internal flowrates are calculated in the same manner as in V_{min} methodology, while in the second step the number of stages is computed using the Underwood equation for each section of DWC [51]. Additionally, modifications of the methods mentioned above have been described in literature as possible tools for DWC design [52]. For the purpose of this thesis V_{min} diagram was chosen as most suitable method for the DWC design as it can provide accurate data to initialise rigorous simulation and it is the most widely used and reliable method for this purpose [53].

3. Methodology

To evaluate the influence of possible improvements to different propylene-to-epichlorohydrin plants, Aspen Plus model of the traditional plant and model of hydrogen peroxide plant with and without dividing wall column distillation were created. Data obtained from these models were used to calculate key parameters of industrial chemical plants such as operative expenditures (OPEX), capital expenditures (CAPEX), carbon footprint and production of by-products. Furthermore, possibilities for future plant improvements were also investigated in terms of heat integration. Finally, a model of DWC was developed to evaluate the influence of this technology on given processes.

3.1. Property model selection

To properly simulate a chemical system, a correct thermodynamic model have to be chosen. It is essential to include all possible binary interactions of components, such as the possibility to form azeotrope and individual properties of components such as electrolyte properties. A practical algorithm to establish an accurate property method was proposed by Kiss [6]:

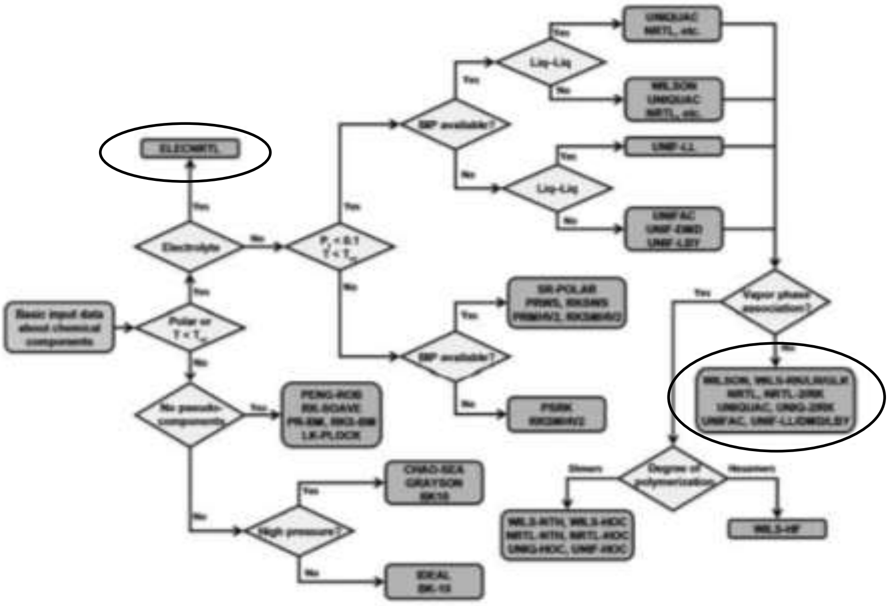


Figure 19. Algorithm for determining property method[6], with highlithed suitable models

Based on the algorithm presented above ELECNRTL, a property method based on the Non-Random Two Liquids (NRTL) model extended with electrolytes properties model was chosen as the most suitable property method, since some of the components present in the plant are electrolytes (hypochlorous acid and calcium hydroxide). Furthermore, NRTL model was proved to be successful in modelling VLE (Vapour-Liquid Equilibrium) and LLE (Liquid-Liquid Equilibrium) of each azeotrope pair present in both processes and it has been reported to provide better accuracy than UNIQAC [54][31]. Validation of other suitable methods shown on figure 20 was not reported in the literature therefore they were excluded. The NRTL is an activity coefficient model proposed by Renon and Prausnitz in 1968 [55], based on three parameters obtained through regression of experimental data [56]. Both methods are based on excess Gibss energy however, ELECNRTL contains additional contributions to this parameter based on electrolyte properties [57].

The NRTL model is based on activity coefficients given by the following equation:

$$ln\,\gamma_i = \frac{\sum_{j=1}^{m}\tau_{ji}G_{ji}x_j}{\sum_{k=1}^{m}G_{ki}x_k} + \sum_{j=1}^{m}\frac{G_{ji}x_j}{\sum_{k=1}^{m}G_{kj}x_k}\left(\tau_{ij} - \frac{\sum_{k=1}^{m}\tau_{kj}G_{kj}x_k}{\sum_{k=1}^{m}G_{kj}x_k}\right) \tag{5}$$

Where:

$$\tau_{ij} = a_{ij} + \frac{b_{ij}}{T} \tag{6}$$

And

$$G_{ij} = e^{-a_{ij}\tau_{ij}} \tag{7}$$

In equation 15, γ is an activity coefficient for component i, x represents the molar fraction of the component. At the same time, m is a number of components in the mixture and T is temperature expressed in Kelvins. Parameters a_{ij} and b_{ij} are binary NRTL parameters related to non-randomness of the mixture [55]. This model is suitable for the given process, because not only it can be used to describe the VLE (vapour-liquid equilibrium), but also LLE (liquid-liquid equilibrium), which is essential for this process because phase splitting between organic, ECH rich phase and aqueous phase is an important part of the process. Several papers have reported successful implementation of LLE using the NRTL method for various compounds [58][59][56]. Since decanter operates under conditions that impose the same temperature and pressure conditions, the LLE is given by following equations[55]:

$$\gamma_i^I x_i^I = \gamma_i^{II} x_i^{II} \tag{8}$$

$$\sum_{i=1}^{N} x_i^I = 1 \tag{9}$$

$$\sum_{i=1}^{N} x_i^{II} = 1 \tag{10}$$

Where activity coefficients γ_i^I and γ_i^{II} are calculated using equation 14. To properly establish values of molar fractions of components in different phases, these four equations (5, 8, 9, 10) have to be solved simultaneously. The VLE is imposed by the condition of equal fugacities of components between different phases. Fugacity of component is given by:

$$f_i^G = py_i\varphi_i \tag{11}$$

Where f_i^G is a component fugacity, p is pressure in bar, y is molar fraction of component in liquid phase and φ_i is the fugacity coefficient of component. At the same time sum of molar fraction of components in each phase has to be equal 1 as stated below:

$$\sum_{i=1}^{N} x_i = 1 \tag{12}$$

$$\sum_{i=1}^{N} y_i = 1 \tag{13}$$

And the pressure of component in vapor phase is given by the following equation:

$$py_{i=}p_i^s\gamma_i x_i \tag{14}$$

Where p_i^s is a vapour pressure of component calculated using Antoine's equation[55].

ELECNRTL method is an extension to the classic NRTL model, suitable to simulate processes that include electrolytes. This model contains two contributions to Gibbs energy, one of them is based on the immediate neighbourhood of species. The second one is based on long-distance ion-ion interactions expressed using the unsymmetric Pitzer-Debye-Huckel formula (PDH) [60]. This contribution provides valuable correction to value of activity coefficient based on ion properties. Furthermore, the reaction in which ECH is produced also occurs in an electrolyte environment. To properly simulate the distillation process, it is key to obtain proper VLE (vapour-liquid equilibrium) data therefore, missing binary parameters of specified components were estimated using the UNIFAC (Universal Quasichemical Functional Group Activity Coefficients) method. This model helps evaluate interactions between molecules based on the functional groups of compounds involved [61]. Since this method is based mainly on functional groups present in the given compound, it does not require experimental data. Additionally, this method has been proven effective for azeotrope search [62].Components properties were imported from Aspen Plus databanks. To avoid excess calculations connected to solid particles it was assumed that milk of lime acts as a solution, instead of suspension. The property model was validated by comparing data obtained using Aspen Plus simulation with data gathered from patents.

3.2. Chlorohydrin process model

To perform a reliable estimation of plant operation using Aspen Plus annual production capacity of epichlorohydrin was assumed to be equal 34 000 tonnes, this scale is similar to the plant operated by Organika Zachem SA in Bydgoszcz, Poland. This plant was chosen as most suitable for this study, because high number of available patents regarding this plant [9][63][17][8][35][15][11][13][10]. The production rate per hour was calculated based on continuous plant operation, since the given plant was operating continuously. Additionally, it was assumed that plant operates 350 days of the year and 24 hours a day, to ensure that enough time is scheduled for maintenance. That leads to hourly production rate of ECH equal to roughly 4100 kg/hr. Furthermore, it was assumed that chlorine required to produce epichlorohydrin is provided by another plant operating within the same chemical complex, since chlorine transportation is expensive and dangerous. This implies that HCl created as a by-product of the process is not converted back to chlorine using oxidation reaction, but sold as hydrochloric acid, as the conversion to chlorine is not economically feasible in given case. Additionally, formation of acrolein during ECH was excluded from the process as no data about reaction rate or conversion for this reaction were found in the literature. The compositions of substrate stream were determined based on specification of commercially available components.

The list components used in base case simulation is shown in table 16 in appendix A. Chlorine obtained in the electrolysis process is usually liquified for purification purposes as well for the ease of storage. This compound is sent to the ECH plant in a liquid form therefore the first step of processing consist of chlorine evaporation, which is performed in an evaporator. In the next step, residual moisture has to be removed from the chlorine gas (water content cannot exceed 5 ppm [35]), to prevent corrosion of the apparatuses. This is usually performed in a column equipped with drying agent such as concentrated sulphuric acid or molecular sieves. For ease of simulation, this step was modelled using separator block, with split fractions specified to meet the required moisture content. Also, at the beginning of process, recycled propylene is mixed with fresh one from the storage. Subsequently, this hydrocarbon is heated using reactor a effluent stream, because use of reactor outlet stream as heating medium provides significant energy savings to the process [63]. The chlorine and propylene streams are then mixed using mixer unit and fed to the stoichiometric reactor. In this type of reactor in Aspen Plus user has to specify each occurring reaction along with conversion of one of the substrates. This is a valuable tool to mimic the real reactor performance when kinetic data are unavailable. The list of the reaction as well as specified conversion is shown in the table below [8]:

Tab. 4 Reactions specified in chlorination reactor

Reaction number	**Conversion in terms of propylene**	**Stoichiometry**
1	0.15815	PROPENE + CHLORINE → ACH + HCL
2	0.0075	PROPENE + CHLORINE → MCPROPEN + HCL
3	0.0051	PROPENE + HCL → MCPROPAN
4	0.0072	PROPENE + 2 CHLORINE → DCPROPEN + 2 HCL
5	0.01082	PROPENE + CHLORINE → 12DCP

This reaction has to be performed with excess propylene to prevent chlorine from entering next steps of the process [8]. As mentioned above, reactor effluent is then used to heat the propylene stream [13]. After this step it is sent to the heat exchanger to cool it to desired temperature [63]. The mixture of hydrocarbons and hydrogen chloride is then sent to the distillation column to remove HCl [10]. It is important to remove this compound as soon as possible as it can react with propylene to form 2-chloropropane (Boiling point 46 ºC), which is almost impossible to remove from ACH (Boiling Point 45 ºC). HCL is removed as liquid distillate while the chlorinated hydrocarbons and propylene mixture is obtained as the bottom stream. Separated hydrogen chloride then undergoes absorption in a column. The HCL distillation column was specified to remove at least 99.9% mass of this component from the feed stream. Deionised water is fed to the top of the column while gas is provided to bottom stage. Water stream was determined to obtain hydrochloric acid concentration equal to 28%. The remaining mixture of hydrocarbons is fed to the propylene column. In this step, propylene is separated from chlorinated hydrocarbons. This separation has to be performed under elevated pressure, because of low boiling point of components. Propylene is obtained as vapour distillate. This apparatus was specified to remove 99.9% of the remaining propylene. The subsequent stage consists of direct sequence of distillation columns to purify the intermediate allyl chloride. First column removes light impurities such as 2-chloropropene. In the second column high boiling impurities are removed i.e. dichloropropene [12][11]. Light Ends column was modelled to recover more than 99.9% of allyl chloride as bottom stream, while removing at least 99% of monochloropropene. The heavy ends columns operated in conditions specified to remove 99.7% mass of heavy fractions, to obtain ACH purity of at least 99.8%. The next stage consists of hydrochlorination reaction where ACH is mixed with aqueous solution of hypochlorous acid to form mixture of dichloropropanols (1,2-dichloropropane-ol and 1,3-dichloropropane-ol). This reactor was simulated as a stoichiometric reactor due to lack of available kinetic data for the reaction. List of the reactions is stated below

Tab. 5 Reactions specified in dichlorpopropanols reactor

	Conversion in terms of ACH	**Stoichiometry**
1.	0.6305	ACH + HCLO → 23DCPOL
2.	0.3110	ACH + HCLO → 13DCPOL
3.	0.0380	ACH + HCL + HCLO → TCP + WATER

The post-reaction mixture is then cooled using heat exchanger, which cools it down to 40 ºC. Then remaining chlorine has to be removed from the solution to prevent plant corrosion. In a commercial plants its performed by mixing the stream with mildly base solution, for example aqueous solution of sodium hydrocarbonate. For the simplicity of simulation this was achieved using separation block, which was specified to remove all remaining chlorine. Then the solution of dichloropropanols is sent to a mixer and mixed with an alkaline agent in this case, milk of lime. This mixture is then fed to the saponification reactor. This reactor is modelled as a PFR reactor with specified kinetics, found in the literature [18]. Dimensions of the reactor were specified to enable 30% conversion of dichloropropanols as specified in the literature. The kinetic equations of reactions, which occur in the reactor are shown below [18]

Tab. 6 Reactions and kinetic equations specified in saponification reactor

	Kinetic equation	**Stoichiometry**
1	$r_1=k_1C_{OH}\text{-}C_{13DCPOL}$	13DCPOL + CAOH2 → 2 ECH + CACL2 + 2 WATER
2	$r_2=k_2C_{OH\text{-}C23DCPOL}$	23DCPOL + CAOH2 → 2 ECH + CACL2 + 2 WATER
3	$r_3=k_2C_{OH}$	CAOH2 + 2 HCL → CACL2 + 2 WATER

Effluent from this reactor is then fed to the stripping column. In this apparatus, reactive distillation is performed, and the rest of the ECH is produced and instantly removed from the reaction environments, which gives a higher yield of reaction. This is caused by preventing the side reaction of ECH hydrolysis from occurring. This column is not equipped with a reboiler or condenser, so the distillate is only vapour. Medium pressure steam is fed to the bottom stage of the column. Additionally, as epichlorohydrin has low solubility in water, two liquid phases are present in this column. Therefore, water was specified as the second liquid phase, present at every stage of the column. Furthermore, convergence for this column had to be specified as azeotropic, because epichlorohydrin forms an azeotrope with water. The vapour distillate is then sent to the heat exchanger in which the condensation occurs. The liquid stream from the condenser is fed to the decanter, where the phase splitting occurs. The aqueous phase is sent back to the distillation column as reflux, while the organic, ECH-rich phase is transported for further purification. The layout of stripping column with heat exchanger and decanter along with specifications is shown on figure 38 in appendix A. Final purification is performed in four distillation columns [19]. Two of them are stripping columns not equipped with a condenser, which means that the vapour distillate is liquified using external heat exchanger. The layout of the ECH purification system is shown on figures 39 and 40 in appendix A. Final ECH purity has to be equal at least 99.9% This base case simulation was used to assess the utility usage, CAPEX and carbon footprint of base case plant. Additionally, the carbon footprint of the plant was evaluated using this model. The simulation results were validated by comparing obtained data with parameters mentioned in the patents issued by Organika Zachem.

3.3. DWC design

To conduct the shortcut simulation of DWC and create a V_{min} graph, the key components have been identified. Additionally, the composition of separated mixture was assumed to contain only these three components to simplify the shortcut calculations of crucial parameters of DWC column and then normalised, so the molar fraction of components sum to unity.

Tab. 7 Values used for shortcut simulation of DWC

Tag	Component	Mole fraction	K-value	Product
MCP	Monochloropropene	0.0702	1.4306	D
ACH	Allyl chloride	0.8367	1.0686	S
DCP	Dichloropropene	0.0931	0.2413	B

The separation task which needs to be performed is to obtain ACH with purity equal to 99.8% mass. Dividing wall column distillation column, which would replace the direct separation system currently used in the commercial process, is simulated using 4 column sequence described in paragraph 2.4. This setup provides the best flexibility and accuracy, but it is hard to initialise [6]. To obtain the data required for proper initialisation of DWC simulation, a V_{min} diagram method was used. In this approach, the internal moral flowrates in each section of the DWC column are estimated by V_{min} graph, which Halvorsen and Skogestad [64] introduced to estimate energy consumption in the distillation column. Data used to create this diagram were calculated based on Aspen Plus simulation of binary splits between the key components, which were as follows: key light: monochloropropene, key heavy: dichloropropene and allyl chloride is a key medium boiling point component. The values of vapour flowrate above the feed stage and the values of distillate flowrate were directly retrieved from the Aspen RadFrac model. The number of stages was set to $4N_{min}$, where N_{min} is the number of stages calculated using the Fenske equation, since it adequately mimics the assumption of an infinite amount of theoretical stages[6]. Furthermore, the K values (x_i/y_i) were obtained directly from the simulation programme to compute the relative volatilities of components. For each split K value at feed stage, of ACH/DCP split was used for calculations. The simulation results are displayed in table 8. and compared with analytical calculations on Figure 22. It can be seen that assumption of constant relative volatilities used to obtain analytical solution is not met for all splits.

Tab. 8. Specified and calculated values for the V_{min} diagram

	Specified		**Calculated**			
Split	**Recoveries**		**D/F**	**V_T/F**	**N_{min}**	**N**
MCP/ACH	$r_{ACH,D}$=0.01	$r_{MCP,B}$=0.01	0.0702177	3.103	39	156
MCP/DCP	$r_{DCP,D}$=0.01	$r_{MCP,B}$=0.01	0.825	1.165	8	32
ACH/DCP	$r_{DCP,D}$=0.01	$r_{MCP,B}$=0.01	0.903	1.30	9	36

Furthermore, V_{min} was also created by solving Underwood's equation. In this approach, calculations are based on the mass balance of a simple distillation column, where feed is provided to the middle of a column, distillate is obtained as a top stream. In contrast, the bottom stream is obtained from the last theoretical stage in a distillation column. Additional assumptions are infinite amount of stages (amount of stages equal $4N_{min}$ is a reasonable estimation as mentioned in chapter 2), constant molar flow and constant molar volatilities [53], which were calculated based on K-values displayed in table 7. and following values of relative volatilities were obtained.

Tab. 9. Relative volatilities of key components

Component	Value of relative volatility (α)
MCP	5.93
ACH	4.43
DCP	1

Parameters above were used by Underwood to define equations for stripping and rectifying sections of distillation column:

$$\sum_i^n \frac{\alpha_i x_i^T}{\alpha_i - \phi} = R + 1 \tag{15}$$

$$\sum_i^n \frac{\alpha_i x_i^B}{\alpha_i - \psi} = B + 1 \tag{16}$$

Where R and B are reflux ratio and boilup ratio respectively, while ϕ and ψ, are Underwood roots for the top and bottom parts of the distillation column. When the values of vapour flow decrease and liquid flow increase, the values of Underwood roots start to be equal. This means that the distillation column has achieved a pinch point [53]. The common roots are called active roots θ^* if their value lies between the values of relative volatilities of components which are split as shown on figure 21.

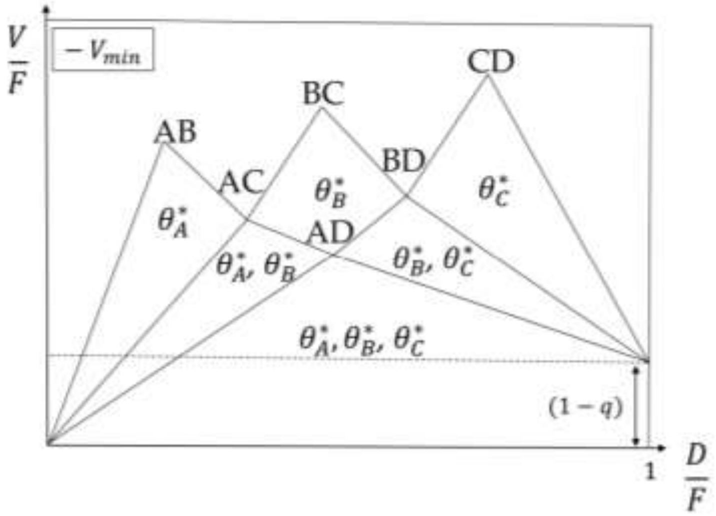


Figure 20. Underwood's roots for different splits [53]

The active roots has to fulfil the following equation [53]:

$$\alpha_1 > \theta_1 > \alpha_2 > \ldots . > \alpha_n \tag{17}$$

Values of active roots can be calculated using mass balance of vapor phase in distillation column:

$$(1-q)F + V^B = V^T \tag{18}$$

Where q is an amount of vapor in a feed stream, in case of given process feed stream is a saturated liquid, therefore q=1, while V^B and V^T can be defined as follows:

$$V^T = \sum_i^n \frac{Fz_i\alpha_i r_i^T}{\alpha_i - \phi} \tag{19}$$

$$V^B = \sum_i^n \frac{Fz_i\alpha_i r_i^B}{\alpha_i - \psi} \tag{20}$$

Which yields with following equation for overall mass balance:

$$F + \sum_i^n \frac{Fz_i\alpha_i r_i^B}{\alpha_i - \psi} = \sum_i^n \frac{Fz_i\alpha_i r_i^T}{\alpha_i - \phi} \tag{21}$$

Dividing both sides by F and rearranging gives:

$$1 = \sum_i^n \frac{z_i\alpha_i r_i^T}{\alpha_i - \theta_i} - \sum_i^n \frac{z_i\alpha_i r_i^B}{\alpha_i - \theta_i} \tag{22}$$

As r^T and r^B has opposite signs as one of them is incoming stream and other is outcoming and for ech component their sum up to unity, the values of recovery cancels out giving:

$$1 = \sum_i^n \frac{z_i\alpha_i}{\alpha_i - \theta_i} \tag{23}$$

Underwood's roots do not depend on component recoveries, only on the condition and composition of the feed stream. In this report, this equation was solved using python function scipy.optimize.fsolve and setting initial guesses to 5.5 and 2. These values were used to calculate the V/F and D/F for three points. For the first split MCP/ACH split, only first Underwood root is active, which gives the following values:

$$\frac{V^T}{F} = \frac{z_{MCP}\alpha_{MCP}}{\alpha_{MCP} - \theta_{MCP}} \tag{24}$$

While D/F is given by:

$$\frac{D}{F} = z_{MCP} \tag{25}$$

For the split between medium and heavy components, only second root is active, therefore:

$$\frac{V^T}{F} = \frac{z_{MCP}\alpha_{MCP}}{\alpha_{MCP}-\theta_{ACH}} + \frac{z_{ACH}\alpha_{ACH}}{\alpha_{ACH}-\theta_{ACH}} \tag{26}$$

$$\frac{D}{F} = z_{MCP} + z_{ACH} \tag{27}$$

For the split when one component is distributed between top and bottom stream both Underwood's roots are active and the recovery of this component in both streams is unknown, but can be calculated using the following expression [53]:

$$\beta = \frac{\alpha_{MCP}z_{MCP}(\alpha_{ACH}-\theta_{MCP})(\alpha_{ACH}-\theta_{ACH})}{\alpha_{ACH}z_{ACH}(\alpha_{MCP}-\theta_{ACH})(\alpha_{MCP}-\theta_{ACH})} \tag{28}$$

And:

$$\frac{V^T}{F} = \frac{z_{MCP}\alpha_{MCP}}{\alpha_{MCP}-\theta_{ACH}} + \frac{z_{ACH}\alpha_{ACH}}{\alpha_{ACH}-\theta_{ACH}} \tag{29}$$

$$\frac{D}{F} = z_{MCP} + \beta z_{ACH} \tag{30}$$

The values of calculated points are shown in the table below:

Tab. 10 Values for V_{min} diagram calculated using Underwood's equation

Split	**D/F**	**V^T/F**
MCP/ACH	0.0702	2.766
MCP/DCP	0.823	1.151
ACH/DCP	0.907	1.192

Additionally, values calculated both analytically and numerically are shown on Figure 22.

