

Simulation of an allyl chloride production process via the propylene chlorination route in ChemCAD[®] simulator

(Simulación de un proceso de producción de cloruro de alilo mediante la ruta de cloración del propileno en el simulador ChemCAD[®])

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Abstract: Allyl chloride is typically used to make intermediates for downstream derivatives such as resins and polymers, and in the production of epichlorohydrin. The present work describes the simulation and conceptual design of an allyl chloride production process via the propylene chlorination route in ChemCAD[®] simulator, to know the mass and energy balances of the intermediate and final streams, the operating and design parameters of some equipment, and other results of interest. The production process consists of a fired heater, a fluidized bed reactor, a waste heat boiler, six shell and tube heat exchangers, two compressors, a gas-liquid absorber and four distillation columns. About 1.336,307 kg/h of allyl chloride are produced at the distillate of the last distillation column with a purity of 99,92 %, while pure propylene, 2-chloropropene and an aqueous solution of HCl 32,4 wt. % are also obtained as byproducts. A first-of-its-kind simulation model was obtained in ChemCAD[®], which could be employed for further optimization studies and productivity increment analysis.

Keywords: Allyl chloride, propylene chlorination, ChemCAD[®], simulation, conceptual design.

Resumen: El cloruro de alilo es típicamente usado para producir intermediarios para derivativos tales como resinas y polímeros, y en la producción de epiclorohidrina. El presente trabajo describe la simulación y diseño conceptual de un proceso de producción de cloruro de alilo mediante la ruta de cloración del propileno en el simulador ChemCAD[®], para conocer los balances de masa y energía de las corrientes intermedias y finales, los parámetros de operación y diseño de algunos equipos, y otros resultados de interés. El proceso de producción consiste en un calentador quemador, un reactor de lecho fluidizado, una caldera de calor residual, seis intercambiadores de calor de tubo y coraza, dos compresores, un absorbedor gas-líquido y cuatro columnas de destilación. Alrededor de 1.336,307 kg/h de cloruro de alilo son producidos en el destilado de la última columna de destilación con una pureza de 99,92 %, mientras que también se obtienen como subproductos propileno puro, 2-cloropropeno y una solución acuosa de HCl al 32,4 % m/m. Se obtuvo un modelo de simulación primero de su tipo en ChemCAD[®], el cual puede ser empleado para posteriores estudios de optimización y análisis de incremento de la productividad.

Palabras clave: Cloruro de alilo, cloración del propileno, ChemCAD[®], simulación, diseño conceptual.

1. INTRODUCTION

Allyl chloride ($3\text{-C}_3\text{H}_5\text{Cl}$) is an important organic intermediate and is mainly used for producing epichlorohydrin, glycerin, and allyl alcohol, where in industry more than 80 % of epichlorohydrin is made from allyl chloride [1]. Additionally, allyl chloride is a common alkylating agent relevant in the manufacture of pharmaceuticals and pesticides. The uses and applications of allyl chloride may vary according to the product grade. The main form of allyl chloride is commercial grade, with 99 wt. % minimum purity [2].

Currently, the production routes of allyl chloride generally include:

- 1) High-temperature propylene chlorination (HTPC) and
- 2) oxychlorination of propylene (OP).

The investment cost of HTPC is comparatively less because no catalyst is needed, while the OP process needs the precious metal catalyst, which can easily lose activity. Consequently, HTPC is generally used in industry [1].

According to [2], while the main commercial production pathway for allyl chloride is the direct high-temperature chlorination of propylene, while examples of other pathways include:

- 1) Thermal dehydrochlorination (cracking) of dichloropropane and
- 2) Oxychlorination using hydrogen chloride and propylene.

However, such processes are either less used or of no commercial interest due to low allyl chloride selectivity and the generation of byproducts with no significant marketable use.

Some authors have studied the allyl chloride production process via propylene chlorination. In this case, in [3] a combined environmental and economic evaluation of an allyl chloride production process via propylene chlorination was performed for a base design and two alternative designs. The environmental analysis was completed using the waste reduction (WAR) algorithm, while the economic analysis was accomplished using the commercial software ICARUS Process Evaluator. All three process options were designed to maintain the process specifications:

- 1) The allyl chloride product stream must have a minimum purity of 99,9 mol%,
- 2) The HCl product stream must be 31,5 wt.%,
- 3) The 2-chloropropene byproduct stream must have a minimum purity of 95 mol%, and
- 4) The 2,3-dichloropropene byproduct stream must have a minimum purity of 95 mol%.