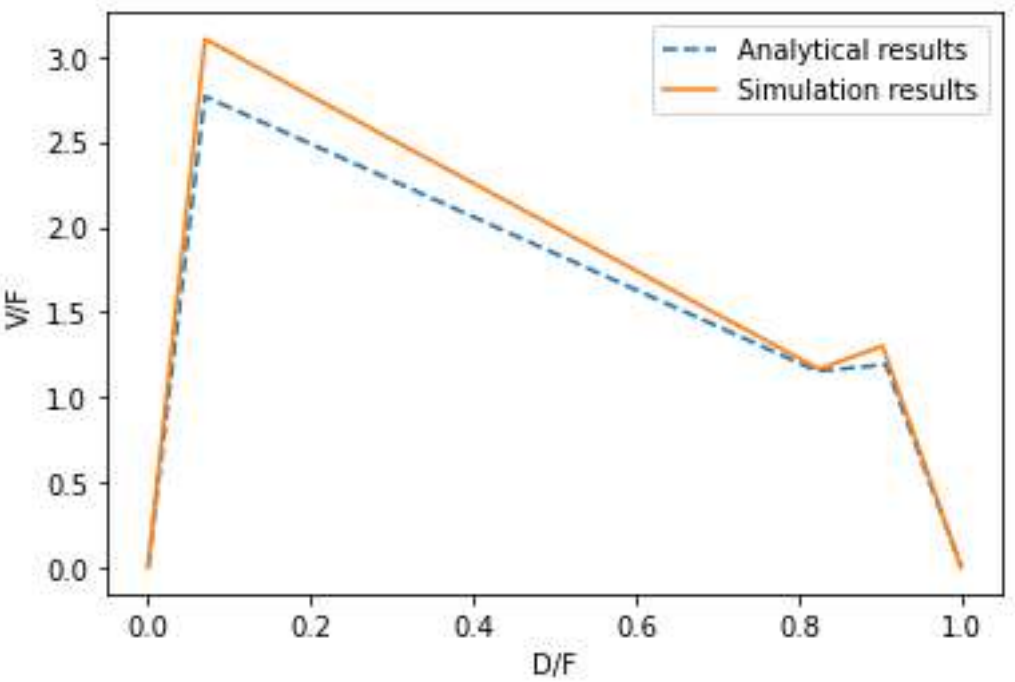


Figure 21. V_{min} diagram for ACH separation

Data shown in table 8 can also be used to quickly evaluate possible energy savings. Comparison between DWC and conventional setup, calculated based on shortcut simulation is shown in table 11:

Tab. 11. Comparison between direct sequence and DWC

	Base case		**DWC**
	Column 1	Column 2	DWC column
Top pressure [bar]	1.9	1.18	1.9
Number of stages	70	30	80
Feed stage	42	15	43
Reflux ratio	56.60	0.3927	42.45
Condenser duty [MW]	-1.597	-0.576	-1.335
Total	-2.173		-1.335
Reboiler duty	1.486	0.529	1.248
Total	2.105		1.248

Energy consumption estimation for DWC column was established using the assumption that the amount of energy required to separate components in such apparatus is determined by energy required to perform the most difficult separation in the system. In case of given system, it is split between monochloropropene and allyl chloride. Values from table 11 indicate that the maximum possible energy savings provided by DWC column are equal about 40 %. In reality, actual savings will be lower, which can be seen once rigorous DWC model is created. In the subsequent step, data obtained using the shortcut simulation were used to calculate internal flowrates of vapour and liquid streams in a distillation column using mass balance equations for each section of dividing wall column. Calculated values of internal molar flowrates and values of reflux and boliup ratio are shown schematically on figure 23.

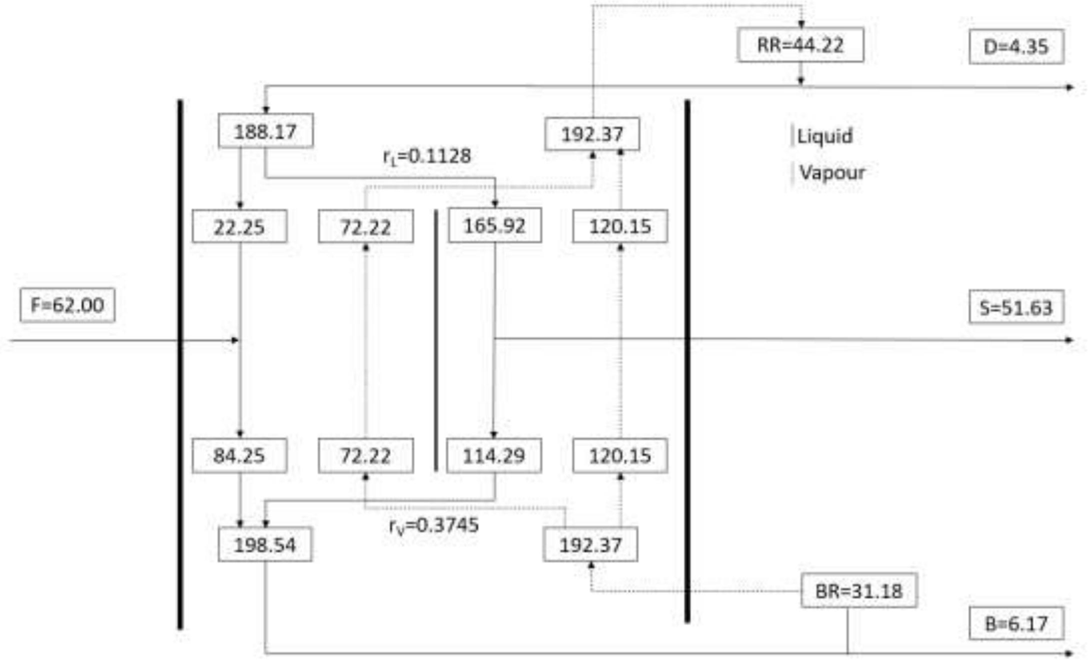


Figure 22. Internal flowrates in DWC based on V_{min} diagram, all flows are in kmol/hr

These values were used to first simulate each section of DWC column as standalone unit. Composition of liquid stream from top of distillation column were assumed to not include any light components and vapour stream from bottom of the column was assumed not to contain any high boiling components, as top column separates light components as distillate and in bottom part of the column all the heavy fractions are separated as bottom stream . To achieve proper values of molar fraction of other compounds composition of assumed components were normalized so the molar fractions sum up to unity. After each section was run as standalone unit the calculated inner streams were connected between columns sections as shown on figure 24.

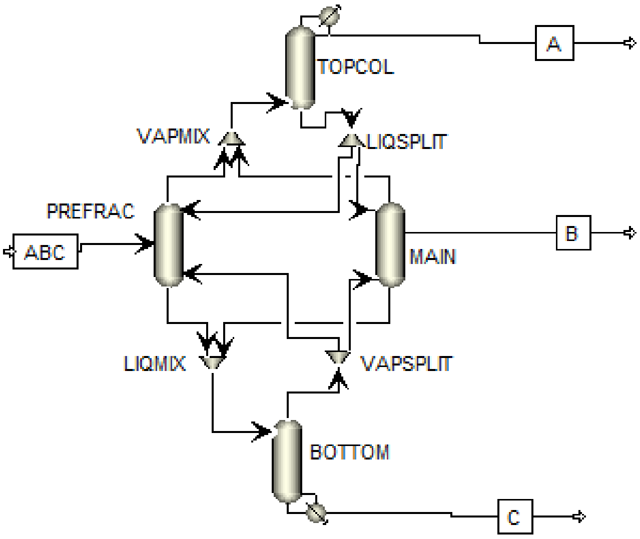


Figure 23. Layout of four column DWC model

To achieve convergence in this system m, the maximum amount of flowsheet evaluation was increased to 500. When the converging DWC model was obtained, it was tuned to achieve desired ACH purity (99.8% mass). The next step of modelling consisted of optimisation according to the algorithm proposed by Dejanovic [50], which is shown on figure 25.

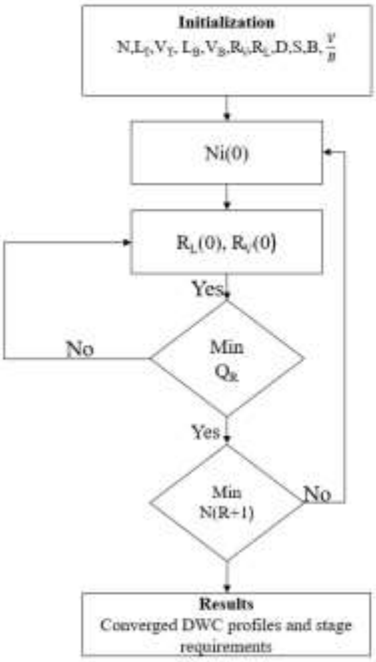


Figure 24. Algorithm for DWC optimisation [45]

3.4. Model of HP based ECH plant

To evaluate the profitability of the oxidation based route, its model has been created in Aspen Plus. Since the novel route also requires allyl chloride as an intermediate product, this part of the plant was copied from the traditional process. Differences are introduced only in the ECH stage as this part consumes the most energy and produces the most significant amount of waste. As this process does not contains electrolytes in opposite to the traditional process, therefore different property method was used, in this case NRTL was most suitable property method, because given process contains polar compounds none of them can be considered an electrolyte. Furthermore, , pressure and temperature ranges allow use of NRTL as this model is not suitable for low and high pressures. Missing binary parameters were imported from the UNIFAC database. The novel process consists of new reactions and compound therefore new component list had to be defined. In this approach trichloropropane, 1,2-dichlorpropanol and 1,3-dichloropropol were excluded as this compounds are not formed in this process. The new components which had to be selected for the simulation were: 1-chloro-3-methoxypropan-2-ol, 1-chloropropane-2,3-diol (CPD), hydrogen peroxide (HP) and methanol, which were chosen as most suitable solvent based on data displayed in table 2. Additionally, since Aspen Plus databases do not include parameters for 1-chloro-3-methoxypropan-2-ol (CMP), this compound was specified by importing the molecular structure and molecular weight of the component, also molecular structure of hydrogen peroxide had to be specified as some important parameters for this compound were also missing. Since this route also uses ACH as intermediate, section of the plant responsible for this compound synthesis and purification was copied from the base case process. For the HP process, epoxidation reaction was modelled in a packed bed reactor and concentration of hydrogen peroxide was assumed to be equal to most commercially available value of 33%. In this approach, ACH stream is mixed with hydrogen peroxide and methanol to obtain uniform solution, which is then heated to desired temperature of 60 ºC and then fed to reactor, which operates at given temperature and pressure equal to 3 bar. The kinetic equations and the values of kinetic parameters are listed below:

1. $ACH + HP \rightarrow ECH + W$
2. $ECH + W \rightarrow CDP$
3. $ECH + MeOH \rightarrow CMP$
4. $HP \rightarrow W + O_2$

$$r_1 = \frac{k_1 b_{HP} C_{HP} C_{AC}}{1 + b_{HP} C_{HP} + b_{ECH} C_{ECH}} \tag{31}$$

$$r_2 = \frac{k_2 b_{ECH} C_{ECH} C_W}{1 + b_{HP} C_{HP} + b_{ECH} C_{ECH}} \tag{32}$$

$$r_3 = \frac{k_2 b_{ECH} C_{ECH} C_M}{1 + b_{HP} C_{HP} + b_{ECH} C_{ECH}} \tag{33}$$

$$r_4 = \frac{k_4 b_{HP} C_{HP}}{1 + b_{HP} C_{HP} + b_{ECH} C_{ECH}} \tag{34}$$

Tab. 12. Values of kinetic parameters for epoxidation reaction

Reaction	k_i^0 $\left[\frac{L}{s \cdot g}\right]$	E_i $\left[\frac{kJ}{mol}\right]$	b_{HP}^0 $\left[\frac{L}{mol}\right]$	b_{ECH}^0 $\left[\frac{L}{mol}\right]$	Q_{HP} $\left[\frac{kJ}{mol}\right]$	Q_{ECH} $\left[\frac{kJ}{mol}\right]$
1	$11.05 \cdot 10^3$	56.75	$3.03 \cdot 10^{-4}$	$5.71 \cdot 10^{-4}$	19.36	18.69
2	$5.94 \cdot 10^3$	70.09	$3.08 \cdot 10^{-4}$	$4.57 \cdot 10^{-4}$	19.56	17.53
3	$1.10 \cdot 10^3$	65.20	$3.05 \cdot 10^{-4}$	$4.79 \cdot 10^{-4}$	19.57	18.58
4	5.11	50.19	$5.70 \cdot 10^{-4}$	$4.27 \cdot 10^{-4}$	19.45	18.55

Reactor was specified as isothermal with constant pressure, pressure and temperature equal to values specified by Danov [28]. It can be seen from table 12 that values of reaction constants were of similar values for first three reactions, which means that it is important to specify appropriate reactor dimensions and amount of used catalyst to achieve high conversion of allyl chloride, yet to prevent side reactions from occurring. Epoxidation reaction is conducted with excess allyl chloride to prevent HP from entering the separation step in which it could lead to the formation of explosive mixture, because it's thermal decompositions products are water and oxygen. As mentioned in chapter 2.1.3. the ratio of HP to ACH was equal to 1:2.77, while the solvent concentration was equal to 65% mass. The post-reaction mixture is then fed to distillation column in which separation of ACH and MeOH occurs. These two compounds forms an azeotropic mixture therefore they have to be separated in the same step, due to low boiling point of this azeotrope these two compounds are obtained as distillate, while ECH, CMP, CDP, and water are obtained as bottom stream. This column removes 99.5 % of MeOH and all ACH present in the feed stream. The distillate stream is recycled and mixed with fresh ACH and HP and fed back to the reactor. Bottom stream form MeOH/ACH column is cooled to 20ºC and fed to the decanter. In this apparatus, phase splitting occurs, where aqueous and organic phases are formed. The organic layer contains ECH, CDP, CMP and some amounts of water, while the aqueous phase consists of water and epichlorohydrin. Organics-rich streams is then fed to the stripping column, where the remaining water is separated. This stripping column is used to remove 98% mass of water from feed stream as vapour distillate, which is then condensed and cooled down to 20ºC and fed back to the decanter as this stream contains significant amount of epichlorohydrin, because azeotrope contains 72% ECH by weight. Additionally aqueous stream is fed to the stripping column to remove remaining ECH, which recovers 99.5% of ECH present in the feed stream. Distillate obtained as azeotropic mixture is condensed, cooled and send back to the decanter. The bottom stream from organic's stripping column is the purified in a distillation column to separate heavy boiling components such as CMP and CDP. This additional separation step also enables to production of ECH of significantly improved purity in comparison to traditional process, because ECH is obtained as top stream, which increases the purity of product. Final purity of ECH was specified as equal 99.9% mass.

3.5. Heat Integration

Energy integration enables significant energy savings which is widely used by companies such as BP and MOL Group[64]. In this approach, streams are divided into two groups- heat sources (hot streams that need to be cooled) and heat sinks (cold streams which need to be heated), while the division is based on whether the stream is above or below the pinch point [65]. The pinch point is established by plotting the cumulative curve (temperature vs enthalpy plot) for both cold and hot streams, as shown on figure 26.

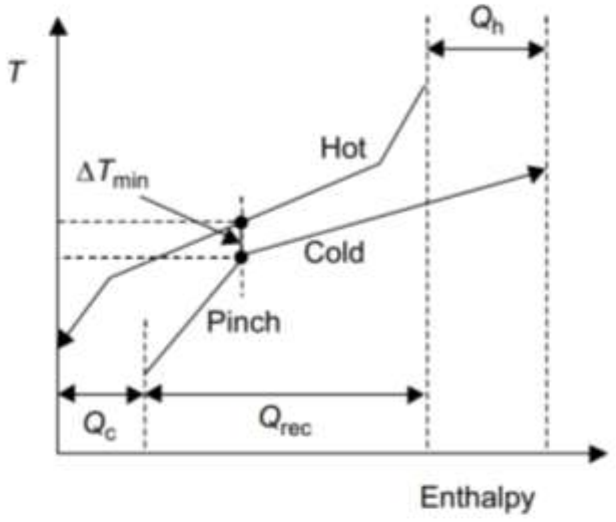


Figure 25. Example of composite curve [66]

As shown on figure 26 minimum cooling and heating requirements can be determined as the difference between enthalpy values of composite curve on the left for colling and on the right for heating. Based on the pinch point analysis, one can establish the heat exchanger configuration necessary to minimise energy usage. This is done by analysing each stream's flowrates and heat capacities and then by matching the appropriate streams until minimum utility requirements are achieved. In reality, sometimes some streams cannot be matched because of safety reasons, complexity of plant control etc. In this report, heat integration of both plant were performed using Aspen Plus built-in tool, Aspen Energy Analyzer. To properly use this programme one has to specify all the utilities required in the simulation i.e. cooling medium for heat exchangers or the parameters of steam used in the reboilers. Aspen Tech has implemented several types of heating and cooling utilities, however in this report utilities used in the Zachem SA plant were used. The list of the utilities applied to the process is shown in the table below.

Tab. 13 Parameters of utilities used in Zachem's ECH plant

Utility	**T_{in} [°C]**	**T_{put} [°C]**
Low pressure steam (p=1.3 bar)	125	124
Medium pressure steam (p=8 bar)	175	174
Liquid propylene	-45	-44
Cooling water	20	25
Air	30	35

Then, once the utilities are specified program performs the pinch points analysis and the stream matching. It can provide useful information about possible heat savings, but not all heat exchangers can be applied as mentioned above. Additionally, to simplify the design and therefore ease of control of the process, amount of splits possible for each stream was set to one. This can limit the possibility of heat recovery, however significantly simplifies the plant operation and safety, which is important in case of handling dangerous compounds such as ECH.

3.6. Equipment sizing

3.6.1. Distillation column sizing

Traditional ECH process consists of many distillation columns and stripping columns. Proper assessment of investment cost requires to perform sizing of each column. As mentioned in patents [12][10][15], the HCl recovery column, propylene recovery column, light ends column, heavy ends column and ECH stripping column are equipped with trays, while the remaining dehydrating column, ECH recovery column and ECH rectification columns are equipped with packing, in this case Raschig's ring are used. Especially in case of ECH stripping column it is important to use trays instead of packing, because a suspension of milk of lime is introduced to this column, which makes it prone to fouling. For the other columns use of a tray instead is caused by the significant height of the column, which implies that for packed column a liquid redistributors will be needed to prevent uneven liquid flow inside the column. To establish the investment cost of distillation tower, column diameter, height, and wall thickness must be calculated. The height of distillation columns depends on the number of trays and tray spacing for the trayed column and on the number of stages and HETP for packed columns. Height of tray column were calculated using equation proposed by Pikoń [2]

$$H_c = N(H + \delta_r) \tag{35}$$

Where:
N- number of trays
H- spacing between stages [m]
δ_r- thickness of the tray [m]

For the purpose of this report, spacing between stages was assumed to be equal 0.6096 m (2 ft) [67], while the tray thickness was neglected due to significantly smaller dimensions than tray spacing [68]. Additionally, spacing between the top and bottom part of the distillation column was assumed to be equal 1.2 and 1.8 meters, respectively based on data provided by Seider [67]. The diameter of each distillation column was established using Aspen Plus built-in tool and then rounded to commercially available value of column diameter. Ratio of downcomer to tray specified was specified to be equal 0.1, while the fractional approach to flooding was set to be equal 0.8. Wall thickness was calculated using procedure proposed by Seider [67]. The results of calculations were used to determine the weight and therefore cost of distillation equipment required for the process, which is displayed in table 35 in appendix B.