Also, [4] used the Integrated Dynamic Decision Analysis (IDDA) approach for reviewing the design of a plant for the production of allyl chloride by chlorination of propylene under exothermic conditions, with the objective of building an objective and documented reference for the decision making about the design alternatives to be adopted for risk minimization.

Likewise, in [2] an allyl chloride production process from propylene and chlorine was described, comprising three major sections: (1) chlorination; (2) propylene recovery; and (3) product treatment.

Similarly, in [5] an allyl chloride production process via high temperature chlorination of propylene was studied and rigorous simulated in Aspen Plus and using dividing wall columns in the separation section.

Finally, in [6] an allyl chloride manufacturing process via propylene chlorination was simulated using Aspen Plus simulator, to demonstrate a methodology developed to optimize processes for sustainability by applying information from the sustainability evaluator and the Oklahoma State University, as well as to convert the multiobjective optimization problem of

sustainability into a single objective problem by using the constraints and the weighted methods.

Nevertheless, to the best of the authors' knowledge, an allyl chloride production process via propylene chlorination has not yet been simulated in ChemCAD® simulator.

Certain chemical company is interested in erecting an allyl chloride production plant via the propylene chlorination route due to the availability of economic resources, raw materials and a guaranteed market for this chemical. Consequently, it is necessary and required to carry out the conceptual design of such a plant to obtain information about its productivity, throughput and equipment operating parameters, as a first step in the development of this chemical process.

In this context, in the present study an allyl chloride production process via the propylene chlorination route was simulated for the first time in ChemCAD® simulator v7.1.2, to know the mass and energy balances of the intermediate and final streams, the operating and design parameters of the main equipment, as well as the required flowrate of utilities and the heat curves in all the shell and tube heat exchangers.

2. MATERIALS AND METHODS

2.1. Physical-chemical properties of allyl chloride

As reported by [7] [8], allyl chloride presents the main physical-chemical properties shown in Table 1.

Table 1. Main physical-chemical properties of allyl chloride.

Property	Value	Units
Other name	3-chloropene	
Molecular weight	76,53	g/mol
Freezing point	-134,5	°C
Boiling point at 101.3 kPa	45,1	°C
Fire point	4	°C
Flash point	4	°C
Specific gravity at 20/4 °C	0,938	-
Liquid density at 25 °C	931	kg/m ³
Critical temperature	240,7	°C
Critical pressure	4.710	kPa
Heat of combustion	24,8	kJ/g
Heat of vaporization at 20 °C	357	J/g
Specific heat, liquid, at 20 °C	1,32	J/g.°C
Solubility at 20 °C, in water	0,33	%
Viscosity at 25 °C	0,3136	cP
Refractive index at 15 °C	1,4153	-

2.2. Description of the allyl chloride production process

Firstly, 3.190 kg/h of gaseous propylene at a temperature and pressure of 25 °C and 11,7 bar are sent to a pressure reduction valve to reduce its pressure to 3,58 bar, thus decreasing its temperature to 10,1 °C. This cold propylene stream is then sent to a fired heater (Fired Heater) to increase its temperature to 548 °C, and the subsequent heated stream is mixed in a mixing nozzle with 1,400 kg/h of a gaseous chlorine stream at a temperature and pressure of 25 °C and 6,44 bar, respectively. The resulting mixed gaseous stream, which has a temperature of 510-515 °C and a

pressure of 3-3,5 bar, is fed to a fluidized bed reactor (Reactor) operating in the temperature and pressure range of 511-525 °C and 3,04-4,50 bar, respectively. According to [9], during the thermal chlorination process, some amounts of carbon can be produced, which has the propensity to deposit on equipment that operates at temperatures greater than 400 °C. For this reason, the reactor chosen for this production process is a fluidized bed with sand (inert solid) on the reaction side. In this case, the sand provide a large surface area on which the carbon can deposit, acts as a scouring agent on the immersed heat transfer tubes in the reactor and prevents the buildup of carbon on the heat transfer surfaces. The carbon deposited preferentially on the sand is removed by combustion in a solid regeneration unit attached to the reactor, while the regenerated sand is sent back to the reactor, thus maintaining a constant inventory of solids inside the reactor.