Most distillation columns have to be equipped with a reflux drum. Reflux drum is usually designed as horizontal cylindrical vessel. The size of this piece of equipment is determined by the liquid phase flowrate for columns with purely liquid distillate, while for the columns with vapour distillate the volume of the reflux vessel has to be calculated also considering the gas phase. The equation required to determine the volume of the reflux drum for distillation column is shown below:

$$V = \frac{L \cdot \tau}{0.75} \qquad (36)$$

Where L is liquid flowrate in m^3/h and τ is assumed residence time

Holdup time was assumed to be equal 10 minutes while the filling factor was assumed to be equal 75% for all columns as no foaming is expected. Additionally, each drum is designed to maintain length to diameter ratio equal 3. The wall thickness of reflux drum was calculated using the same equation as for the distillation column.

3.6.2. Decanter sizing

Decanter is an important equipment in ECH production, because it enables the separation of ECH and water, since the water-ECH azeotrope is heterogeneous. This apparatus uses the difference in density of immiscible liquids to separate them into two liquid phases. For the proper decanter operation it is important to ensure an appropriate volume and, therefore residence time, which enables complete separation of liquid phases. The residence time can be calculated using following equation [69]:

$$\tau = \frac{100\mu}{\rho_A - \rho_B} \qquad (37)$$

Where μ is density in cP and ρ is in kg/m^3.

Data required to obtain the residence time shown above were directly obtained from Aspen Plus. Another important parameter for decanter design is height of a second phase outlet. However the value of this parameter will not influence the size and therefore cost of the vessel, therefore calculation of this parameter will be omitted from this report.

In case of decanter calculations the ratio of length to diameter were assumed to be equal 2 instead of three as for classic vessel, to ensure proper phase splitting in the decanter. To calculate the wall thickness and therefore the decanter weight, same algorithm as for reflux drum were used.

3.6.3. Reactor design

Dimensions of chlorination were specified based on the residence time mentioned in the patent obtained by Organika Zachem [9], whose value was within 0.5-3 s interval. Additionally, chlorination reactor can be assumed to be PFR. For this report, value of residence time, equal 2 seconds were assumed. The reactor volume was determined by multiplying the residence time by the inlet flowrate of the reactant mixture. Please note that slight volume changes of the reaction changes of reacting mixture occurs, but this can be neglected due to significant volume of excess propylene in the reactor.

In industrially operating plant hydrochlorination reaction is performed by stripping chorine gas through aqueous solution of allyl chloride in case of ECH plant or simultaneous stripping of propylene and chlorine gas in case of propylene oxide [26][1]. Therefore the best model for rigorous simulation of this kind of reaction is bubble column reactor. However, as kinetic and mass transfer data were unavailable in the literature, this reactor was simulated as stoichiometric reactor with residence time equal 8 s [17], but for cost analysis this reactor was considered as PFR. Which is fed with two premixed liquid streams, where one consists of an aqueous solution of hypochlorite acid and the second consists of aqueous solution of ACH. The volume of this reactor was also calculated by multiplying combined inlet liquid streams by the specified residence time. This reactor is only used in base case process, because hydrochlorination reaction is not used for the HP route.

Saponification reactor used in the base case process was specified to obtain 30% conversion as specified in literature [18] additionally, this reactor also operates as a PRF reactor. To ensure this conversion a residence time of 30 s was required.

For the HP route epoxidation reaction occurs between allyl chloride and hydrogen peroxide, which occurs in a packed bed PFR. Therefore this reactor was also specified as plug flow reactor, but in this case it is filled with catalytic bed, which consists of TS-1 zeolite. In case of this reactor, the residence time was unknown, therefore the reactor volume were established based on condition that all hydrogen peroxide needs to react in the reactor, with known kinetic parameters.

All the calculations considering wall thickness were performed in the same way as for the reflux drums and other equipment.

3.6.4. Heat exchangers design

Heat exchangers, including reboilers and condensers were performed using Aspen Energy Analyser. Data from the Aspen Plus simulation were imported to Aspen Energy Analyzer, and then for the base case and then by selecting heat exchanger tab, all the necessary data are shown. Data retrieved from this programme contained crucial heat exchanger parameters such as the heat load and the area of heat exchange. Additionally the cost of each heat exchanger was also established using this programme.

4. Results and discussion

4.1. DWC dimensions

The final values of internal flows along with stage requirements are shown on figure 27. The total energy requirements for designed DWC column are shown in a table 14. It can be seen that actual values of internal flows and especially values of liquid and vapour split ratios vary significantly from the values obtained from shortcut simulations. Values of internal flowrates and stage requirement obtained using the algorithm shown on figure 25 are shown below

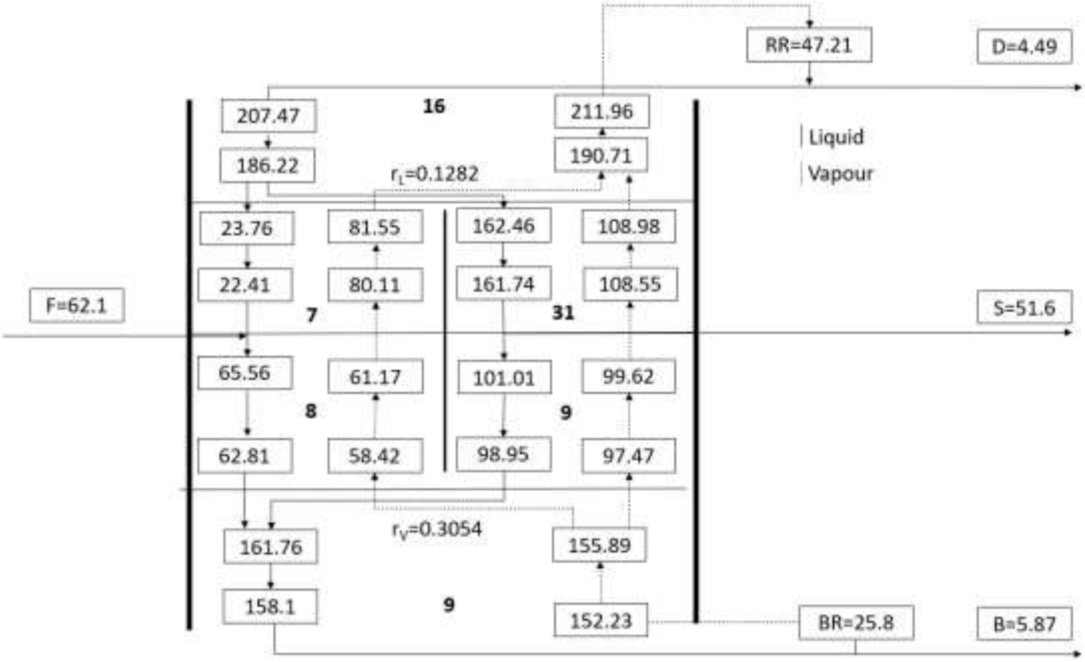


Figure 26. Final values of internal flowrates and stage requirements

Comparison between two column setup and DWC are shown in table 14.

Tab.14. Comparison between two column setup and DWC

	Base case		**Final DWC**	**Difference [%]**
	Column 1	Column 2	DWC column	
Top pressure [bar]	1.9	1.19	1.9	-
Number of stages	70	30	80	-20
Feed stage	42	15	43	-
Reflux ratio	56.60	0.3927	46.19	-
Condenser duty [MW]	-1.597	-0.576	-1.471	-
Total	-2.173		-1.471	-32
Reboiler duty	1.486	0.529	1.342	-
Total	2.105		1.342	-36

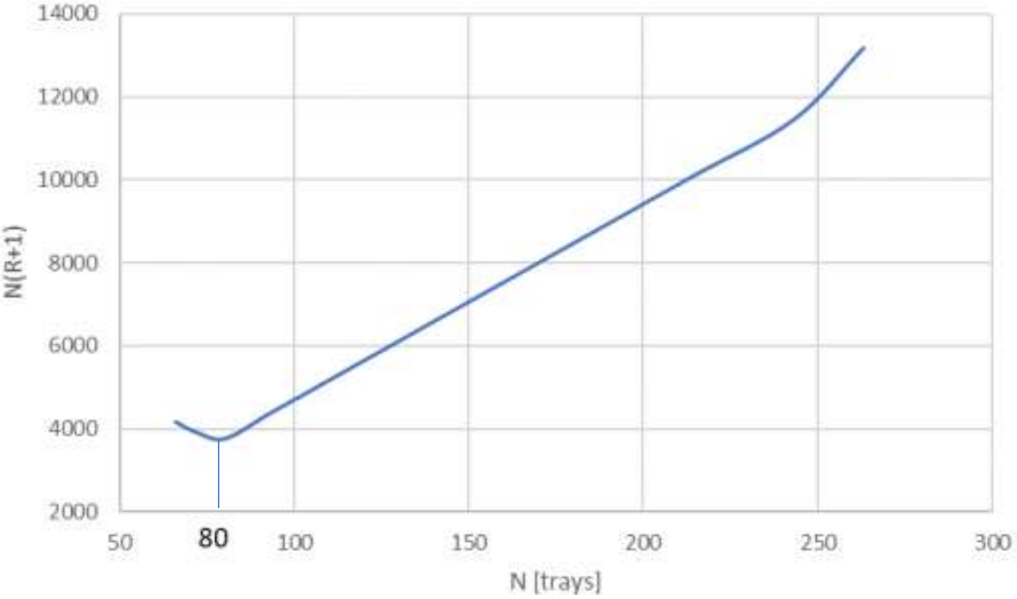


Figure 27. Number of trays determination for DWC

Optimal number of stages required to perform separation was established by gradually decreasing the number of trays for each DWC section, while maintaining product purity. For the majority of points decrease in number of stages did not affect the product purity, however when the number of trays in a column has decreased below 80, reflux ratio had to be significantly increase to maintain desired purity, which lead to increase in value N(R+1). Feed stage was established by performing an analysis of influence of feed stage on ACH purity.

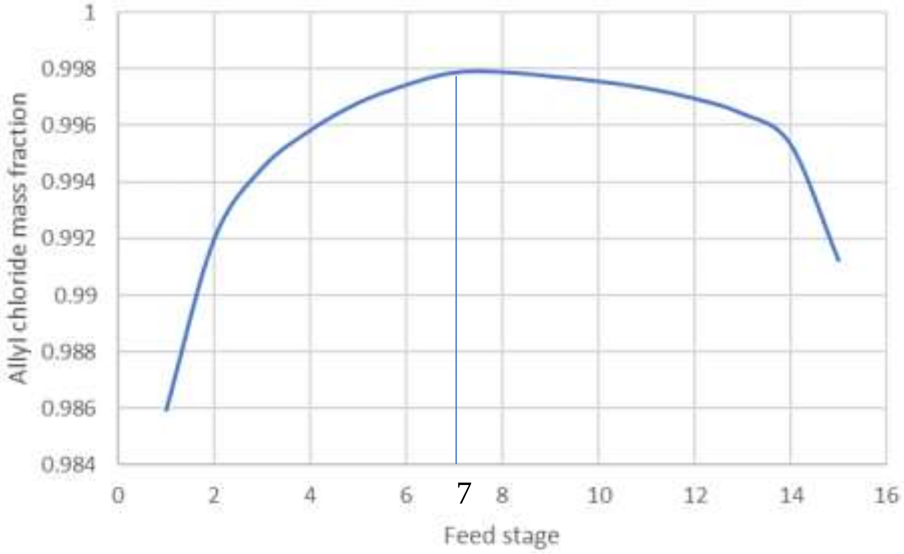


Figure 28. Influence of feed stage on ACH purity

As shown on figure 29 the highest purity can be obtained when feed is provided on 7th tray of the prefractionator, while keeping values of remaining parameters as specified in table 14. Another parameter determined by sensitivity analysis is the stage from which side stream is obtained. The graph obtained to determine proper tray is displayed below:

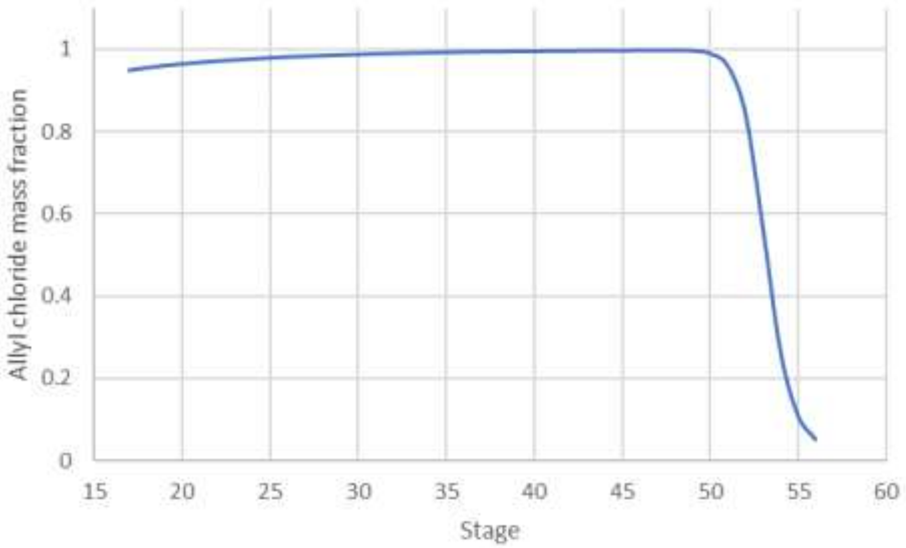


Figure 29. Allyl chloride mass fraction in middle part of main column

As shown on figure 30, DWC provides a wide window of stages from which sidestream can be obtained. However, the highest purity is reported on the 47th tray, therefore this tray was chosen to obtain ACH stream as it provides purity, which meets the requirements mentioned in chapter 3.1. Furthermore, the product purity was plotted as a function of vapour and liquid split value, to ensure that proper values of these parameters were obtained. The results of this analysis are displayed on graphs below.

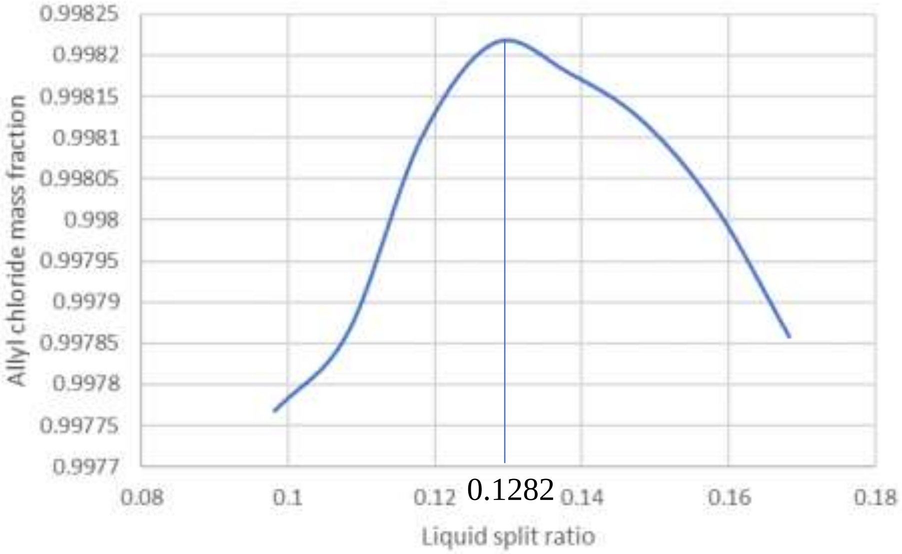


Figure 30. Allyl chloride mass fraction as function of liquid split ratio

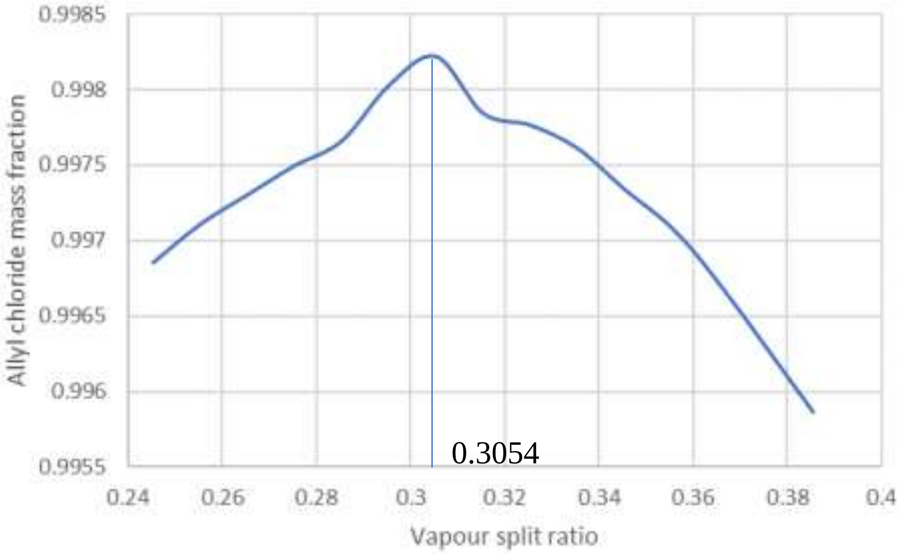


Figure 31. Allyl chloride mass fraction as function of vapour split ratio

As shown on figures 25 and 26, the liquid and vapour splits that offer the best quality of intermediate product are 0.1282 and 0.3054, respectively. To investigate if the dividing wall inside the column has to be insulated to prevent heat transfer through the temperature profile of the column was plotted.

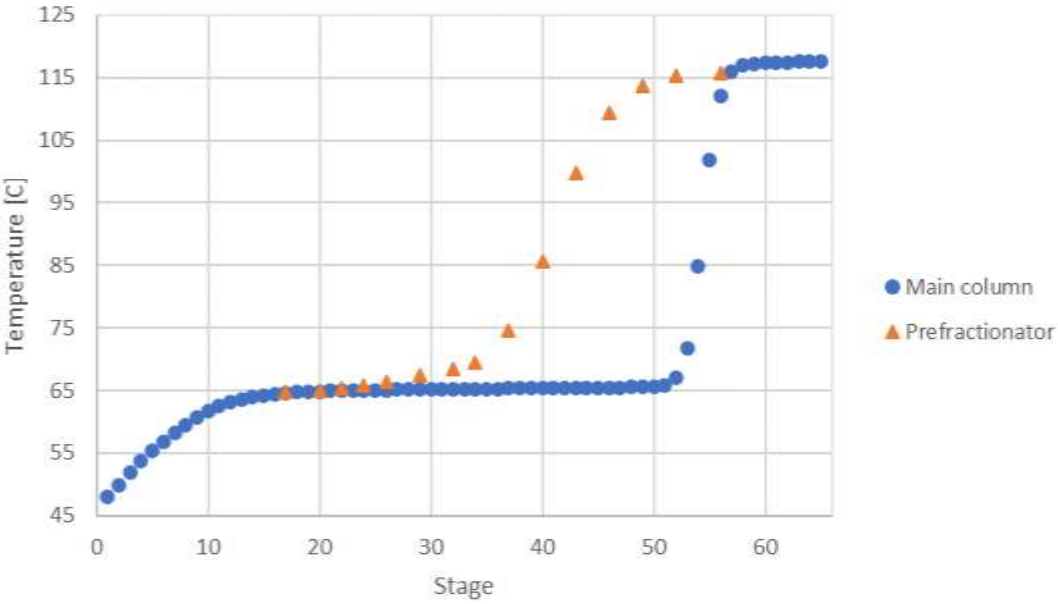


Figure 32. Temperature profile in DWC

Figure 33 depicts temperature profile in both prefractionator and main column. This graph indicates that the temperature difference between these two sections can reach up to 50ºC, meaning the inner wall needs to be insulated to reduce undesired heat transfer between two parts of DWC [70].

To determine the cost of dividing wall column, it's dimensions have to be calculated. Diameter of the column was determined using the correlation for the flooding condition proposed by Prekumar and Rangaiah[71]. This method assumes that vapour flowrate is within 70-90% of flooding velocity. For the purpose of this report value of 80% was chosen. The correlations for the flooding velocity are following:

$$V_{max} = 0.07\sqrt{\frac{\rho_L - \rho_V}{\rho_V}} = 0.916 \tag{38}$$

The active velocity is equal 80% of this value as stated above:

$$V_{act} = 0.8 \cdot V_{max} = 0.733 \tag{39}$$

Column diameter is determined using following equation:

$$D = \sqrt{\frac{4G}{\pi \rho_V V_{act}}} = 1.3\ m \approx 1.4\ m \tag{40}$$

Please note that values of vapour flowrate used in the equation above were taken from the bottom part of the column, because this part has the largest vapour flowrate, which dictates the column diameter. Diameter was round up to closest commercially available column diameter. The height of DWC column can be determined using the same algorithm as for the classical column. Since this column is equipped in structure packing, because it offers lower HETP than trayed and random packed column. Mellapak provided by Sulzer was chosen as most suitable packing, with HETP equal 0.4 m [72].

Total height of packing can be determined by

$$H = N \cdot HETP = 26 \tag{41}$$

Additionally, spacing between top and bottom of distillation column adds, another 3 meters to column height. Moreover spacing between layers of structured packing and liquid redistributors has to be considered. It was assumed that liquid redistributor is required before and after the partition wall and also in the middle of each section of DWC column. Spacing between structured packing layers was assumed to be equal 0.4 m for each liquid distributor. This sums up to total column height of 31 m. The wall thickness and weight of DWC column were calculated in the same manner as normal column.

4.2. Chlorohydrin process

For the traditional process as steam is fed directly to the distillation column it is not considered by Aspen Plus as utility, because it is defined as inlet stream. Therefore in energy requirements calculations the amount of energy carried by this stream was added to amount of energy consumed by the plant determined by simulation programme. The energy equivalent of steam feed to the ECH stripping column is equal 9 MW. This value was calculated based on the steam parameters (7 bar, 165 ºC). Since wastewater production is one of the most significant drawbacks of ECH manufacturing, the economic effect of sewage treatment on plant profitability. Based on results of simulation base case plant produces almost 200 m^3/hr of wastewater which consist of very diluted stream of calcium chloride with some residuals of organic compounds. For the purpose of this report it was assumed that total wastewater stream from base case plant is bottom stream from ECH stripping column, as flowrate of this stream is significantly higher than any other waste stream present in the model. In industrial practice it is crucial to maintain amount of organics in the wastewater as low as possible, because it has drastically negative influence on microorganisms used for wastewater treatment [73]. Several methods for treatment of such stream have been reported however, in the most widely used approach pre-treated wastewater from ECH is sent to the municipal wastewater treatment facility and then discharged to the river [74]. For the purpose of economic evaluation of the process it was assumed that the cost of wastewater treatment is similar to municipal wastewater treatment, because after pre-treatment at chemical plant this stream was send to the municipal wastewater treatment facility [15]. In literature several prices for wastewater treatment costs have been reported, however for the purpose of this thesis the value of 1.48 USD per m^3 was assumed for the plant located in Netherlands, because cost of sewage treatment was available for this location. The annual cost related to wastewater treatment was calculated by multiplying the volumetric flowrate of wastewater by number of hours which plant operates thought whole year. Then this total volume of sewage in m^3 where multiplied by the cost of treatment of one cubic meter of wastewater as stated by the report by United Nations Environment Programme [75]. Raw material prices can be key to plants' profitability, therefore it is important to include their prices in economic analysis of the process. The usage of component was computed by multiplying the raw material flowrate in kg/hr by the annual operational hours of the plant. Then the annual usage of components was multiplied by the raw material pricesin [USD/ton]. The following components were specified as raw material for base case process: propylene, chlorine, milk of lime, water. Prices of products were based on their current market value [76][77].

4.3. HP process

In the HP process, utility usage has been directly retrieved from Aspen Plus simulation. In case of this plant the highest energy consumption was reported by the column used to separate ACH and MeOH from post-epoxidation mixture. This process exhibits significantly lower wastewater production, but the composition of sewage stream my impose specific difficulties during its treatment, as this stream consists of certain amounts of chlorinated organic compounds such as CDP and CMP. However, in case of significantly smaller stream the costs related to the wastewater treatment are almost less significant. The annual cost of this operation was calculated using the same algorithm as for the base case process. In case of this process cost of raw materials is higher than for the base case, due to higher cost of hydrogen peroxide in comparison to chlorine. Although in case of this process chlorine which normally would be used for the production of dichloropropanols can be sold as product instead. Please note that this potential income has not been incorporated into both processes' cost evaluation.

4.4. Comparison between technologies

A comparison of technological parameters for both parameters is displayed in table 15. Values used for this comparison are based on data shown in Appendix B.

Tab. 15 Comparison between chlorohydrin and HP process

Parameter	Base case	HP process	Difference in %
Investment cost [1000 USD]	21687	21139	-2.5
Raw material cost [mln USD]	39.8	51.8	+30
Annual production capacity [tonnes]	34524	39160	+12
Annual sales [mln USD]	82.65	93.95	+14
Annual operating costs [mln USD]	52.04	61.09	+17
Annual profit [mln USD]	30.61	32.86	+7
Amount of produced wastewater [kg/kg pf ECH]	48.29	1.04	-98
Yield [%]	71	78	+10
Atom efficiency in terms of chlorine	0.476	0.895	+88
Energy demand [MJ/kg ECH]	40.28	39.43	-2
CO_2 emissions [kg/kg ECH]	1.17	1.13	-3

The novel route offers slightly lower investment cost, which is mainly caused by the smaller number of distillation columns needed to obtain desired ECH purity. However, the investment cost for HP process is mainly determined by the price of ACH/MeOH column, since its significant dimensions (diameter of 3.4 m and height equal 44 m). Additionally, all supporting equipment for this column also has significant dimensions, as shown in tables 35 and 36 in appendix B. HP route also requires fewer decanters and reactors, which improves the economic parameters of novel process. The most significant improvement has been observed in terms of wastewater formation, as the HP process can reduce amount of produced wastewater by almost 98%. This is important, because it can provide annual savings of nearly 2 mln USD and decrease investment costs for wastewater treatment unit. Please note that CAPEX required for pre-treatment of sewage, before sending to the municipal wastewater treatment plant, since it is outside battery limits for the process. Moreover, a novel route provides higher ECH yield in terms of propylene, which means that less by-products are formed during the processing. This is very important now, since the propylene prices are increasing steadily [78] and this compound is the most expensive raw material used. On the other hand prices of raw materials for novel process are significantly higher than for base case, however it can change considerably, because chlorine prices are strongly dependent on electricity prices, which has been increasing steadily due to shortages on fossil fuel market. Additionally, current geopolitical situation implies that this shortage may continue in the future, which may lead to increased chlorine prices. Moreover, chlorine prices are highly dependent on sodium hydroxide prices because these compounds are both products of brine electrolysis. When caustic soda is in high demand, the chlorine prices tend to go down, but if the chlorine demand is high and energy is expensive, it could have significant negative influence on plant’s profitability. Therefore HP process is more independent from chlorine prices, which may be beneficial, because of reasons described above. The decrease of energy per kg of ECH and CO_2 emission per kg of ECH is mainly caused by improved yield of the process, since the energy consumption for both cases is similar. However, chlorohydrin route is an older process, which was developed and improved over past 60 years, while the hydrogen peroxide route has been only studied as simulations and hasn’t been applied in industry, which implies that there is significant field for optimisation. For example, it can be studied if the ACH reactor effluent can be used as heat source for the ACH/MeOH column. It can provide significant savings, as this column has the highest energy consumption in the whole plant. Another parameter that has been improved by applying the HP process is atom efficiency in chlorine. In the chlorohydrin route all chlorine used in the dichloropropanols formation is not present in the final product. This approach is very inefficient because the solution containing the chlorine atoms cannot be recirculated back to electrolyser and thus has to be discharged as wastewater. In the HP route almost all the chlorine used in the process is transformed to product, either as ECH or HCl and sold to the customer. Please note that HCl formed in the chlorination step also can be sold as product, therefore it was included in calculations of overall atom efficiency of the process.

Overall novel route offers higher profits than classical process, even with significantly higher raw material prices. Furthermore, due to reasons described above the profitability of the plant may increase in the future.

4.5. Influence of DWC

Dividing wall column distillation can be applied to both traditional and novel process of ECH production. For both processes DWC column offers about 5% savings in investment cost for the whole plant, while maintaining desired purity of ACH. Thanks to this technology and introduction of structured packing, two columns with significant dimensions were replaced by one apparatus with more compact dimensions. This change may significantly impact the plant’s profitability, since reduced investment cost can provide shorter payback time for the plant. Additionally more compact design will require less area, which can provide further investment cost savcosts. Figures 31 depicts DWC’s influence on plants’ energy requirements.

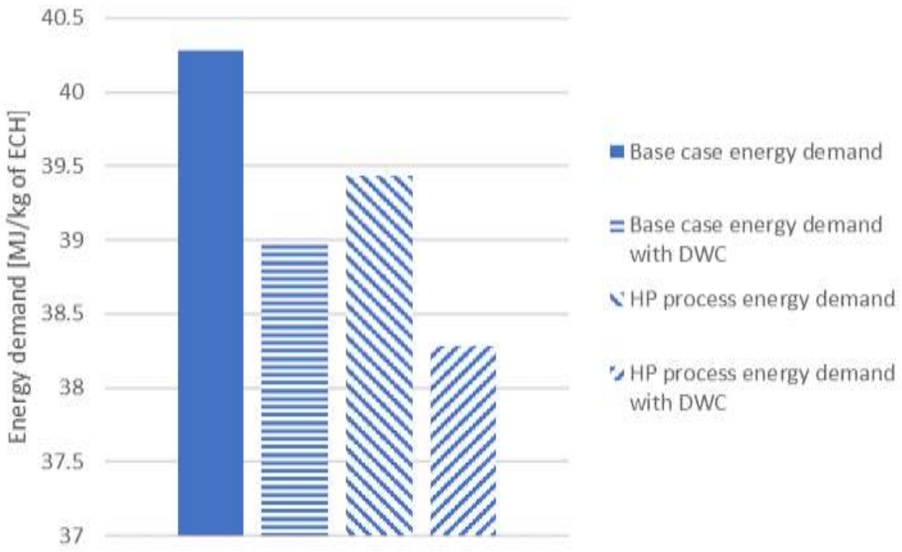


Figure 33. Energy requirements for given cases

As shown above, a decrease in operational cost is also possible with DWC applied. However, the savings in this matter does not exceed 5% of total energy consumption, which translates to about 390 000 USD savings per year. This value may not seem significant, but for the plants with higher production capacity this may lead to substantial decrease in OPEX. Influence of DWC on CAPEX is shown on figure below.

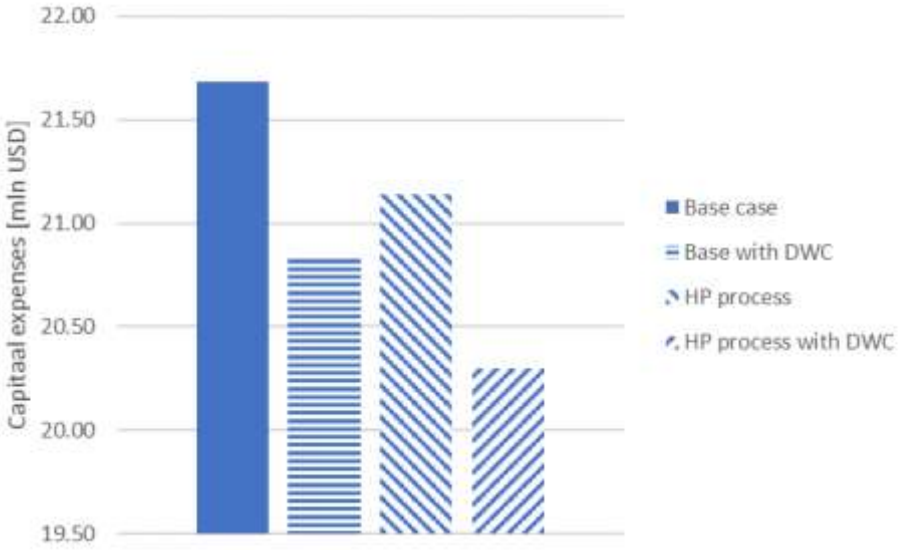


Figure 34. Influence of DWC on capital expenses

Application of this distillation technique can lead to decrease in capital expenses equal to about 4%. This change is mainly caused by reduced number of columns and supporting equipment in ACH section of the plant.

5. Conclusions

This report concluded that oxidation based epoxidation reaction of ACH to ECH is possible when using methanol as solvent. This may have significant impact on future plants and process profitability, since methanol is one of the most common chemical compounds used in the chemical industry. This implies that this compound is easily accessible and cheap, which makes it very suitable for the industrial applications. Additionally proposed separation scheme simplifies the purification of ECH and enables higher purities than sequences discussed in the literature.

The comparison between two different processes of ECH production strongly indicates that HP process can provide significant savings, equal 98% in wastewater production, while also achieving lower energy consumption and carbon dioxide emission per tonne of product. This can be beneficial for the future ECH, plants, as it will not be so dependent on proximity of wastewater treatment unit. Additionally reduced amount of sewage implies that not only operational costs connected to wastewater treatment can decrease, but also significant savings in CAPEX for this purpose can be reported for this route, however exact number has not been established in this report, as wastewater treatment is outside battery limits for given process.

Another important advantage of novel route is an increase in ECH yield from 71% to 78% with respect to propylene. Importance of this parameter is crucial for profitability of current and future ECH, since propylene market is expected to experience fluctuations caused by global macroeconomic situation. Introduction of novel epoxidation reaction has significantly limited by-products formation on this stage, however selectivity of propylene chlorination can be improved to achieve higher yields. As chlorination of propylene is an equilibrium reaction, it may be beneficial to recycle some amounts of both light and heavy by-products back to chlorination reactor to shift the equilibrium towards ACH.

Application of DWC has not introduced savings which would allow to achieve goal mentioned in the introduction as energy consumption with applied DWC was lower by 3.5% instead of 5%. When compared to the original two-column setup DWC offers 34% savings in comparison to the classic approach. This is equal about 390 000 USD less spent on utilities and carbon emissions per year. However, the savings provided by introduction of this unit could be beneficial for plants, with higher production capacities. Exact window of DWC application to this process can be investigated. Additionally, CAPEX of the plant has decreased almost by 5 % which, means that optimisation goal was almost met for this parameter. This can lead to more straightforward implementation of novel route, because of shorter payback time.

Furthermore, the atom efficiency of the process in terms of chlorine has increased by 88% to 0.895. This change has significant impact on profitability of the whole chemical complex, since chlorine which would be used for chlorination reaction can be sold and therefore generate additional profit. Another benefit of the process is increase in production capacity equal 13%. This also indicates that in case of novel process, less by-products is formed in epoxidation step.

Additionally, the hydrogen peroxide route can be partly retrofitted to existing ECH plants based on chlorohydrin route, which would further decrease the investment cost of such plant. Since both plants use the same intermediate product, only the ECH part of the traditional plant can be replaced by the novel route, while leaving the ACH part from the old process. This approach appears to be the most profitable solution, as only about 55% of investment costs, which translates to about 11 mln USD, is required to perform this modification, while in the same time, this plant will benefit from every improvement provided by the novel process.

Finally, it was established that the raw material costs for the novel route are 30% higher than ones for traditional process. Currently ,it decreases the profitability, but in the future chlorine market can undergo significant fluctuations in EU due to imposed quota on CO_2 emissions, which can significantly increase the electricity and therefore chlorine prices. Proper market analysis of the chlorine and other product should be conducted to establish the profitability window for the novel process. Additionally ,as novel routes to produce hydrogen oxide are being investigated its price is expected to decrease in future, further promoting oxidation route

6. Future recommendations

As the formation of explosive mixture of ACH/MeOH and hydrogen peroxide presents possible threat to plant safe operation it is essential to establish proper control strategy for this plant. Special attention should be paid to the DWC column, epoxidation reactor and ACH/MeOH column as these three pieces of equipment operate in series. Dividing wall column should maintain desired purity of ACH to prevent light chlorinated compounds from entering reactor as well as above mentioned distillation column, because this may lead to formation of other explosive mixtures.

Additionally, further optimisation of the plant can be performed, to reduce operating cost of Hydrogen peroxide plant. The complexity of the studied process indicates that the best results may be obtained using the superstructure approach. This technique can provide good overview on the overall plant's performance, therefore enabling proper optimisation.

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Appendix A

Tab. 16 List of components for base case process

Component ID	Type	Component name	Alias
PROPENE	Conventional	PROPYLENE	C3H6-2
CHLORINE	Conventional	CHLORINE	CL2
WATER	Conventional	WATER	H2O
ETHANE	Conventional	ETHANE	C2H6
PROPANE	Conventional	PROPANE	C3H8
MCPROPAN	Conventional	ISOPROPYL-CHLORIDE	
MCPROPEN	Conventional	2-CHLOROPROPENE	C3H5CL-D0
ACH	Conventional	ALLYL-CHLORIDE	C3H5CL
12DCP	Conventional	1,2-DICHLOROPROPANE	C3H6CL2
DCPROPEN	Conventional	2,3-DICHLOROPROPENE	C3H4CL2
13DCPOL	Conventional	1,3-DICHLORO-2-PROPANOL	C3H6CL2O-D1
23DCPOL	Conventional	2,3-DICHLORO-1-PROPANOL	C3H6CL2O-D2
TCP	Conventional	1,2,3-TRICHLOROPROPANE	C3H5CL3
ECH	Conventional	ALPHA-EPICHLOROHYDRIN	C3H5CLO
CAOH2	Conventional	CALCIUM-HYDROXIDE	CA(OH)2
CACL2	Conventional	CALCIUM-CHLORIDE	CACL2
NITROGEN	Conventional	NITROGEN	N2
HCLO	Conventional	HYPOCHLOROUS-ACID	HCLO