The chlorination reactions are exothermic (Table 2), thus the heat produced by these reactions is removed using the commercially available heat transfer medium (or coolant) Dowtherm A[®]. The hot gaseous crude allyl chloride stream coming from the fluidized bed reactor at a temperature and pressure of 510-515 °C and 2,5-3,0 bar, which contains unreacted propylene along with the reaction products, is sent to a waste-heat boiler (Waste-Heat Boiler) which utilizes the heat content of this stream to generate low pressure saturated steam (162 °C and 6 bar). The outlet cooled gaseous stream of the waste-heat boiler, at a temperature of 200 °C, is then sent to a shell and tube heat exchanger (Cooler 1) to reduce its temperature to 50 °C against cooling water at 30 °C, and then to another shell and tube heat exchanger (Cooler 2) to be cooled to -50 °C against propylene at -62 °C. The cooled liquid mixture leaving Cooler 2 is fed to a phase separator (Phase Separator) operating at -50 °C and 1,5 bar, where a vapor stream is obtained at the top and a liquid phase is generated at the bottom of this equipment.

The bottom stream of the Phase Separator is sent to a first distillation column (Propylene Column) operating at 1,5 bar, where almost all the propylene and hydrogen chloride are obtained at the top stream of this distillation column, while the bottom stream contains almost all the allyl chloride and both chloroprenes. The top stream of this first distillation column is mixed with the top stream generated in the phases separator, and the resulting two phase mixture rich in propylene and hydrogen chloride with traces of allyl chloride (temperature of -56 °C) is heated to 10 °C in a shell and tube heat exchanger (Heater 1) using low pressure saturated steam (162 °C, 6,5 bar). The resultant heated gaseous mixture is sent to a gas-liquid absorber (Absorber) where almost all the hydrogen chloride contained on it is absorbed by 1,480 kg/h of deionized water, thus obtaining at the bottom of this absorber a stream of aqueous hydrogen chloride (32,4 wt.%), with traces of propylene. This bottom stream is at a temperature of 120-123 °C, thus a shell and tube heat exchanger (Cooler 3) is employed to cool it to 35 °C using cooling water at 30 °C as coolant.

The bottom stream of the first distillation column is pumped to a second distillation column (Concentration Column) to remove almost all the propylene that remains in the feed stream, which is obtained at the top stream, while the bottom stream of this distillation column contains the concentrated allyl chloride and both chloroprenes. The top stream of the Concentration Column is mixed with the top stream of the gas-liquid absorber, to obtain a stream rich in propylene, which is sent to a granular filter (Adsorption Filter) which contains activated carbon and where all the components, except propylene, are removed by absorption, thus obtaining a gaseous stream of pure propylene at the top exit of this filter. This gaseous top stream of pure propylene obtained in the filter is first compressed to 10 bar in a adiabatic reciprocating compressor (Compressor 1), then it is cooled to 40 °C in a shell and tube heat exchanger (Cooler 4) against cooling water at 30 °C.

Next, this cooled stream is compressed again to 20 bar in a adiabatic centrifugal compressor (Compressor 2), and the resulting compressed gaseous stream is condensed by means of a shell and tube heat exchanger (Condenser) using cooling water at 2 °C, thus obtaining a liquid stream of pure propylene at 45 °C and 20 bar, which could be recycled back to the allyl chloride

production process. The bottom stream of the second distillation column is pumped to a third distillation column (2-Chloropropene Column), in order to remove the 2-chloropropene at the top stream, while the bottom stream of this third distillation column is pumped to a fourth distillation column (Allyl Chloride Column) to remove the 2,3-chloropropene at the bottom of this column, thus obtaining 1.337,3 kg/h of a concentrated stream of allyl chloride at the top with a purity of 99,92 %, being 2-chloropropene the main impurity found on it.

Figure 1 presents the process flow diagram of the allyl chloride production process previously described.