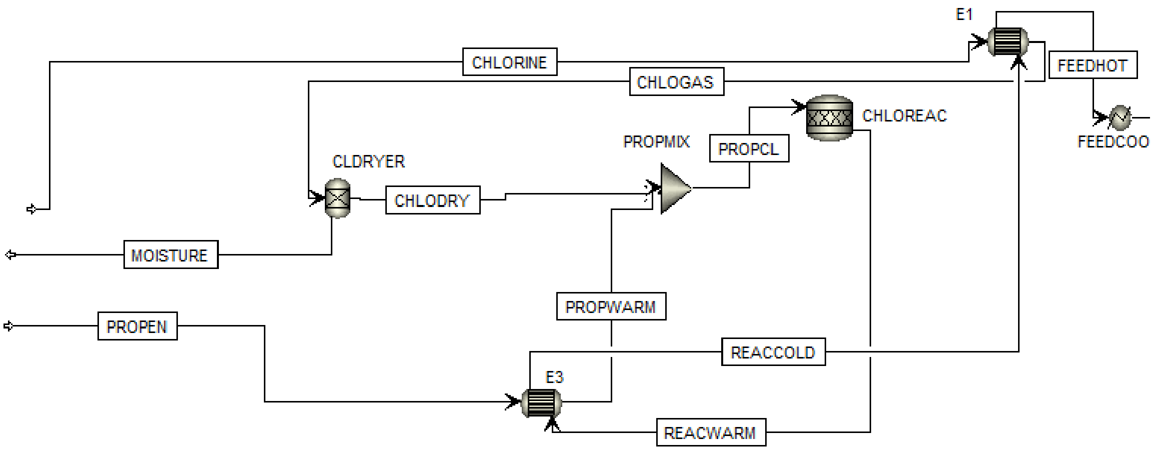

Figure 35. Layout of chlorination section for base case process

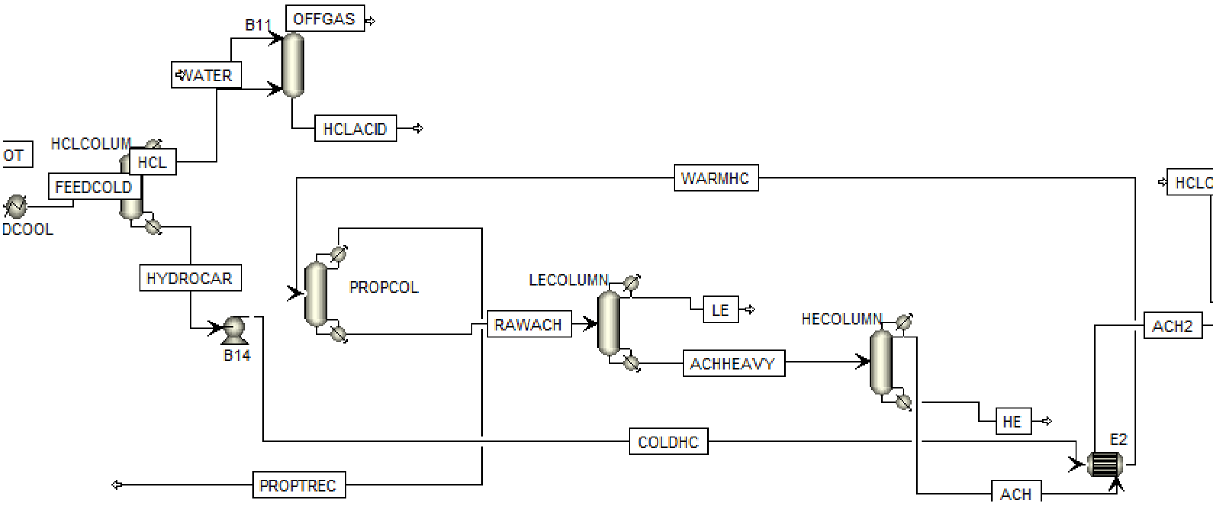

Figure 36. Layout of ACH purification section

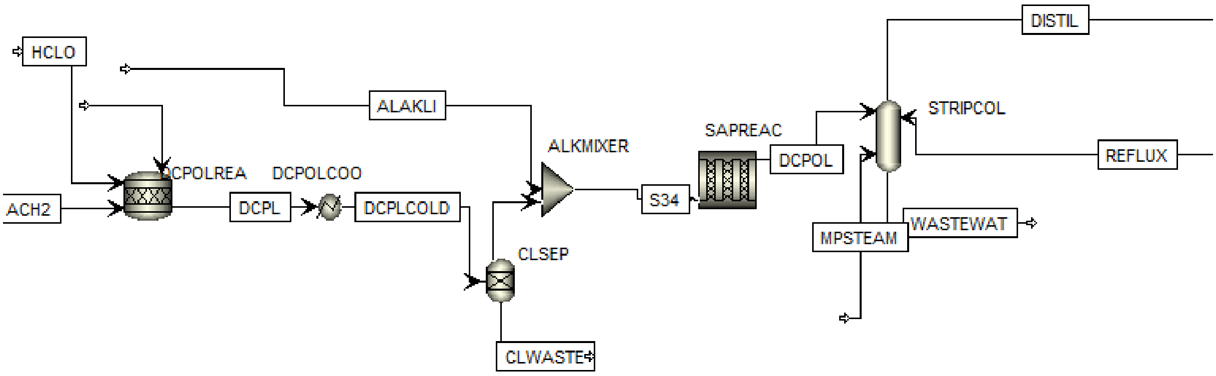

Figure 37. Hydrochlorination part of ECH plant

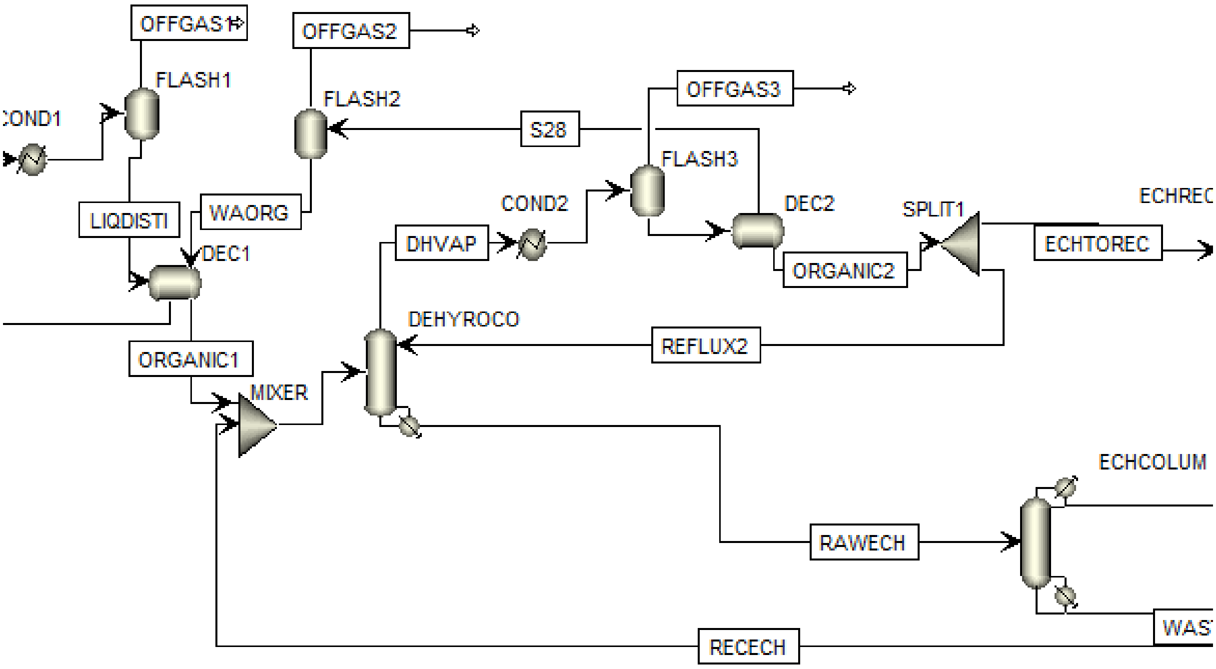

Figure 38. Purification of ECH

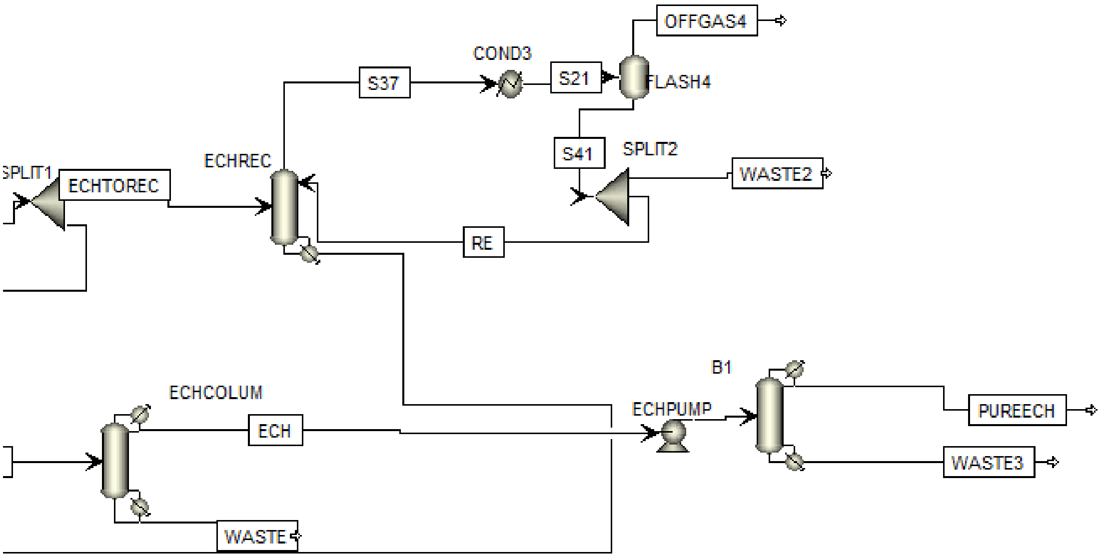

Figure 39. Final stage of ECH purification

Tab. 17. Stream summary for base case process

Mass Flow kg/hr	ACH	ACH2	ACHHEAVY	ALAKLI	CHLODRY	CHLOGAS
CHLORINE	0.00	0.00	0.00	0.00	4446.60	4446.60
WATER	0.00	0.00	0.00	14320.32	0.00	0.20
MCPROPAN	0.40	0.40	0.40	0.00	0.00	0.00
ACH	3974.51	3974.51	3975.60	0.00	0.00	0.00
12DCP	0.42	0.42	401.66	0.00	0.00	0.00
DCPROPEN	0.73	0.73	262.51	0.00	0.00	0.00
CAOH2	0.00	0.00	0.00	3580.08	0.00	0.00
NITROGEN	0.00	0.00	0.00	0.00	8.70	8.70
Mass Frac						
CHLORINE	0.0000	0.0000	0.0000	0.0000	0.9980	0.9980
WATER	0.0000	0.0000	0.0000	0.8000	0.0000	0.0000
MCPROPAN	0.0001	0.0001	0.0001	0.0000	0.0000	0.0000
ACH	0.9996	0.9996	0.8568	0.0000	0.0000	0.0000
12DCP	0.0001	0.0001	0.0866	0.0000	0.0000	0.0000
DCPROPEN	0.0002	0.0002	0.0566	0.0000	0.0000	0.0000
CAOH2	0.0000	0.0000	0.0000	0.2000	0.0000	0.0000
NITROGEN	0.0000	0.0000	0.0000	0.0000	0.0020	0.0020
Total Flow kmol/hr	51.95	51.95	57.88	843.22	63.02	63.03
Total Flow kg/hr	3976.06	3976.06	4640.17	17900.40	4455.30	4455.50
Total Flow cum/hr	4.43	4.30	5.27	29.37	417.51	417.58
Temperature C	49.93	30.00	80.21	80.00	72.78	72.78
Pressure bar	1.18	1.18	2.60	0.45	4.20	4.20
Vapor Frac	0.00	0.00	0.00	0.00	1.00	1.00
Liquid Frac	1.00	1.00	1.00	1.00	0.00	0.00
Solid Frac	0.00	0.00	0.00	0.00	0.00	0.00
Enthalpy kcal/mol	-6.59	-7.22	-8.41	-72.12	0.33	0.32
Enthalpy kcal/kg	-86.05	-94.31	-104.85	-3397.35	4.68	4.53
Enthalpy Gcal/hr	-0.34	-0.37	-0.49	-60.81	0.02	0.02

Entropy cal/mol-K	-55.49	-57.57	-53.75	-23.06	-1.66	-1.66
Entropy cal/gm-K	-0.73	-0.75	-0.67	-1.09	-0.02	-0.02
Density kmol/cum	11.73	12.08	10.99	28.71	0.15	0.15
Density kg/cum	897.81	924.44	881.00	609.52	10.67	10.67
Average MW	76.53	76.53	80.17	21.23	70.69	70.68
Liq Vol 60F cum/hr	4.27	4.27	4.84	28.79	3.21	3.21

Tab. 18. Stream summary for base case process

Mass Flow kg/hr	CHLORINE	CHLORINE	CLWASTE	COLDHC	DCPL	DCPLCOLD	DCPOL
PROPENE	0.00	0.00	0.00	11215.90	0.00	0.00	0.00
CHLORINE	4446.60	4446.60	60.65	0.03	60.65	60.65	0.00
WATER	0.20	0.20	0.00	0.00	134649.00	134649.00	149129.00
HCL	0.00	0.00	0.00	10.80	1747.04	1747.04	1747.04
PROPANE	0.00	0.00	0.00	6.70	0.00	0.00	0.00
MCPROPAN	0.00	0.00	0.00	131.61	0.40	0.40	0.40
MCPROPEN	0.00	0.00	0.00	188.57	0.00	0.00	0.00
ACH	0.00	0.00	0.00	3976.33	81.48	81.48	81.48
12DCP	0.00	0.00	0.00	401.66	0.42	0.42	0.42
DCPROPEN	0.00	0.00	0.00	262.51	0.73	0.73	0.73
13DCPOL	0.00	0.00	0.00	0.00	2083.43	2083.43	1707.19
23DCPOL	0.00	0.00	0.00	0.00	4223.80	4223.80	3458.56
TCP	0.00	0.00	0.00	0.00	290.97	290.97	290.97
ECH	0.00	0.00	0.00	0.00	0.00	0.00	818.82
CAOH2	0.00	0.00	0.00	0.00	0.00	0.00	3252.23
CACL2	0.00	0.00	0.00	0.00	0.00	0.00	491.08
NITROGEN	8.70	8.70	0.00	0.00	32.45	32.45	32.45
HCLO	0.00	0.00	18.23	0.00	18.23	18.23	0.00
Mass Frac							
PROPENE	0.0000	0.0000	0.0000	0.6926	0.0000	0.0000	0.0000
CHLORINE	0.9980	0.9980	0.7689	0.0000	0.0004	0.0004	0.0000
WATER	0.0000	0.0000	0.0000	0.0000	0.9404	0.9404	0.9262
HCL	0.0000	0.0000	0.0000	0.0007	0.0122	0.0122	0.0109
PROPANE	0.0000	0.0000	0.0000	0.0004	0.0000	0.0000	0.0000
MCPROPAN	0.0000	0.0000	0.0000	0.0081	0.0000	0.0000	0.0000
MCPROPEN	0.0000	0.0000	0.0000	0.0116	0.0000	0.0000	0.0000
ACH	0.0000	0.0000	0.0000	0.2455	0.0006	0.0006	0.0005
12DCP	0.0000	0.0000	0.0000	0.0248	0.0000	0.0000	0.0000
DCPROPEN	0.0000	0.0000	0.0000	0.0162	0.0000	0.0000	0.0000
13DCPOL	0.0000	0.0000	0.0000	0.0000	0.0146	0.0146	0.0106
23DCPOL	0.0000	0.0000	0.0000	0.0000	0.0295	0.0295	0.0215
TCP	0.0000	0.0000	0.0000	0.0000	0.0020	0.0020	0.0018
ECH	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0051
CAOH2	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0202

CACL2	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0031
NITROGEN	0.0020	0.0020	0.0000	0.0000	0.0002	0.0002	0.0002
HCLO	0.0000	0.0000	0.2311	0.0000	0.0001	0.0001	0.0000
Total Flow kmol/hr	63.03	63.03	1.20	329.00	7576.40	7576.40	8427.26
Total Flow kg/hr	4455.50	4455.50	78.88	16194.12	143189.00	143189.00	161010.00
Total Flow cum/hr	3.02	3.02	23.09	23.95	142.73	144.43	1148.29
Temperature C	-5.00	-5.00	63.00	-25.78	40.00	63.00	74.00
Pressure bar	4.20	4.20	1.00	6.50	1.10	1.00	0.70
Vapor Frac	0.00	0.00	0.69	0.00	0.00	0.00	0.00
Liquid Frac	1.00	1.00	0.31	1.00	1.00	1.00	1.00
Solid Frac	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Enthalpy kcal/mol	-4.82	-4.82	-7.21	-2.50	-67.80	-67.37	-67.63
Enthalpy kcal/kg	-68.21	-68.21	-109.98	-50.76	-3587.36	-3564.84	-3539.55
Enthalpy Gcal/hr	-0.30	-0.30	-0.01	-0.82	-513.67	-510.45	-569.90
Entropy cal/mol-K	-20.12	-20.12	55.86	-56.37	-38.20	-36.90	-34.98
Entropy cal/gm-K	-0.28	-0.28	0.85	-1.15	-2.02	-1.95	-1.83
Density kmol/cum	20.85	20.85	0.05	13.74	53.08	52.46	7.34
Density kg/cum	1473.69	1473.69	3.42	676.23	1003.19	991.43	140.22
Average MW	70.68	70.68	65.58	49.22	18.90	18.90	19.11
Liq Vol 60F cum/hr	3.21	3.21	0.06	26.78	142.57	142.57	170.19

Tab. 19. Stream summary for base case process

Mass Flow kg/hr	DHVAP	DISTIL	ECH	ECHTOREC	FEEDCOLD	FEEDHOT
PROPENE	0.00	0.00	0.00	0.00	11215.90	11215.90
CHLORINE	0.00	0.00	0.00	0.00	0.03	0.03
WATER	85.45	16319.04	0.00	9.25	0.00	0.00
HCL	0.00	0.00	0.00	0.00	2295.28	2295.28
ETHANE	0.00	0.00	0.00	0.00	1.00	1.00
PROPANE	0.00	0.00	0.00	0.00	6.70	6.70
MCPROPAN	0.57	0.42	0.00	0.28	131.61	131.61
MCPROPEN	0.00	0.00	0.00	0.00	188.57	188.57
ACH	120.99	181.22	0.00	60.16	3976.33	3976.33
12DCP	0.38	0.43	0.18	0.23	401.66	401.66
DCPROPEN	0.64	0.79	0.33	0.39	262.51	262.51
13DCPOL	0.00	23.84	0.01	0.00	0.00	0.00
23DCPOL	0.00	222.79	0.00	0.00	0.00	0.00
TCP	0.06	295.22	45.75	0.04	0.00	0.00
ECH	561.87	5557.28	4153.15	344.12	0.00	0.00
NITROGEN	36.04	127.76	0.00	5.53	8.70	8.70

HCLO	0.00	0.00	0.00	0.00	0.00	0.00
Mass Frac						
PROPENE	0.0000	0.0000	0.0000	0.0000	0.6066	0.6066
CHLORINE	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
WATER	0.1060	0.7180	0.0000	0.0220	0.0000	0.0000
HCL	0.0000	0.0000	0.0000	0.0000	0.1241	0.1241
ETHANE	0.0000	0.0000	0.0000	0.0000	0.0001	0.0001
PROPANE	0.0000	0.0000	0.0000	0.0000	0.0004	0.0004
MCPROPAN	0.0007	0.0000	0.0000	0.0007	0.0071	0.0071
MCPROPEN	0.0000	0.0000	0.0000	0.0000	0.0102	0.0102
ACH	0.1501	0.0080	0.0000	0.1432	0.2151	0.2151
12DCP	0.0005	0.0000	0.0000	0.0005	0.0217	0.0217
DCPROPEN	0.0008	0.0000	0.0001	0.0009	0.0142	0.0142
13DCPOL	0.0000	0.0010	0.0000	0.0000	0.0000	0.0000
23DCPOL	0.0000	0.0098	0.0000	0.0000	0.0000	0.0000
TCP	0.0001	0.0130	0.0109	0.0001	0.0000	0.0000
ECH	0.6971	0.2445	0.9890	0.8193	0.0000	0.0000
NITROGEN	0.0447	0.0056	0.0000	0.0132	0.0005	0.0005
HCLO	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
Total Flow kmol/hr	13.70	976.77	45.20	5.23	392.00	392.00
Total Flow kg/hr	806.00	22728.79	4199.42	420.00	18488.30	18488.30
Total Flow cum/hr	785.17	68662.42	3.76	3.81	1805.86	7601.46
Temperature C	74.51	74.85	70.58	16.78	-29.00	220.00
Pressure bar	0.50	0.41	0.20	1.00	2.00	2.10
Vapor Frac	1.00	1.00	0.00	0.03	0.47	1.00
Liquid Frac	0.00	0.00	1.00	0.97	0.53	0.00
Solid Frac	0.00	0.00	0.00	0.00	0.00	0.00
Enthalpy kcal/mol	-30.72	-54.94	-34.14	-33.24	-4.44	2.54
Enthalpy kcal/kg	-522.25	-2361.24	-367.48	-413.59	-94.13	53.93
Enthalpy Gcal/hr	-0.42	-53.67	-1.54	-0.17	-1.74	1.00
Entropy cal/mol-K	-27.00	-9.96	-77.67	-71.08	-41.64	-19.62
Entropy cal/gm-K	-0.46	-0.43	-0.84	-0.88	-0.88	-0.42
Density kmol/cum	0.02	0.01	12.03	1.37	0.22	0.05
Density kg/cum	1.03	0.33	1117.75	110.17	10.24	2.43
Average MW	58.83	23.27	92.90	80.37	47.16	47.16
Liq Vol 60F cum/hr	0.76	21.92	3.57	0.38	30.16	30.16

Tab. 20. Stream summary for base case process

Mass Flow kg/hr	HCL	HCLACID	HCLO	HE	HYDROCAR	LE
PROPENE	0.00	0.00	0.00	0.00	11215.90	0.00
CHLORINE	0.00	0.00	60.65	0.00	0.03	0.00
WATER	0.00	2580.51	97938.01	0.00	0.00	0.00
HCL	2284.48	1053.26	1819.00	0.00	10.80	0.00
ETHANE	1.00	0.02	0.00	0.00	0.00	0.00

PROPANE	0.00	0.00	0.00	0.00	6.70	0.00
MCPROPAN	0.00	0.00	0.00	0.00	131.61	131.21
MCPROPEN	0.00	0.00	0.00	0.00	188.57	186.62
ACH	0.00	0.00	0.00	1.09	3976.33	0.73
12DCP	0.00	0.00	0.00	401.24	401.66	0.00
DCPROPEN	0.00	0.00	0.00	261.78	262.51	0.00
NITROGEN	8.70	0.41	32.45	0.00	0.00	0.00
HCLO	0.00	0.00	2687.00	0.00	0.00	0.00
Mass Frac						
PROPENE	0.0000	0.0000	0.0000	0.0000	0.6926	0.0000
CHLORINE	0.0000	0.0000	0.0006	0.0000	0.0000	0.0000
WATER	0.0000	0.7101	0.9551	0.0000	0.0000	0.0000
HCL	0.9958	0.2898	0.0177	0.0000	0.0007	0.0000
ETHANE	0.0004	0.0000	0.0000	0.0000	0.0000	0.0000
PROPANE	0.0000	0.0000	0.0000	0.0000	0.0004	0.0000
MCPROPAN	0.0000	0.0000	0.0000	0.0000	0.0081	0.4119
MCPROPEN	0.0000	0.0000	0.0000	0.0000	0.0116	0.5858
ACH	0.0000	0.0000	0.0000	0.0016	0.2455	0.0023
12DCP	0.0000	0.0000	0.0000	0.6042	0.0248	0.0000
DCPROPEN	0.0000	0.0000	0.0000	0.3942	0.0162	0.0000
NITROGEN	0.0038	0.0001	0.0003	0.0000	0.0000	0.0000
HCLO	0.0000	0.0000	0.0262	0.0000	0.0000	0.0000
Total Flow kmol/hr	63.00	172.14	5539.51	5.92	329.00	4.12
Total Flow kg/hr	2294.18	3634.20	102537.00	664.12	16194.12	318.55
Total Flow cum/hr	1.97	3.57	102.55	0.67	23.92	0.38
Temperature C	-79.91	-44.81	20.00	129.74	-26.32	47.07
Pressure bar	1.55	1.20	0.22	2.58	2.00	1.90
Vapor Frac	0.00	0.00	0.00	0.00	0.00	0.00
Liquid Frac	1.00	1.00	1.00	1.00	1.00	1.00
Solid Frac	0.00	0.00	0.00	0.00	0.00	0.00
Enthalpy kcal/mol	-26.47	-62.20	-67.55	-31.19	-2.51	-22.39
Enthalpy kcal/kg	-726.82	-2946.42	-3649.39	-278.26	-51.05	-289.47
Enthalpy Gcal/hr	-1.67	-10.71	-374.20	-0.18	-0.83	-0.09
Entropy cal/mol-K	-20.86	-39.05	-35.85	-66.09	-56.42	-66.25
Entropy cal/gm-K	-0.57	-1.85	-1.94	-0.59	-1.15	-0.86
Density kmol/cum	32.02	48.18	54.02	8.85	13.75	10.97
Density kg/cum	1165.94	1017.11	999.84	992.28	676.91	848.20
Average MW	36.42	21.11	18.51	112.10	49.22	77.34
Liq Vol 60F cum/hr	3.38	4.13	103.56	0.57	26.78	0.36

Tab. 21. Stream summary for base case process

Mass Flow kg/hr	LIQDISTI	MOISTURE	MPSTEAM	OFFGAS	OFFGAS2
WATER	16319.04	0.20	16000.00	31.19	0.02
HCL	0.00	0.00	0.00	1231.23	0.00
ETHANE	0.00	0.00	0.00	0.98	0.00
PROPANE	0.00	0.00	0.00	0.00	0.00