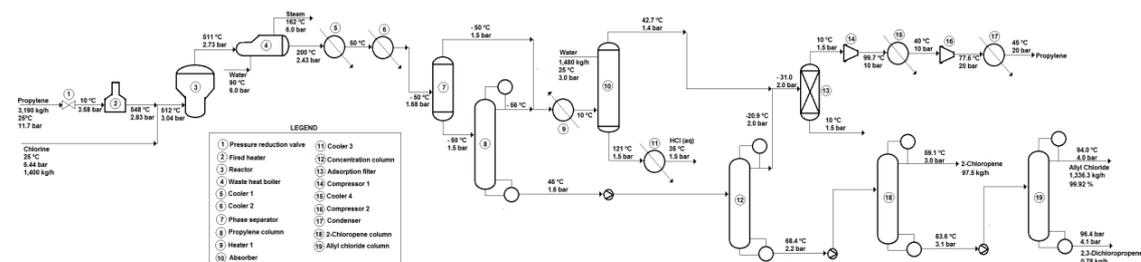


Figure 1. Process flow diagram of the allyl chloride production process.

2.3. Reactions and stoichiometry

The following table shows the main reactions that occur in the fluidized bed reactor, along with their stoichiometry, percentage conversion and standard heat of reactions [9].

Table 2. Stoichiometry, percentage conversion and standard heat of reaction of the main reactions involved in the fluidized bed reactor.

No.	Stoichiometry	Conversion	Heat of reaction
1	Allyl chloride formation $C_3H_6 + Cl_2 \rightarrow C_3H_5Cl + HCl$	80%	$\Delta H_{298} = -112 \text{ kJ/mol}$
2	2-chloropropene formation $C_3H_6 + Cl_2 \rightarrow C_3H_5Cl + HCl$	16%	$\Delta H_{298} = -121 \text{ kJ/mol}$
3	Dichloropropene formation $C_3H_6 + 2Cl_2 \rightarrow C_3H_4Cl_2 + 2HCl$	3%	$\Delta H_{298} = -222 \text{ kJ/mol}$
4	Carbon formation $C_3H_6 + 3Cl_2 \rightarrow 3C + 6HCl$	1%	$\Delta H_{298} = -306 \text{ kJ/mol}$

2.4. Selection of the thermodynamic model

The selected thermodynamic model of this study was Soave-Redlich-Kwong (SRK) with no vapor phase association; immiscible water/hydrocarbon solubility; a global enthalpy model of SRK; an ideal gas heat capacity of Design Institute for Physical Properties (DIPPR) and steam table of International Association for the Properties of Water and Steam (IAPWS-IF97).

2.5. Design parameters of the main equipment

The design parameters of the main equipment involved in the allyl chloride production process simulated in ChemCAD® are shown in Table 3. Those design parameters were selected following rules of thumbs and suggestions reported in [10], [11], [12], [13] and [14], as well as taking into account some suggestions of the simulator itself.

Table 3. Design parameters of the main equipment involved in the allyl chloride production process simulated in ChemCAD®.

Equipment	Design parameters
Fired heater	Type: Cylindrical type. Design type: Process heater. Tube material: Carbon steel. Efficiency: 0,75
Reactor	Type: Plug Flow. Length of tubes: 2,5 m. Diameter of tubes: 0,060 m. Number of tubes: 150. Number of steps: 1. Material: Stainless steel 304
Waste heat boiler	Area: 57,0 m ² . Type: Shell and tube/Fixed head. Material: Stainless steel 304.
Cooler 1	Area: 52,0 m ² . Type: Shell and tube/U tube. Material: Stainless steel 304.
Cooler 2	Area: 50,0 m ² . Type: Shell and tube/Fixed head. Material: Stainless steel 304.
Phase Separator	Type: Cylindrical tank. Material: Stainless steel 316. Diameter: 1,8 m. Height: 3,5 m.
Propylene Column	Type: Cylindrical. Material: Carbon steel. Diameter: 2,5 m. Tray type: Sieve.
Heater 1	Area: 85,0 m ² . Type: Shell and tube/Fixed head. Material: Stainless steel 347.
Absorber	Type: Cylindrical. Number of stages: 18. Material: Carbon steel. Diameter: 2,0 m. Height: 3,0 m.
Cooler 3	Area: 70,0 m ² . Type: Shell and tube/U tube. Material: Stainless steel 304.
Concentration Column	Type: Cylindrical. Material: Carbon steel. Diameter: 1,8 m.

	Tray type: Sieve.
Adsorption Filter	Material: Carbon steel. Diameter: 1,5 m. Height: 2,2 m.
Compressor 1	Type: Reciprocating/Adiabatic. Driver type: Belt drive coupling. Motor RPM: 3.600. Motor type: Explosion proof.
Cooler 4	Area: 50,0 m ² . Type: Shell and tube/Fixed head. Material: Carbon steel.
Compressor 2	Type: Centrifugal/Adiabatic. Driver type: Belt drive coupling. Motor RPM: 3.600. Motor type: Explosion proof.
Condenser	Area: 50,0 m ² . Type: Shell and tube/U tube. Material: Stainless steel 316.
2-Chloropropene Column	Type: Cylindrical. Material: Carbon steel. Diameter: 1,6 m. Tray type: Sieve.
Allyl Chloride Column	Type: Cylindrical. Material: Carbon steel. Diameter: 1,6 m. Tray type: Sieve.

2.6. Mass flowrate of utilities and heat curves of the heat exchangers

In this work, the mass flowrate of the utilities selected to cool/heat process streams in the shell and tube heat exchangers, as well as the heat curves of those shell and tube heat exchangers, were obtained. The selected utilities were cooling water at 30 °C and 3,0 bar, propylene at -62 °C and 0,5 bar, saturated steam at 162 °C and 6,5 bar, and chilled water at 2 °C and 3,0 bar. The mass flowrate of the utilities were calculated by employing the “Utility option” on the “Specifications” tab for each shell and tube heat exchanger, while the heat curves were obtained selecting the “Heat Curves” option.

3. RESULTS AND DISCUSSION

The following figures display the flowsheet of the allyl chloride production process simulated in ChemCAD[®] simulator, corresponding to the reaction (Figure 2a) and the separation/purification (Figure 2b) sections.