MCPROPAN	0.42	0.00	0.00	0.00	0.00
MCPROPEN	0.00	0.00	0.00	0.00	0.00
ACH	181.22	0.00	0.00	0.00	0.79
12DCP	0.43	0.00	0.00	0.00	0.00
DCPROPEN	0.79	0.00	0.00	0.00	0.00
13DCPOL	23.84	0.00	0.00	0.00	0.00
23DCPOL	222.79	0.00	0.00	0.00	0.00
TCP	295.22	0.00	0.00	0.00	0.00
ECH	5557.28	0.00	0.00	0.00	0.08
NITROGEN	127.76	0.00	0.00	8.29	0.74
Mass Frac					
WATER	0.7180	1.0000	1.0000	0.0245	0.0143
HCL	0.0000	0.0000	0.0000	0.9682	0.0000
ETHANE	0.0000	0.0000	0.0000	0.0008	0.0000
MCPROPAN	0.0000	0.0000	0.0000	0.0000	0.0004
MCPROPEN	0.0000	0.0000	0.0000	0.0000	0.0000
ACH	0.0080	0.0000	0.0000	0.0000	0.4819
12DCP	0.0000	0.0000	0.0000	0.0000	0.0001
DCPROPEN	0.0000	0.0000	0.0000	0.0000	0.0001
13DCPOL	0.0010	0.0000	0.0000	0.0000	0.0000
23DCPOL	0.0098	0.0000	0.0000	0.0000	0.0000
TCP	0.0130	0.0000	0.0000	0.0000	0.0000
ECH	0.2445	0.0000	0.0000	0.0000	0.0482
NITROGEN	0.0056	0.0000	0.0000	0.0065	0.4550
Total Flow kmol/hr	976.77	0.01	888.14	35.83	0.04
Total Flow kg/hr	22728.79	0.20	16000.00	1271.69	1.63
Total Flow cum/hr	21.92	0.00	4472.68	888.70	0.96
Temperature C	20.00	72.78	165.00	32.74	26.00
Pressure bar	1.00	4.20	7.00	1.02	1.00
Vapor Frac	0.00	0.00	1.00	1.00	1.00
Liquid Frac	1.00	1.00	0.00	0.00	0.00
Solid Frac	0.00	0.00	0.00	0.00	0.00
Enthalpy kcal/mol	-65.83	-67.41	-56.70	-23.54	-2.54
Enthalpy kcal/kg	-2829.17	-3741.76	-3147.13	-663.34	-60.54
Enthalpy Gcal/hr	-64.30	0.00	-50.35	-0.84	0.00
Entropy cal/mol-K	-41.85	-36.31	-11.43	2.35	-9.29
Entropy cal/gm-K	-1.80	-2.02	-0.63	0.07	-0.22
Density kmol/cum	44.56	54.19	0.20	0.04	0.04
Density kg/cum	1036.96	976.22	3.58	1.43	1.69
Average MW	23.27	18.02	18.02	35.49	41.91
Liq Vol 60F cum/hr	21.92	0.00	16.03	1.86	0.00

Tab. 22. Stream summary for base case process

Mass Flow kg/hr	OFFGAS3	OFFGAS4	ORGANIC1	ORGANIC2	PROPCL	PROPEN
PROPENE	0.00	0.00	0.00	0.00	13825.80	13825.80
CHLORINE	0.00	0.00	0.00	0.00	4446.60	0.00

WATER	1.00	0.09	79.86	14.85	0.00	0.00
HCL	0.00	0.00	0.00	0.00	199.50	199.50
ETHANE	0.00	0.00	0.00	0.00	1.00	1.00
PROPANE	0.00	0.00	0.00	0.00	6.70	6.70
MCPROPAN	0.12	0.04	0.40	0.44	0.00	0.00
ACH	20.53	4.90	84.59	96.56	0.00	0.00
12DCP	0.01	0.00	0.42	0.37	0.00	0.00
DCPROPEN	0.00	0.00	0.73	0.63	0.00	0.00
13DCPOL	0.00	0.00	20.44	0.00	0.00	0.00
23DCPOL	0.00	0.00	163.70	0.00	0.00	0.00
TCP	0.00	0.00	290.97	0.06	0.00	0.00
ECH	2.51	0.25	4192.87	552.36	0.00	0.00
NITROGEN	26.18	3.74	32.70	8.88	8.70	0.00
Mass Frac						
PROPENE	0.0000	0.0000	0.0000	0.0000	0.7478	0.9852
CHLORINE	0.0000	0.0000	0.0000	0.0000	0.2405	0.0000
WATER	0.0198	0.0096	0.0164	0.0220	0.0000	0.0000
HCL	0.0000	0.0000	0.0000	0.0000	0.0108	0.0142
ETHANE	0.0000	0.0000	0.0000	0.0000	0.0001	0.0001
PROPANE	0.0000	0.0000	0.0000	0.0000	0.0004	0.0005
MCPROPAN	0.0024	0.0050	0.0001	0.0007	0.0000	0.0000
ACH	0.4078	0.5433	0.0174	0.1432	0.0000	0.0000
12DCP	0.0001	0.0003	0.0001	0.0005	0.0000	0.0000
DCPROPEN	0.0001	0.0002	0.0001	0.0009	0.0000	0.0000
13DCPOL	0.0000	0.0000	0.0042	0.0000	0.0000	0.0000
23DCPOL	0.0000	0.0000	0.0336	0.0000	0.0000	0.0000
TCP	0.0000	0.0000	0.0598	0.0001	0.0000	0.0000
ECH	0.0498	0.0273	0.8615	0.8193	0.0000	0.0000
NITROGEN	0.5199	0.4143	0.0067	0.0132	0.0005	0.0000
Total Flow kmol/hr	1.29	0.21	55.44	8.39	397.23	334.21
Total Flow kg/hr	50.35	9.02	4866.66	674.15	18488.30	14033.00
Total Flow cum/hr	31.87	4.98	4.14	0.61	4697.08	1372.99
Temperature C	26.00	20.00	20.00	20.00	328.25	45.00
Pressure bar	1.00	1.00	1.00	1.00	4.20	6.00
Vapor Frac	1.00	1.00	0.00	0.00	1.00	1.00
Liquid Frac	0.00	0.00	1.00	1.00	0.00	0.00
Solid Frac	0.00	0.00	0.00	0.00	0.00	0.00
Enthalpy kcal/mol	-3.10	-1.90	-39.08	-33.24	9.31	4.57
Enthalpy kcal/kg	-79.27	-43.26	-445.12	-413.59	199.97	108.80
Enthalpy Gcal/hr	0.00	0.00	-2.17	-0.28	3.70	1.53
Entropy cal/mol-K	-7.51	-10.78	-77.72	-71.14	-17.19	-35.98
Entropy cal/gm-K	-0.19	-0.25	-0.89	-0.89	-0.37	-0.86
Density kmol/cum	0.04	0.04	13.39	13.83	0.08	0.24
Density kg/cum	1.58	1.81	1175.69	1111.25	3.94	10.22
Average MW	39.12	43.89	87.79	80.37	46.54	41.99
Liq Vol 60F cum/hr	0.08	0.01	4.15	0.61	30.08	26.87

Tab. 23. Stream summary for base case process

Mass Flow kg/hr	PROPTREC	PROPWARM	PUREECH	RAWACH	RAWECH	RE
PROPENE	11215.90	13825.80	0.00	0.00	0.00	0.00
WATER	0.00	0.00	0.00	0.00	0.00	82.46
HCL	10.80	199.50	0.00	0.00	0.00	0.00
ETHANE	0.00	1.00	0.00	0.00	0.00	0.00
PROPANE	6.70	6.70	0.00	0.00	0.00	0.00
MCPROPAN	0.00	0.00	0.00	131.61	0.00	2.09
MCPROPEN	1.95	0.00	0.00	186.62	0.00	0.00
ACH	0.00	0.00	0.00	3976.33	0.00	497.30
12DCP	0.00	0.00	0.18	401.66	0.18	2.04
DCPROPEN	0.00	0.00	0.33	262.51	0.33	3.52
13DCPOL	0.00	0.00	0.00	0.00	20.44	0.00
23DCPOL	0.00	0.00	0.00	0.00	163.70	0.00
TCP	0.00	0.00	0.83	0.00	290.97	0.00
ECH	0.00	0.00	4110.46	0.00	4153.15	269.72
NITROGEN	0.00	0.00	0.00	0.00	0.00	16.17
Mass Frac						
PROPENE	0.9983	0.9852	0.0000	0.0000	0.0000	0.0000
WATER	0.0000	0.0000	0.0000	0.0000	0.0000	0.0944
HCL	0.0010	0.0142	0.0000	0.0000	0.0000	0.0000
ETHANE	0.0000	0.0001	0.0000	0.0000	0.0000	0.0000
PROPANE	0.0006	0.0005	0.0000	0.0000	0.0000	0.0000
MCPROPAN	0.0000	0.0000	0.0000	0.0265	0.0000	0.0024
MCPROPEN	0.0002	0.0000	0.0000	0.0376	0.0000	0.0000
ACH	0.0000	0.0000	0.0000	0.8019	0.0000	0.5695
12DCP	0.0000	0.0000	0.0000	0.0810	0.0000	0.0023
DCPROPEN	0.0000	0.0000	0.0001	0.0529	0.0001	0.0040
13DCPOL	0.0000	0.0000	0.0000	0.0000	0.0044	0.0000
23DCPOL	0.0000	0.0000	0.0000	0.0000	0.0354	0.0000
TCP	0.0000	0.0000	0.0002	0.0000	0.0629	0.0000
ECH	0.0000	0.0000	0.9997	0.0000	0.8972	0.3089
NITROGEN	0.0000	0.0000	0.0000	0.0000	0.0000	0.0185
Total Flow kmol/hr	267.01	334.21	44.44	62.00	48.29	14.64
Total Flow kg/hr	11235.39	14033.00	4111.79	4958.73	4628.76	873.30
Total Flow cum/hr	850.88	2839.74	3.91	6.07	4.26	0.88
Temperature C	2.43	345.00	117.78	117.98	104.86	20.00
Pressure bar	6.37	6.00	1.00	6.62	0.64	1.00
Vapor Frac	1.00	1.00	0.00	0.00	0.00	0.00
Liquid Frac	0.00	0.00	1.00	1.00	1.00	1.00
Solid Frac	0.00	0.00	0.00	0.00	0.00	0.00
Enthalpy kcal/mol	4.27	11.00	-32.06	-7.80	-34.93	-31.84
Enthalpy kcal/kg	101.55	261.98	-346.46	-97.55	-364.42	-533.95
Enthalpy Gcal/hr	1.14	3.68	-1.42	-0.48	-1.69	-0.47
Entropy cal/mol-K	-39.17	-22.08	-72.42	-50.06	-74.52	-54.34
Entropy cal/gm-K	-0.93	-0.53	-0.78	-0.63	-0.78	-0.91

Density kmol/cum	0.31	0.12	11.36	10.21	11.34	16.59
Density kg/cum	13.20	4.94	1051.43	816.65	1086.99	989.06
Average MW	42.08	41.99	92.53	79.98	95.85	59.63
Liq Vol 60F cum/hr	21.58	26.87	3.50	5.20	3.89	0.88

Tab. 24. Stream summary for base case process

Mass Flow kg/hr	REACCOLD	REACWARM	RECECH	REFLUX	REFLUX2	S1
PROPENE	11215.90	11215.90	0.00	0.00	0.00	0.00
WATER	0.00	0.00	0.00	16308.77	5.60	0.00
HCL	2295.28	2295.28	0.00	0.00	0.00	0.00
ETHANE	1.00	1.00	0.00	0.00	0.00	0.00
PROPANE	6.70	6.70	0.00	0.00	0.00	0.00
MCPROPAN	131.61	131.61	0.00	0.02	0.17	0.00
MCPROPEN	188.57	188.57	0.00	0.00	0.00	0.00
ACH	3976.33	3976.33	0.00	99.74	36.40	0.00
12DCP	401.66	401.66	0.00	0.01	0.14	0.18
DCPROPEN	262.51	262.51	0.00	0.07	0.24	0.33
13DCPOL	0.00	0.00	0.00	3.41	0.00	0.01
23DCPOL	0.00	0.00	0.00	59.09	0.00	0.00
TCP	0.00	0.00	0.04	4.25	0.02	45.75
ECH	0.00	0.00	313.91	1371.34	208.24	4153.15
NITROGEN	8.70	8.70	0.00	95.31	3.35	0.00
Mass Frac						
PROPENE	0.6066	0.6066	0.0000	0.0000	0.0000	0.0000
WATER	0.0000	0.0000	0.0000	0.9090	0.0220	0.0000
HCL	0.1241	0.1241	0.0000	0.0000	0.0000	0.0000
ETHANE	0.0001	0.0001	0.0000	0.0000	0.0000	0.0000
PROPANE	0.0004	0.0004	0.0000	0.0000	0.0000	0.0000
MCPROPAN	0.0071	0.0071	0.0000	0.0000	0.0007	0.0000
MCPROPEN	0.0102	0.0102	0.0000	0.0000	0.0000	0.0000
ACH	0.2151	0.2151	0.0000	0.0056	0.1432	0.0000
12DCP	0.0217	0.0217	0.0000	0.0000	0.0005	0.0000
DCPROPEN	0.0142	0.0142	0.0000	0.0000	0.0009	0.0001
13DCPOL	0.0000	0.0000	0.0000	0.0002	0.0000	0.0000
23DCPOL	0.0000	0.0000	0.0000	0.0033	0.0000	0.0000
TCP	0.0000	0.0000	0.0001	0.0002	0.0001	0.0109
ECH	0.0000	0.0000	0.9999	0.0764	0.8193	0.9890
NITROGEN	0.0005	0.0005	0.0000	0.0053	0.0132	0.0000
Total Flow kmol/hr	392.00	392.00	3.39	925.32	3.16	45.20
Total Flow kg/hr	18488.30	18488.30	313.95	17941.99	254.16	4199.42
Total Flow cum/hr	8219.02	11749.78	0.30	17.86	2.31	3.76
Temperature C	259.27	485.00	117.78	20.00	16.78	70.75
Pressure bar	2.10	2.10	1.00	1.00	1.00	1.20
Vapor Frac	1.00	1.00	0.00	0.00	0.03	0.00
Liquid Frac	0.00	0.00	1.00	1.00	0.97	1.00
Solid Frac	0.00	0.00	0.00	0.00	0.00	0.00

Enthalpy kcal/mol	3.37	8.85	-32.06	-67.49	-33.24	-34.13
Enthalpy kcal/kg	71.46	187.72	-346.47	-3480.69	-413.59	-367.41
Enthalpy Gcal/hr	1.32	3.47	-0.11	-62.45	-0.11	-1.54
Entropy cal/mol-K	-18.01	-9.47	-72.42	-39.80	-71.08	-77.65
Entropy cal/gm-K	-0.38	-0.20	-0.78	-2.05	-0.88	-0.84
Density kmol/cum	0.05	0.03	11.36	51.82	1.37	12.03
Density kg/cum	2.25	1.57	1051.41	1004.87	110.17	1117.53
Average MW	47.16	47.16	92.53	19.39	80.37	92.90
Liq Vol 60F cum/hr	30.16	30.16	0.27	17.85	0.23	3.57

Tab. 25. Stream summary for base case process

Mass Flow kg/hr	S4	S18	S20	S21	S25	S26
WATER	16319.04	134649.00	36675.67	91.70	79.86	85.45
HCL	0.00	1747.04	0.00	0.00	0.00	0.00
MCPROPAN	0.42	0.40	0.00	2.36	0.40	0.57
ACH	181.22	81.48	0.00	557.46	84.59	120.99
12DCP	0.43	0.42	0.00	2.27	0.42	0.38
DCPROPEN	0.79	0.73	0.00	3.91	0.73	0.64
13DCPOL	23.84	2083.43	0.00	0.00	20.44	0.00
23DCPOL	222.79	4223.80	0.00	0.00	163.70	0.00
TCP	295.22	290.97	0.00	0.00	291.01	0.06
ECH	5557.28	0.00	0.00	299.93	4506.78	561.87
NITROGEN	127.76	32.45	0.00	21.70	32.70	36.04
Mass Frac						
WATER	0.7180	0.9409	1.0000	0.0936	0.0154	0.1060
HCL	0.0000	0.0122	0.0000	0.0000	0.0000	0.0000
MCPROPAN	0.0000	0.0000	0.0000	0.0024	0.0001	0.0007
ACH	0.0080	0.0006	0.0000	0.5692	0.0163	0.1501
12DCP	0.0000	0.0000	0.0000	0.0023	0.0001	0.0005
DCPROPEN	0.0000	0.0000	0.0000	0.0040	0.0001	0.0008
13DCPOL	0.0010	0.0146	0.0000	0.0000	0.0039	0.0000
23DCPOL	0.0098	0.0295	0.0000	0.0000	0.0316	0.0000
TCP	0.0130	0.0020	0.0000	0.0000	0.0562	0.0001
ECH	0.2445	0.0000	0.0000	0.3063	0.8699	0.6971
NITROGEN	0.0056	0.0002	0.0000	0.0222	0.0063	0.0447
Total Flow kmol/hr	976.77	7575.20	2035.81	16.48	58.83	13.70
Total Flow kg/hr	22728.79	143110.00	36675.67	979.35	5180.61	806.00
Total Flow cum/hr	479.06	144.36	36.74	5.96	18.37	32.56
Temperature C	40.00	63.00	20.00	20.00	25.20	26.00
Pressure bar	0.41	1.00	1.00	1.00	1.00	1.00
Vapor Frac	0.01	0.00	0.00	0.01	0.01	0.09
Liquid Frac	0.99	1.00	1.00	0.99	0.99	0.91
Solid Frac	0.00	0.00	0.00	0.00	0.00	0.00
Enthalpy kcal/mol	-65.39	-67.38	-68.36	-31.47	-38.67	-39.70
Enthalpy kcal/kg	-2810.00	-3566.73	-3794.47	-529.42	-439.15	-674.75
Enthalpy Gcal/hr	-63.87	-510.43	-139.16	-0.52	-2.28	-0.54

Entropy cal/mol-K	-40.37	-36.92	-39.29	-53.79	-77.28	-54.61
Entropy cal/gm-K	-1.73	-1.95	-2.18	-0.91	-0.88	-0.93
Density kmol/cum	2.04	52.48	55.42	2.77	3.20	0.42
Density kg/cum	47.44	991.36	998.33	164.42	282.07	24.75
Average MW	23.27	18.89	18.02	59.44	88.06	58.83
Liq Vol 60F cum/hr	21.92	142.51	36.75	1.00	4.42	0.76

Tab. 26. Stream summary for base case process

Mass Flow kg/hr	S28	S29	S34	S37	S41	WAORG
WATER	69.61	84.45	148970.00	91.70	91.62	69.59
HCL	0.00	0.00	1747.04	0.00	0.00	0.00
MCPROPAN	0.00	0.44	0.40	2.36	2.32	0.00
ACH	3.90	100.46	81.48	557.46	552.56	3.11
12DCP	0.00	0.37	0.42	2.27	2.27	0.00
DCPROPEN	0.00	0.63	0.73	3.91	3.91	0.00
13DCPOL	0.00	0.00	2083.43	0.00	0.00	0.00
23DCPOL	0.00	0.00	4223.80	0.00	0.00	0.00
TCP	0.00	0.06	290.97	0.00	0.00	0.00
ECH	7.00	559.36	0.00	299.93	299.69	6.92
CAOH2	0.00	0.00	3580.08	0.00	0.00	0.00
NITROGEN	0.99	9.87	32.45	21.70	17.97	0.24
Mass Frac						
WATER	0.8541	0.1118	0.9252	0.0936	0.0944	0.8713
HCL	0.0000	0.0000	0.0109	0.0000	0.0000	0.0000
MCPROPAN	0.0000	0.0006	0.0000	0.0024	0.0024	0.0000
ACH	0.0478	0.1329	0.0005	0.5692	0.5695	0.0390
12DCP	0.0000	0.0005	0.0000	0.0023	0.0023	0.0000
DCPROPEN	0.0000	0.0008	0.0000	0.0040	0.0040	0.0000
13DCPOL	0.0000	0.0000	0.0129	0.0000	0.0000	0.0000
23DCPOL	0.0000	0.0000	0.0262	0.0000	0.0000	0.0000
TCP	0.0000	0.0001	0.0018	0.0000	0.0000	0.0000
ECH	0.0859	0.7402	0.0000	0.3063	0.3089	0.0867
CAOH2	0.0000	0.0000	0.0222	0.0000	0.0000	0.0000
NITROGEN	0.0121	0.0131	0.0002	0.0222	0.0185	0.0031
Total Flow kmol/hr	4.03	12.41	8418.41	16.48	16.27	3.99
Total Flow kg/hr	81.50	755.65	161010.00	979.35	970.33	79.87
Total Flow cum/hr	0.08	0.69	2806.16	526.61	0.98	0.08
Temperature C	20.00	26.00	63.24	70.49	20.00	26.00
Pressure bar	1.00	1.00	0.45	0.88	1.00	1.00
Vapor Frac	0.00	0.00	0.01	1.00	0.00	0.00
Liquid Frac	1.00	1.00	0.99	0.00	1.00	1.00
Solid Frac	0.00	0.00	0.00	0.00	0.00	0.00
Enthalpy kcal/mol	-66.35	-43.49	-67.86	-22.43	-31.84	-66.83
Enthalpy kcal/kg	-3277.23	-714.42	-3547.90	-377.35	-533.94	-3335.98
Enthalpy Gcal/hr	-0.27	-0.54	-571.25	-0.37	-0.52	-0.27
Entropy cal/mol-K	-39.86	-59.49	-35.49	-25.57	-54.34	-39.66

Entropy cal/gm-K	-1.97	-0.98	-1.86	-0.43	-0.91	-1.98
Density kmol/cum	49.17	17.92	3.00	0.03	16.59	50.10
Density kg/cum	995.33	1090.70	57.38	1.86	989.06	1003.57
Average MW	20.24	60.87	19.13	59.44	59.63	20.03
Liq Vol 60F cum/hr	0.08	0.69	171.30	1.00	0.98	0.08