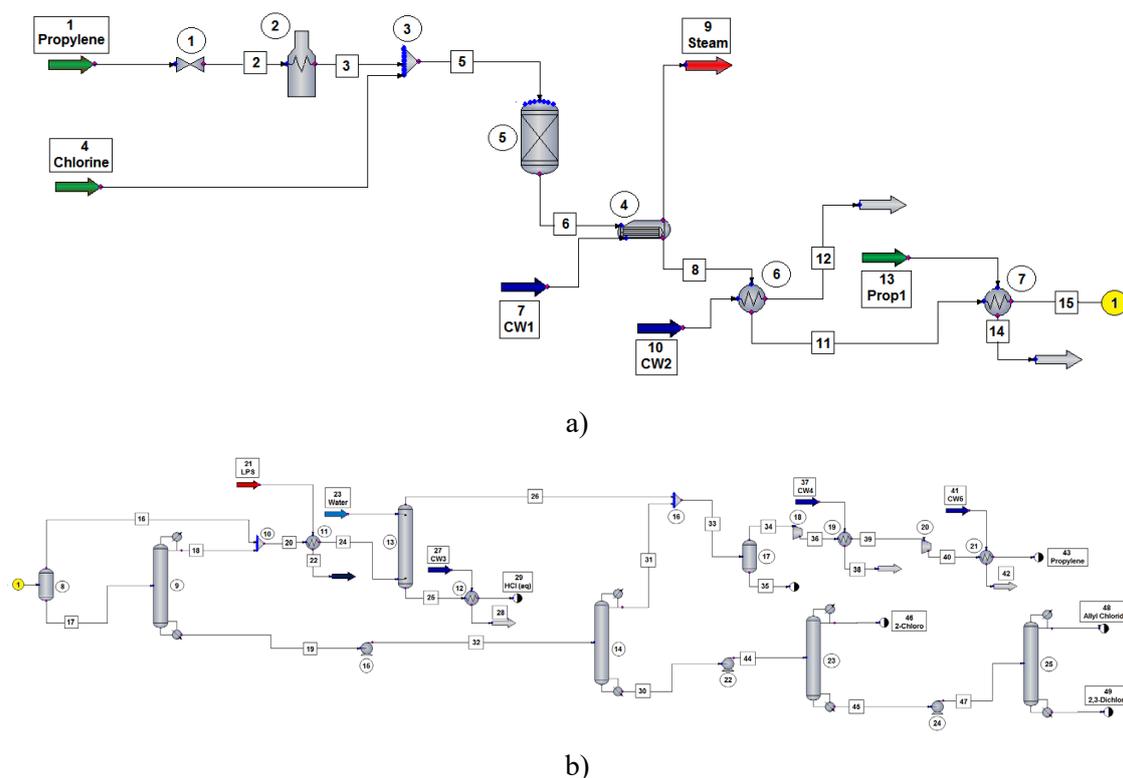


Figure 2. Flowsheet of the allyl chloride production process simulated in ChemCAD[®], corresponding to the sections of a: Reaction, b: Separation/purification.

3.1. Mass and energy balances of selected intermediate and final streams

Table 4 shows the mass and energy balances of selected intermediate and final streams, which were obtained through the simulation of the allyl chloride production process in ChemCAD[®] simulator. The results involve the temperature, pressure, flowrate, enthalpy and vapor mole fraction of those selected streams. Refer to Figure 2 to know to which stream number the mass and energy balances are referred to.

Table 4. Temperature, pressure, flowrate, enthalpy and vapor mole fraction of selected intermediate and final streams.

Parameter	Stream number (refer to Figure 2)				
	5	6	15	16	17
Temperature (°C)	511,72	511	-50	-50	-50
Pressure (bar)	3,04	2,73	1,68	1,5	1,5
Vapor fraction	1	1	0	0,99	0
Enthalpy (MJ/h)	5.470,2	3.270,97	-3.105,02	-352,51	-2.640,88
	Mass flowrate (kg/h)				
Allyl chloride	0	1.392,014	1.392,014	0,891	1.391,123
2-Chloropropene	0	117,836	117,836	0	117,836
2,3-Dichloropropene	0	0,789	0,789	0	0,789
Propylene	3.190	2.359,438	2.359,438	110,894	2.248,544
Chlorine	1.400	0,005	0,005	0	0,005
Hydrogen chloride	0	719,901	719,901	151,179	568,721

Carbon	0	5,32x10 ⁻⁵	5,32x10 ⁻⁵	0	5,32x10 ⁻⁵
Water	0	0	0	0	0
TOTAL	4.590	4.589,983	4.589,983	262,964	4.327,018

Table 4. Continued...

Parameter	Stream number (refer to Figure 2)				
	24	29	26	19	31
Temperature (°C)	10	35	42,52	45,87	-20,94
Pressure (bar)	1,5	1,5	1,4	1,6	2
Vapor fraction	1	0	0	0	0
Enthalpy (MJ/h)	-802,25	-24.489	-357,651	-521,061	-13,182
	Mass flowrate (kg/h)				
Allyl chloride	14,802	0,198	14,604	1.377,212	13,772
2-Chloropropene	10,042	0,415	9,627	107,795	9,328
2,3-Dichloropropene	3,562x10 ⁻⁵	7,322x10 ⁻⁷	3,489x10 ⁻⁵	0,789	4,412x10 ⁻⁵
Propylene	2.336,952	63,062	2.273,891	22,485	22,261
Chlorine	0,005	0,005	9,528x10 ⁻⁶	0,0001	0,0001
Hydrogen chloride	719,731	718,368	1,363	0,169	0,169
Carbon	7,389x10 ⁻¹⁶	0	0	5,321x10 ⁻⁵	7,389x10 ⁻¹⁶
Water	0	1.436,153	43,847	0	0
TOTAL	3.081,532	2.218,201	2.343,332	1.508,450	45,530

Table 4. Continued...