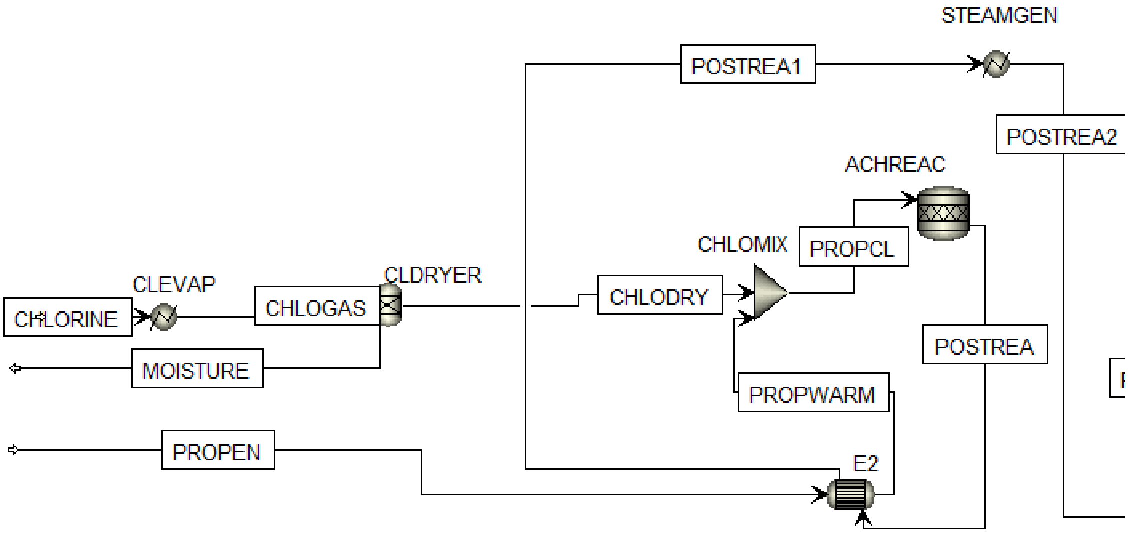

Figure 40. Chlorination section for HP process

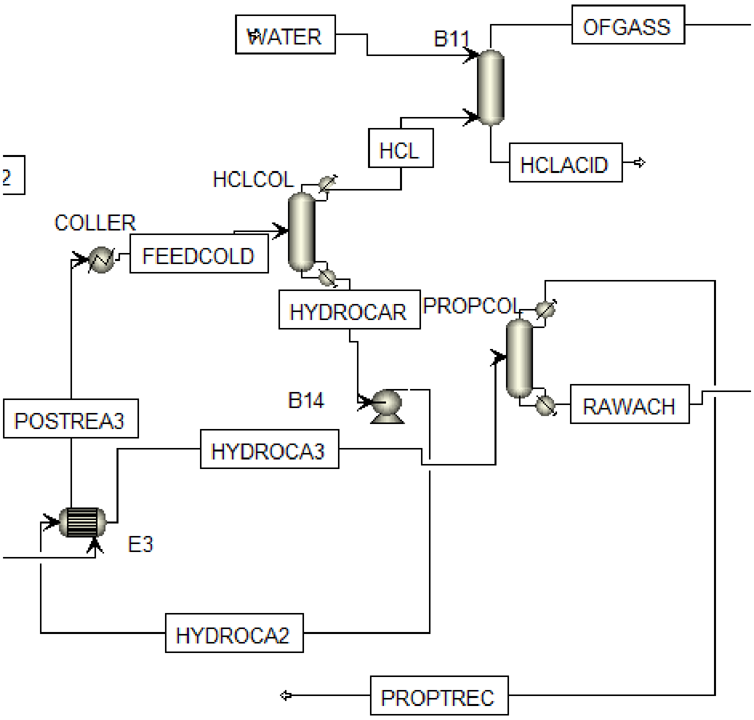

Figure 41. Purification of ACH

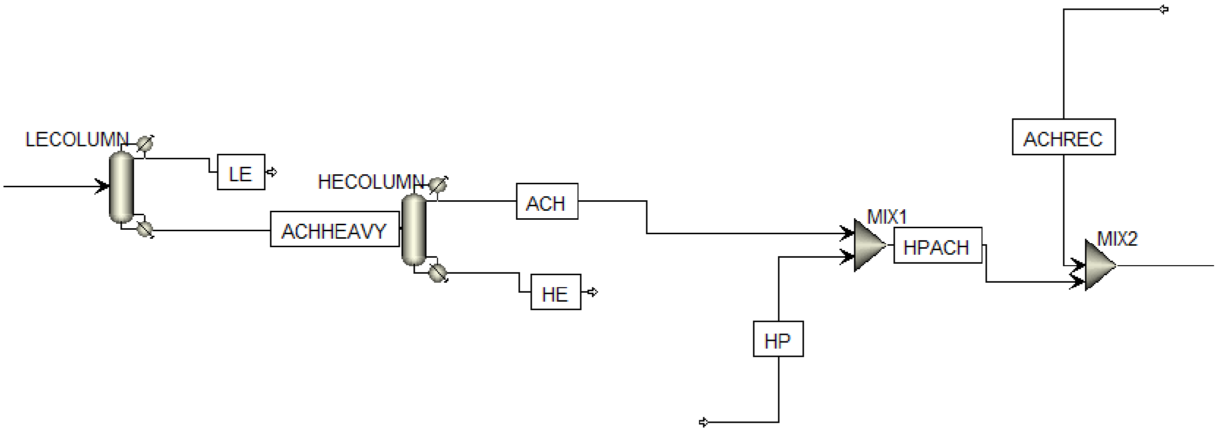

Figure 42. Second stage of ACH purification

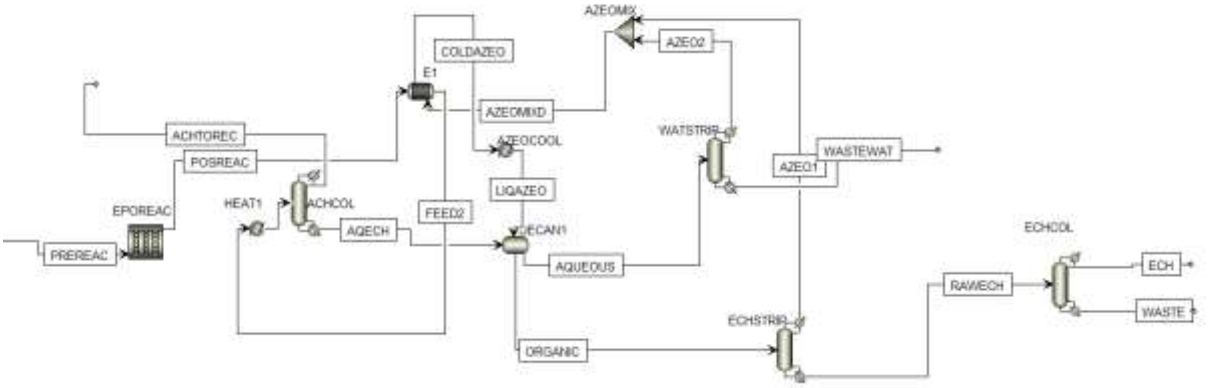

Figure 43. Layout of epoxidation stage and ECH purification

Tab. 27. Stream summary for HP process

Mass Flow kg/hr	ACH	ACHHEAVY	ACHREC	ACHTOREC	AQECH	AQUEOUS
WATER	0.00	0.00	0.00	0.00	4350.63	4621.73
MCPROPAN	0.21	0.21	0.00	0.21	0.00	0.00
MCPROPEN	0.00	0.00	0.00	0.00	0.00	0.00
ACH	3975.07	3975.79	6999.05	7102.14	0.00	0.00
12DCP	0.22	401.66	0.00	0.22	0.00	0.00
DCPROPEN	0.39	262.51	0.00	0.39	0.00	0.00
ECH	0.00	0.00	13.18	6.43	4671.78	508.29
METHANOL	0.00	0.00	19182.20	19089.06	90.53	321.65
HP	0.00	0.00	0.00	0.00	25.22	25.18
CMP	0.00	0.00	1.00	0.00	11.12	6.72
CDP	0.00	0.00	1.00	0.00	11.69	9.12
OXYGEN	0.00	0.00	15.00	14.94	0.00	0.00
Mass Frac						
WATER	0.0000	0.0000	0.0000	0.0000	0.4749	0.8414
MCPROPAN	0.0001	0.0000	0.0000	0.0000	0.0000	0.0000
MCPROPEN	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000

ACH	0.9998	0.8568	0.2670	0.2709	0.0000	0.0000
12DCP	0.0001	0.0866	0.0000	0.0000	0.0000	0.0000
DCPROPEN	0.0001	0.0566	0.0000	0.0000	0.0000	0.0000
ECH	0.0000	0.0000	0.0005	0.0002	0.5100	0.0925
METHANOL	0.0000	0.0000	0.7318	0.7282	0.0099	0.0586
HP	0.0000	0.0000	0.0000	0.0000	0.0028	0.0046
CMP	0.0000	0.0000	0.0000	0.0000	0.0012	0.0012
CDP	0.0000	0.0000	0.0000	0.0000	0.0013	0.0017
OXYGEN	0.0000	0.0000	0.0006	0.0006	0.0000	0.0000
Total Flow kmol/hr	51.95	57.88	690.74	689.10	295.75	272.95
Total Flow kg/hr	3975.88	4640.17	26211.43	26213.39	9160.98	5492.68
Total Flow cum/hr	4.43	5.27	31.16	33.27	9.57	5.51
Temperature C	49.93	80.06	20.00	61.30	112.49	20.00
Pressure bar	1.18	2.60	1.00	2.00	2.30	1.00
Vapor Frac	0.00	0.00	0.00	0.00	0.00	0.00
Liquid Frac	1.00	1.00	1.00	1.00	1.00	1.00
Solid Frac	0.00	0.00	0.00	0.00	0.00	0.00
Enthalpy kcal/mol	-6.58	-8.41	-50.39	-49.25	-60.14	-67.21
Enthalpy kcal/kg	-86.00	-104.91	-1328.00	-1294.72	-1941.42	-3339.92
Enthalpy Gcal/hr	-0.34	-0.49	-34.81	-33.94	-17.79	-18.35
Entropy cal/mol-K	-55.49	-53.77	-57.21	-54.04	-39.59	-40.47
Entropy cal/gm-K	-0.73	-0.67	-1.51	-1.42	-1.28	-2.01
Density kmol/cum	11.73	10.99	22.17	20.71	30.89	49.52
Density kg/cum	897.79	881.22	841.10	787.99	956.93	996.42
Average MW	76.53	80.17	37.95	38.04	30.98	20.12
Liq Vol 60F cum/hr	4.27	4.84	31.70	31.69	8.49	5.50

Tab. 28. Stream summary for HP process

Mass Flow kg/hr	AZEO1	AZEO2	AZEOMIXD	CHLODRY	CHLOGAS	CHLORINE
CHLORINE	0.00	0.00	0.00	4446.60	4446.60	4446.60
WATER	81.91	272.62	354.52	0.00	0.20	0.20
ECH	1400.13	505.92	1906.11	0.00	0.00	0.00
NITROGEN	0.00	0.00	0.00	8.70	8.70	8.70
METHANOL	60.92	231.26	292.18	0.00	0.00	0.00
HP	0.13	0.06	0.19	0.00	0.00	0.00
CMP	0.11	0.03	0.14	0.00	0.00	0.00
Mass Frac						
CHLORINE	0.0000	0.0000	0.0000	0.9980	0.9980	0.9980
WATER	0.0531	0.2699	0.1389	0.0000	0.0000	0.0000

ECH	0.9073	0.5010	0.7466	0.0000	0.0000	0.0000
NITROGEN	0.0000	0.0000	0.0000	0.0020	0.0020	0.0020
METHANOL	0.0395	0.2290	0.1144	0.0000	0.0000	0.0000
HP	0.0001	0.0001	0.0001	0.0000	0.0000	0.0000
CMP	0.0001	0.0000	0.0001	0.0000	0.0000	0.0000
Total Flow kmol/hr	21.58	27.82	49.41	63.02	63.03	63.03
Total Flow kg/hr	1543.19	1009.89	2553.13	4455.30	4455.50	4455.50
Total Flow cum/hr	682.56	829.86	1523.28	158.25	158.28	3.02
Temperature C	107.19	85.63	97.68	50.00	50.00	-5.00
Pressure bar	1.00	1.00	1.00	10.70	10.70	6.28
Vapor Frac	1.00	1.00	1.00	1.00	1.00	0.00
Liquid Frac	0.00	0.00	0.00	0.00	0.00	1.00
Solid Frac	0.00	0.00	0.00	0.00	0.00	0.00
Enthalpy kcal/mol	-32.95	-48.23	-41.55	0.20	0.19	-4.82
Enthalpy kcal/kg	-460.82	-1328.70	-804.10	2.89	2.74	-68.21
Enthalpy Gcal/hr	-0.71	-1.34	-2.05	0.01	0.01	-0.30
Entropy cal/mol-K	-38.91	-20.87	-28.48	-3.96	-3.96	-20.12
Entropy cal/gm-K	-0.54	-0.57	-0.55	-0.06	-0.06	-0.28
Density kmol/cum	0.03	0.03	0.03	0.40	0.40	20.85
Density kg/cum	2.26	1.22	1.68	28.15	28.15	1473.72
Average MW	71.49	36.30	51.68	70.69	70.68	70.68
Liq Vol 60F cum/hr	1.35	1.00	2.35	3.21	3.21	3.21

Tab. 29. Stream summary for HP process

Mass Flow kg/hr	COLDAZEO	ECH	FEED2	FEEDCOLD	HCL	HCLACID
PROPENE	0.00	0.00	0.00	11215.90	0.00	0.00
CHLORINE	0.00	0.00	0.00	0.03	0.00	0.00
WATER	354.52	1.51	4350.63	0.00	0.00	2584.15
HCL	0.00	0.00	0.00	2295.28	2284.48	1126.70
ETHANE	0.00	0.00	0.00	1.00	1.00	0.02
PROPANE	0.00	0.00	0.00	6.70	0.00	0.00
MCPROPAN	0.00	0.00	0.21	131.61	0.00	0.00
MCPROPEN	0.00	0.00	0.00	188.57	0.00	0.00
ACH	0.00	0.00	7102.14	3976.33	0.00	0.00
12DCP	0.00	0.00	0.22	401.66	0.00	0.00
DCPROPEN	0.00	0.00	0.39	262.51	0.00	0.00
ECH	1906.11	4622.76	4678.21	0.00	0.00	0.00
NITROGEN	0.00	0.00	0.00	8.70	8.70	0.09

METHANOL	292.18	0.15	19179.60	0.00	0.00	0.00
HP	0.19	0.10	25.22	0.00	0.00	0.00
CMP	0.14	0.05	11.12	0.00	0.00	0.00
CDP	0.00	0.00	11.69	0.00	0.00	0.00
OXYGEN	0.00	0.00	14.94	0.00	0.00	0.00
Mass Frac						
PROPENE	0.0000	0.0000	0.0000	0.6066	0.0000	0.0000
CHLORINE	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
WATER	0.1389	0.0003	0.1230	0.0000	0.0000	0.6964
HCL	0.0000	0.0000	0.0000	0.1241	0.9958	0.3036
ETHANE	0.0000	0.0000	0.0000	0.0001	0.0004	0.0000
PROPANE	0.0000	0.0000	0.0000	0.0004	0.0000	0.0000
MCPROPAN	0.0000	0.0000	0.0000	0.0071	0.0000	0.0000
MCPROPEN	0.0000	0.0000	0.0000	0.0102	0.0000	0.0000
ACH	0.0000	0.0000	0.2008	0.2151	0.0000	0.0000
12DCP	0.0000	0.0000	0.0000	0.0217	0.0000	0.0000
DCPROPEN	0.0000	0.0000	0.0000	0.0142	0.0000	0.0000
ECH	0.7466	0.9996	0.1322	0.0000	0.0000	0.0000
NITROGEN	0.0000	0.0000	0.0000	0.0005	0.0038	0.0000
METHANOL	0.1144	0.0000	0.5422	0.0000	0.0000	0.0000
HP	0.0001	0.0000	0.0007	0.0000	0.0000	0.0000
CMP	0.0001	0.0000	0.0003	0.0000	0.0000	0.0000
CDP	0.0000	0.0000	0.0003	0.0000	0.0000	0.0000
OXYGEN	0.0000	0.0000	0.0004	0.0000	0.0000	0.0000
Total Flow kmol/hr	49.41	50.05	984.85	392.00	63.00	174.35
Total Flow kg/hr	2553.13	4624.56	35374.36	18488.30	2294.18	3710.96
Total Flow cum/hr	1155.20	4.35	42.37	1946.69	1.91	3.33
Temperature C	87.00	109.71	63.89	-29.00	-92.86	-48.10
Pressure bar	1.00	0.80	3.50	2.00	1.55	1.20
Vapor Frac	0.78	0.00	0.00	0.49	0.00	0.00
Liquid Frac	0.22	1.00	1.00	0.51	1.00	1.00
Solid Frac	0.00	0.00	0.00	0.00	0.00	0.00
Enthalpy kcal/mol	-43.60	-32.46	-52.88	-4.34	-26.69	-61.81
Enthalpy kcal/kg	-843.69	-351.28	-1472.18	-92.11	-732.81	-2904.07
Enthalpy Gcal/hr	-2.15	-1.62	-52.08	-1.70	-1.68	-10.78
Entropy cal/mol-K	-34.10	-73.19	-49.59	-41.29	-21.99	-38.57
Entropy cal/gm-K	-0.66	-0.79	-1.38	-0.88	-0.60	-1.81
Density kmol/cum	0.04	11.50	23.24	0.20	32.93	52.32
Density kg/cum	2.21	1062.66	834.90	9.50	1199.08	1113.67
Average MW	51.68	92.39	35.92	47.16	36.42	21.28
Liq Vol 60F cum/hr	2.35	3.94	40.18	30.16	3.38	4.24

Tab. 30. Stream summary for HP process

Mass Flow kg/hr	HE	HP	HPACH	HYDROCA2	HYDROCA3	HYDROCAR
PROPENE	0.00	0.00	0.00	11215.90	11215.90	11215.90
WATER	0.00	3440.92	3440.92	0.00	0.00	0.00
HCL	0.00	0.00	0.00	10.80	10.80	10.80
PROPANE	0.00	0.00	0.00	6.70	6.70	6.70
MCPROPAN	0.00	0.00	0.21	131.61	131.61	131.61
MCPROPEN	0.00	0.00	0.00	188.57	188.57	188.57
ACH	0.72	0.00	3975.07	3976.33	3976.33	3976.33
12DCP	401.44	0.00	0.22	401.66	401.66	401.66
DCPROPEN	262.12	0.00	0.39	262.51	262.51	262.51
HP	0.00	1746.14	1746.14	0.00	0.00	0.00
CMP	0.00	0.00	0.00	0.00	0.00	0.00
CDP	0.00	0.00	0.00	0.00	0.00	0.00
OXYGEN	0.00	0.00	0.00	0.00	0.00	0.00
Mass Frac						
PROPENE	0.0000	0.0000	0.0000	0.6926	0.6926	0.6926
WATER	0.0000	0.6634	0.3755	0.0000	0.0000	0.0000
HCL	0.0000	0.0000	0.0000	0.0007	0.0007	0.0007
PROPANE	0.0000	0.0000	0.0000	0.0004	0.0004	0.0004
MCPROPAN	0.0000	0.0000	0.0000	0.0081	0.0081	0.0081
MCPROPEN	0.0000	0.0000	0.0000	0.0116	0.0116	0.0116
ACH	0.0011	0.0000	0.4338	0.2455	0.2455	0.2455
12DCP	0.6043	0.0000	0.0000	0.0248	0.0248	0.0248
DCPROPEN	0.3946	0.0000	0.0000	0.0162	0.0162	0.0162
HP	0.0000	0.3366	0.1906	0.0000	0.0000	0.0000
Total Flow kmol/hr	5.92	242.33	294.29	329.00	329.00	329.00
Total Flow kg/hr	664.29	5187.06	9162.94	16194.12	16194.12	16194.12
Total Flow cum/hr	0.67	4.62	8.77	23.93	549.51	23.91
Temperature C	129.79	20.00	25.83	-26.10	16.00	-26.64
Pressure bar	2.58	1.00	1.00	6.50	6.50	2.00
Vapor Frac	0.00	0.00	0.00	0.00	0.44	0.00
Liquid Frac	1.00	1.00	1.00	1.00	0.56	1.00
Solid Frac	0.00	0.00	0.00	0.00	0.00	0.00
Enthalpy kcal/mol	-31.21	-63.57	-53.51	-2.51	0.33	-2.52
Enthalpy kcal/kg	-278.32	-2969.91	-1718.56	-50.93	6.70	-51.23
Enthalpy Gcal/hr	-0.18	-15.41	-15.75	-0.82	0.11	-0.83
Entropy cal/mol-K	-66.11	-41.60	-44.11	-56.40	-46.38	-56.46
Entropy cal/gm-K	-0.59	-1.94	-1.42	-1.15	-0.94	-1.15

Density kmol/cum	8.85	52.40	33.56	13.75	0.60	13.76
Density kg/cum	992.37	1121.55	1044.85	676.64	29.47	677.32
Average MW	112.12	21.40	31.14	49.22	49.22	49.22
Liq Vol 60F cum/hr	0.57	4.66	8.93	26.78	26.78	26.78

Tab. 31. Stream summary for HP process

Mass Flow kg/hr	LE	LIQAZEO	MOISTURE	OFGASS	ORGANIC	POSREAC
WATER	0.00	354.52	0.20	27.55	83.41	4350.63
HCL	0.00	0.00	0.00	1157.78	0.00	0.00
ETHANE	0.00	0.00	0.00	0.98	0.00	0.00
PROPANE	0.00	0.00	0.00	0.00	0.00	0.00
MCPROPAN	131.40	0.00	0.00	0.00	0.00	0.21
MCPROPEN	186.62	0.00	0.00	0.00	0.00	0.00
ACH	0.54	0.00	0.00	0.00	0.00	7102.14
12DCP	0.00	0.00	0.00	0.00	0.00	0.22
DCPROPEN	0.00	0.00	0.00	0.00	0.00	0.39
ECH	0.00	1906.11	0.00	0.00	6069.60	4678.21
NITROGEN	0.00	0.00	0.00	8.61	0.00	0.00
METHANOL	0.00	292.18	0.00	0.00	61.06	19179.60
HP	0.00	0.19	0.00	0.00	0.23	25.22
CMP	0.00	0.14	0.00	0.00	4.55	11.12
CDP	0.00	0.00	0.00	0.00	2.58	11.69
OXYGEN	0.00	0.00	0.00	0.00	0.00	14.94
Mass Frac						
WATER	0.0000	0.1389	1.0000	0.0231	0.0134	0.1230
HCL	0.0000	0.0000	0.0000	0.9689	0.0000	0.0000
ETHANE	0.0000	0.0000	0.0000	0.0008	0.0000	0.0000
PROPANE	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
MCPROPAN	0.4125	0.0000	0.0000	0.0000	0.0000	0.0000
MCPROPEN	0.5858	0.0000	0.0000	0.0000	0.0000	0.0000
ACH	0.0017	0.0000	0.0000	0.0000	0.0000	0.2008
12DCP	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
DCPROPEN	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
ECH	0.0000	0.7466	0.0000	0.0000	0.9756	0.1322
NITROGEN	0.0000	0.0000	0.0000	0.0072	0.0000	0.0000
METHANOL	0.0000	0.1144	0.0000	0.0000	0.0098	0.5422
HP	0.0000	0.0001	0.0000	0.0000	0.0000	0.0007
CMP	0.0000	0.0001	0.0000	0.0000	0.0007	0.0003
CDP	0.0000	0.0000	0.0000	0.0000	0.0004	0.0003
OXYGEN	0.0000	0.0000	0.0000	0.0000	0.0000	0.0004
Total Flow kmol/hr	4.12	49.41	0.01	33.62	72.20	984.85

Total Flow kg/hr	318.56	2553.13	0.20	1194.92	6221.43	35374.36
Total Flow cum/hr	0.38	2.34	0.00	835.80	5.31	42.11
Temperature C	47.01	20.00	50.00	31.80	20.00	60.00
Pressure bar	1.90	1.00	10.70	1.02	1.00	3.50
Vapor Frac	0.00	0.00	0.00	1.00	0.00	0.00
Liquid Frac	1.00	1.00	1.00	0.00	1.00	1.00
Solid Frac	0.00	0.00	0.00	0.00	0.00	0.00
Enthalpy kcal/mol	-22.41	-52.36	-67.81	-23.42	-38.45	-52.98
Enthalpy kcal/kg	-289.75	-1013.12	-3764.22	-659.03	-446.21	-1475.03
Enthalpy Gcal/hr	-0.09	-2.59	0.00	-0.79	-2.78	-52.18
Entropy cal/mol-K	-66.28	-59.23	-37.53	2.37	-79.23	-49.88
Entropy cal/gm-K	-0.86	-1.15	-2.08	0.07	-0.92	-1.39
Density kmol/cum	10.97	21.07	53.82	0.04	13.60	23.39
Density kg/cum	848.25	1088.90	969.50	1.43	1171.93	840.03
Average MW	77.34	51.68	18.02	35.54	86.17	35.92
Liq Vol 60F cum/hr	0.36	2.35	0.00	1.75	5.34	40.18

Tab. 32. Stream summary for HP process

Mass Flow kg/hr	POSTREA	POSTREA1	POSTREA2	POSTREA3	PREREAC	PROPCL
PROPENE	11215.90	11215.90	11215.90	11215.90	0.00	13825.80
CHLORINE	0.03	0.03	0.03	0.03	0.00	4446.60
WATER	0.00	0.00	0.00	0.00	3440.92	0.00
HCL	2295.28	2295.28	2295.28	2295.28	0.00	199.50
ETHANE	1.00	1.00	1.00	1.00	0.00	1.00
PROPANE	6.70	6.70	6.70	6.70	0.00	6.70
MCPROPAN	131.61	131.61	131.61	131.61	0.21	0.00
MCPROPEN	188.57	188.57	188.57	188.57	0.00	0.00
ACH	3976.33	3976.33	3976.33	3976.33	10974.12	0.00
12DCP	401.66	401.66	401.66	401.66	0.22	0.00
DCPROPEN	262.51	262.51	262.51	262.51	0.39	0.00
ECH	0.00	0.00	0.00	0.00	13.18	0.00
NITROGEN	8.70	8.70	8.70	8.70	0.00	8.70
METHANOL	0.00	0.00	0.00	0.00	19182.20	0.00
HP	0.00	0.00	0.00	0.00	1746.14	0.00
CMP	0.00	0.00	0.00	0.00	1.00	0.00
CDP	0.00	0.00	0.00	0.00	1.00	0.00
OXYGEN	0.00	0.00	0.00	0.00	15.00	0.00
Mass Frac						

PROPENE	0.6066	0.6066	0.6066	0.6066	0.0000	0.7478
CHLORINE	0.0000	0.0000	0.0000	0.0000	0.0000	0.2405
WATER	0.0000	0.0000	0.0000	0.0000	0.0973	0.0000
HCL	0.1241	0.1241	0.1241	0.1241	0.0000	0.0108
ETHANE	0.0001	0.0001	0.0001	0.0001	0.0000	0.0001
PROPANE	0.0004	0.0004	0.0004	0.0004	0.0000	0.0004
MCPROPAN	0.0071	0.0071	0.0071	0.0071	0.0000	0.0000
MCPROPEN	0.0102	0.0102	0.0102	0.0102	0.0000	0.0000
ACH	0.2151	0.2151	0.2151	0.2151	0.3102	0.0000
12DCP	0.0217	0.0217	0.0217	0.0217	0.0000	0.0000
DCPROPEN	0.0142	0.0142	0.0142	0.0142	0.0000	0.0000
ECH	0.0000	0.0000	0.0000	0.0000	0.0004	0.0000
NITROGEN	0.0005	0.0005	0.0005	0.0005	0.0000	0.0005
METHANOL	0.0000	0.0000	0.0000	0.0000	0.5423	0.0000
HP	0.0000	0.0000	0.0000	0.0000	0.0494	0.0000
CMP	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
CDP	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
OXYGEN	0.0000	0.0000	0.0000	0.0000	0.0004	0.0000
Total Flow kmol/hr	392.00	392.00	392.00	392.00	985.03	397.23
Total Flow kg/hr	18488.30	18488.30	18488.30	18488.30	35374.36	18488.30
Total Flow cum/hr	11766.65	9516.22	4816.85	3383.75	40.16	2866.26
Temperature C	485.00	340.00	185.00	48.69	21.34	247.56
Pressure bar	2.10	2.10	3.10	3.10	1.00	6.00
Vapor Frac	1.00	1.00	1.00	1.00	0.00	1.00
Liquid Frac	0.00	0.00	0.00	0.00	1.00	0.00
Solid Frac	0.00	0.00	0.00	0.00	0.00	0.00
Enthalpy kcal/mol	8.86	5.21	1.87	-0.52	-51.32	7.58
Enthalpy kcal/kg	187.93	110.45	39.55	-10.94	-1429.16	162.96
Enthalpy Gcal/hr	3.47	2.04	0.73	-0.20	-50.56	3.01
Entropy cal/mol-K	-9.46	-14.80	-21.83	-27.96	-52.39	-20.99
Entropy cal/gm-K	-0.20	-0.31	-0.46	-0.59	-1.46	-0.45
Density kmol/cum	0.03	0.04	0.08	0.12	24.53	0.14
Density kg/cum	1.57	1.94	3.84	5.46	880.94	6.45
Average MW	47.16	47.16	47.16	47.16	35.91	46.54
Liq Vol 60F cum/hr	30.16	30.16	30.16	30.16	40.63	30.08

Tab. 33.Stream summary for HP process

Mass Flow kg/hr	PROPEN	PROPTREC	PROPWARM	RAWACH	RAWECH	S27
PROPENE	13825.80	11215.90	13825.80	0.00	0.00	0.00
CHLORINE	0.00	0.03	0.00	0.00	0.00	0.00
WATER	0.00	0.00	0.00	0.00	1.51	4350.63
HCL	199.50	10.80	199.50	0.00	0.00	0.00
ETHANE	1.00	0.00	1.00	0.00	0.00	0.00
PROPANE	6.70	6.70	6.70	0.00	0.00	0.00
MCPROPAN	0.00	0.00	0.00	131.61	0.00	0.21
MCPROPEN	0.00	1.95	0.00	186.62	0.00	0.00
ACH	0.00	0.00	0.00	3976.33	0.00	7102.14
12DCP	0.00	0.00	0.00	401.66	0.00	0.22
DCPROPEN	0.00	0.00	0.00	262.51	0.00	0.39
ECH	0.00	0.00	0.00	0.00	4669.46	4678.21
METHANOL	0.00	0.00	0.00	0.00	0.15	19179.60
HP	0.00	0.00	0.00	0.00	0.10	25.22
CMP	0.00	0.00	0.00	0.00	4.44	11.12
CDP	0.00	0.00	0.00	0.00	2.58	11.69
OXYGEN	0.00	0.00	0.00	0.00	0.00	14.94
Mass Frac						
PROPENE	0.9852	0.9983	0.9852	0.0000	0.0000	0.0000
CHLORINE	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
WATER	0.0000	0.0000	0.0000	0.0000	0.0003	0.1230
HCL	0.0142	0.0010	0.0142	0.0000	0.0000	0.0000
ETHANE	0.0001	0.0000	0.0001	0.0000	0.0000	0.0000
PROPANE	0.0005	0.0006	0.0005	0.0000	0.0000	0.0000
MCPROPAN	0.0000	0.0000	0.0000	0.0265	0.0000	0.0000
MCPROPEN	0.0000	0.0002	0.0000	0.0376	0.0000	0.0000
ACH	0.0000	0.0000	0.0000	0.8019	0.0000	0.2008
12DCP	0.0000	0.0000	0.0000	0.0810	0.0000	0.0000
DCPROPEN	0.0000	0.0000	0.0000	0.0529	0.0000	0.0000
ECH	0.0000	0.0000	0.0000	0.0000	0.9981	0.1322
METHANOL	0.0000	0.0000	0.0000	0.0000	0.0000	0.5422
HP	0.0000	0.0000	0.0000	0.0000	0.0000	0.0007
CMP	0.0000	0.0000	0.0000	0.0000	0.0009	0.0003
CDP	0.0000	0.0000	0.0000	0.0000	0.0006	0.0003
OXYGEN	0.0000	0.0000	0.0000	0.0000	0.0000	0.0004
Total Flow kmol/hr	334.21	267.01	334.21	62.00	50.62	984.85
Total Flow kg/hr	14033.00	11235.39	14033.00	4958.73	4678.24	35374.36
Total Flow cum/hr	1473.43	960.44	2474.57	6.07	4.46	2438.20
Temperature C	45.00	2.44	261.17	117.58	119.02	100.00
Pressure bar	6.00	6.37	6.00	6.62	1.05	3.50
Vapor Frac	1.00	1.00	1.00	0.00	0.00	0.28

Liquid Frac	0.00	0.00	0.00	1.00	1.00	0.72
Solid Frac	0.00	0.00	0.00	0.00	0.00	0.00
Enthalpy kcal/mol	4.69	4.44	8.98	-7.82	-32.15	-49.77
Enthalpy kcal/kg	111.70	105.63	213.78	-97.75	-347.90	-1385.66
Enthalpy Gcal/hr	1.57	1.19	3.00	-0.48	-1.63	-49.02
Entropy cal/mol-K	-35.73	-38.76	-25.61	-50.10	-72.24	-41.20
Entropy cal/gm-K	-0.85	-0.92	-0.61	-0.63	-0.78	-1.15
Density kmol/cum	0.23	0.28	0.14	10.22	11.36	0.40
Density kg/cum	9.52	11.70	5.67	817.31	1049.83	14.51
Average MW	41.99	42.08	41.99	79.98	92.42	35.92
Liq Vol 60F cum/hr	26.87	21.58	26.87	5.20	3.98	40.18

Tab. 34. Stream summary for HP process

Mass Flow kg/hr	WASTE	WASTEWAT	WATER
WATER	0.00	4349.12	2611.70
ECH	46.71	2.37	0.00
METHANOL	0.00	90.39	0.00
HP	0.00	25.12	0.00
CMP	4.39	6.69	0.00
CDP	2.58	9.12	0.00
Mass Frac			
WATER	0.0000	0.9702	1.0000
ECH	0.8702	0.0005	0.0000
METHANOL	0.0000	0.0202	0.0000
HP	0.0000	0.0056	0.0000
CMP	0.0818	0.0015	0.0000
CDP	0.0480	0.0020	0.0000
Total Flow kmol/hr	0.56	245.13	144.97
Total Flow kg/hr	53.68	4482.79	2611.70
Total Flow cum/hr	0.05	4.89	2.64
Temperature C	121.15	99.11	30.00
Pressure bar	1.00	1.05	1.50
Vapor Frac	0.00	0.00	0.00
Liquid Frac	1.00	1.00	1.00
Solid Frac	0.00	0.00	0.00
Enthalpy kcal/mol	-40.52	-66.70	-68.17

Enthalpy kcal/kg	-425.25	-3647.51	-3784.20
Enthalpy Gcal/hr	-0.02	-16.35	-9.88
Entropy cal/mol-K	-77.90	-35.02	-38.67
Entropy cal/gm-K	-0.82	-1.91	-2.15
Density kmol/cum	11.28	50.08	54.90
Density kg/cum	1075.16	915.87	989.12
Average MW	95.28	18.29	18.02
Liq Vol 60F cum/hr	0.04	4.50	2.62

Appendix B

Tab. 35. Base case distillation column sizing

Column	No of stages	Height [m]	Diameter [m]	wall thickness [m]	weight [kg]	Material	Cost [USD]
HCl column	40	27	1.2	0.006	18710	Carbon steel	592100
Propylene column	25	18	1.4	0.008	14915	Carbon steel	464700
LE column	70	46	1.6	0.008	41311	Carbon steel	1512300
HE column	30	21	0.8	0.006	9675	Carbon steel	364500
ECH stripper	14	12	3.0	0.012	22971	Stainless steel	98874
Dehydration column	20	15	0.8	0.006	6986	Stainless steel	255000
ECH recycle column	27	19	0.6	0.006	6616	Stainless steel	303800
ECH column	26	19	2.4	0.008	27420	Stainless steel	697700
ECH final column	22	16	1.6	0.006	24137	Stainless steel	291300

Tab. 36. HP process distillation column sizing

Column	No of stages	Height [m]	Diameter [m]	wall thickness [m]	weight [kg]	Material	Cost [USD]
HCl column	40	27	1.2	0.006	18710	Carbon stell	592100
Propylene column	25	18	1.4	0.008	14915	Carbon steel	464700
LE column	70	46	1.6	0.008	41311	Carbon steel	1512300
HE column	30	21	0.8	0.006	9675	Carbon steel	364500
ACH/MeOH column	68	44	3.4	0.012	28040	Stainless steel	1968522
ECH stripper	6	7	0.6	0.006	2038	Stainless steel	169300
Water stripper	3	5	0.8	0.006	2854	Stainless steel	190400
ECH column	20	15	0.8	0.008	8788	Stainless steel	271900

Tab. 37. Reflux drum sizing for base case

Reflux drum	Liquid flowrate [m^3/hr]	Volume [m^3]	Diameter calc [m]	Diameter [m]	Length [m]	Wall thickness [m]	Material	Weight [kg]	Cost [USD]
HCl column	10.79	2.40	0.339	0.4	1.2	0.006	Carbon Steel	1070	16929
Propylene column	-	-	0.954	1	3	0.008	Carbon Steel	662	28137
LE column	21.26	4.73	0.669	0.8	2.4	0.008	Carbon Steel	940	23987
HE column	1.74	0.388	0.0548	0.2	0.6	0.006	Carbon Steel	600	14928
ECH column	22.29	4.963	0.702	0.8	2.4	0.013	Stainless steel	950	24034

Tab. 38.Reflux drums sizing for HP process

Reflux drum	Liquid flowrate [m^3/hr]	Volume [m^3]	Diameter [m]	Length [m]	Wall thickness [m]	Material	Weight [kg]	Cost [USD]
HCl column	10.79	2.40	0.4	1.2	0.006	Carbon steel	237	16929
Propylene column	-	6.75	1	3	0.008	Carbon steel	1473	28137
LE column	21.26	4.73	0.8	2.4	0.008	Carbon steel	944	23987
HE column	1.74	0.388	0.2	0.6	0.006	Carbon steel	60	14928
ACH/MeOH column	11.0	10	1.4	4.2	0.012	Stainless steel	2890	37455
ECH column	5.7	6	1	3	0.006	Stainless steel	1470	28119

Tab. 39. Decanter sizing for base case

Decanter	Inlet flowrate [m3/hr]	Residence time [hr]	Decanter volume [m3]	Nominal diameter [m]	Lenght [m]	Wall thickness [m]	Material	Weight [kg]	Cost [USD]
1	22.362	0.5464	12.22	2.8	5.6	0.006	Stainless steel	2988	25138
2	0.745	0.5464	0.4071	0.6	1.2	0.006	Stainless steel	308	4718

Tab. 40. Decanter sizing for HP process

Decanter	Inlet flowrate [m3/hr]	Residence time [hr]	Decanter volume [m3]	Nominal diameter [m]	Lenght [m]	Wall thickness [m]	Material	Weight [kg]	Cost [USD]
1	11.911	0.546	6.508	2.2	4.4	0.006	Satinless steel	1846	19198

Tab. 41. Reactor sizing for base case

	Inlet flowrate [m3/hr]	Residence time [hr]	Reactor volume [m3]	Diameter [m]	Lenght [m]	Wall thickness [m]	Material	Weight [kg]	Cost [USD]
Chlorination reactor	3271.96	0.0006	1.815	1.2	2.4	0.006	Ferritic steel	1879	109873
Hydrchlorination reactor	142.45	0.0022	0.316	0.6	1.2	0.006	Stainless steel with PTFE lighning	1680	470318
Saponification reactor	2806.45	0.008	23.37	4	8	0.006	Stainless steel with PTFE ligning	6096	375641

Tab. 42. Reactor sizing for HP process

	Inlet flowrate [m3/hr]	Residence time [hr]	Reactor volume [m^3]	Diameter [m]	Lenght [m]	Wall thickness [m]	Material	Weight [kg]	Cost [USD]
Chlorination reactor	3271.96	0.0006	1.815	1.2	2.4	0.006	Ferritic steel	1879	109873
Epoxidation reactor	-	-	-	-	5	0.006	Stainless stell with PTFE lining	1279	110111

Tab. 43. Heat exchangers sizing for base case

Heat exchanger	Load [kJ/h]	Cost [USD]	Area [m2]	Shells
Condenser@LECOLUMN	5749759	23838	35	1
Condenser@HECOLUMN	2076955	15292	11	1
Condenser@ECHCOLUM	12238860	24031	36	1
Reboiler@ECHCOLUM	12055180	30639	58	1
Reboiler@LECOLUMN	5351909	13778	7	1
Reboiler@HECOLUMN	1907885	13024	5	1
Reboiler@PROPCOL	2633066	11761	3	1
Reboiler@ECHREC	692374	13547	8	1
Reboiler@DEHYROCO	1096832	12547	5	1
Condenser@PROPCOL	8147112	11546	15	1

Reboiler@HCLCOLUM	3322043	10546	11	1
Condenser@HCLCOLUM	6478834	15545	14	1
E3	9412501	44122	128	1
E1	291566	15678	3	1
E2	1754830	24787	35	1
COND1	42967401	49456	131	1
COND2	534251	11802	3	1
COND3	632715	12439	4	1
COOLER1	12817500	22861	43	1
HEATER1	13501378	16429	14	1
	Total	393667		

Tab. 44.Heat exchangers sizing for HP process

HP proces				
Heat exchanger	Load [kJ/h]	Cost [USD]	Area [m2]	Shells
Condenser@LECOLUMN	5749759	23838	35.3	1
Condenser@HECOLUMN	2076955	15292	10.6	1
Reboiler@LECOLUMN	5351909	13778	7.0	1
Reboiler@HECOLUMN	1907885	13024	5.3	1
Reboiler@PROPCOL	2633066	11761	2.7	1
Condenser@PROPCOL	8147112	11546	15.1	1
Reboiler@HCLCOLUM	3322043	10546	11.0	1
Condenser@HCLCOLUM	6478834	15545	14.2	1
Reboiler@ACHCOL	44042633	29727	54.9	1
Condenser@ACHCOL	104559439	1500703	647.5	13
Reboiler@WATSTRIP	1831180	12412	4.0	1
Reboiler@ECHSTRIP	2730919	11516	2.2	1
Rebolier@ECHCOL	2272973	19102	20.9	1
Condenser@ECHCOL	2288228	33562	68.6	1
E1	7131518	30943	45.2	1
E2	500892	10675	4.1	1
	Total	1763970		

Tab. 45. Wastewater data for base case process

Base case	
Annual amount of wastewater [m3]	1663200
Wastewater treatment cost per m3 [USD/m3]	1.481
Annual wastewater treatment costs	2463199

Tab. 46. Wastewater data for HP process

Base case	
Annual amount of wastewater [m3]	13695
Wastewater treatment cost per m3 [USD/m3]	1.481
Annual wastewater treatment costs	20282

Tab. 47. Raw materials usage and cost for base case process

Base case			
Material	Annual usage [ton/year]	Cost [USD/ton]	Annual cost [mln USD]
Chlorine	68704	175	12.0
Propylene	22862	1048	24.0
Milk of lime	31360	85	2.6
Water	1328235	0.87	1.2
		Total	39.8

Tab. 48. Raw materials usage and cost for HP process

HP process			
Material	Annual usage [tonnes/year]	Cost [USD/tonne]	Annual cost [mln USD]
Chlorine	38952	175	6.8
Propylene	22862	1048	24.0
Hydrogen peroxide (34% solution)	43570	483	21.0
		Total	51.8

Tab. 49. Carbon footprint data for base case process

Base case	
CO2 emmision [kg/hr]	5856
Annual CO2 emmision [kg]	49190400
Annual CO2 emmision cost [USD]	4427136
CO2 emmision[kg CO2 per kg of ECH]	1.17

Tab. 50. Carbon footprint data for HP process

HP proccess	
CO2 emmision [kg/hr]	5297
Annual CO2 emmision [kg]	44494800
Annual CO2 emmision cost [USD]	4004532
CO2 emmision[kg CO2 per kg of ECH]	1.13