Parameter	Stream number (refer to Figure 2)				
	44	33	34	35	39
Temperature (°C)	68,41	-31,01	10	10	40
Pressure (bar)	3	2	1,5	1,5	10
Vapor fraction	0	0,45	1	0,18	1
Enthalpy (MJ/h)	-462,04	-370,83	1.004,49	-712,05	1.064,12
	Mass flowrate (kg/h)				
Allyl chloride	1.363,44	28,376	0	28,375	0
2-Chloropropene	98,467	18,955	0	18,955	0
2,3-Dichloropropene	0,789	7,901x10 ⁻⁵	0	7,901x10 ⁻⁵	0
Propylene	0,225	2.296,151	2.273,19	22,961	2.273,19
Chlorine	5,587x10 ⁻⁶	0,0001	0	0,0001	0
Hydrogen chloride	6,489x10 ⁻⁵	1,532	0	1,532	0
Carbon	5,321x10 ⁻⁵	7,39x10 ⁻¹⁶	0	7,39x10 ⁻¹⁶	0
Water	0	48,847	0	43,847	0
TOTAL	1.462,921	2.388,861	2.273,19	115,670	2.273,19

Table 4. Final...

Parameter	Stream number (refer to Figure 2)				
	46	47	48	49	43
Temperature (°C)	59,10	83,65	94,04	96,39	45
Pressure (bar)	3	3,5	4	4.1	20
Vapor fraction	0	0	0	0	0

Enthalpy (MJ/h)	-57,36	-372,82	-345,29	-3,94	355,820
	Mass flowrate (kg/h)				
Allyl chloride	13,634	1.349,805	1.336,307	13,498	0
2-Chloropropene	97,482	0,984	0,984	0,0001	0
2,3-Dichloropropene	1,096x10 ⁻¹¹	0,789	0,0079	0,781	0
Propylene	0,225	0	0	0	2.273,19
Chlorine	5,587x10 ⁻⁶	0	0	0	0
Hydrogen chloride	6,489x10 ⁻⁵	0	0	0	0
Carbon	7,389x10 ⁻¹⁶	5,321x10 ⁻⁵	7,39x10 ⁻¹⁶	5,32x10 ⁻⁵	0
Water	0	0	0	0	0
TOTAL	111,341	1.351,578	1.337,298	14,279	2.273,19

The outlet stream of the fluidized bed reactor (stream 6 in Figure 2a) contains allyl chloride in 30,32 %, unreacted propylene in 51,40 % and 15,68 % of hydrogen chloride. About 830,562 kg/h of propylene reacts with almost all the 1,400 kg/h of chlorine, in order to produce 1.392,014 kg/h of allyl chloride. It's worth noting that an insignificant amount of carbon is produced in the reactor (5,32x10⁻⁵ kg/h) which agrees with the values suggested by [9].

In the phase separator, a vapor stream is obtained at the top of this equipment (stream 16) with a total mass flowrate of 262,964 kg/h and with the following composition: 42,17 % of propylene and 57,49 % of hydrogen chloride with traces amounts of allyl chloride, while at the bottom a liquid stream (stream 17) is obtained with a total mass flowrate of 4.327,018 kg/h, where the main chemicals found on it are propylene (51,96 %), allyl chloride (32,15 %) and hydrogen chloride (13,14 %).

In the propylene column, about 99,00 % of the allyl chloride fed to this distillation column is obtained at the bottom (stream 18, 1.377,212 kg/h), while 91,48 % of the 2-chloropropene fed to this column is also obtained at the bottom (107,795 kg/h). Concerning the propylene component, about 99,00 % of this chemical is recovered at the distillate stream (stream 18) in this distillation column (data not shown), with a mass flowrate of 2.226,059 kg/h, while 568,552 kg/h of hydrogen chloride are also obtained in this distillate stream. The composition of the distillate stream in the propylene column is 78,97 % propylene and 20,17 % hydrogen chloride, with minor traces of allyl chloride and 2-chloropropene (data not shown).

In the absorber, a liquid stream having a total mass flowrate of 2.218,201 kg/h is obtained at the bottom (stream 25) with the following mass concentration: hydrogen chloride (32,4 %), water (64,74 %) and propylene (0,028 %), that is, an aqueous solution of hydrochloric acid is obtained at the bottom stream of this equipment, which could be commercialized as a byproduct. The top stream of the absorber (stream 26) contains propylene with a mass concentration of 97,04 % and a mass flowrate of 2.273,891 kg/h, with traces of allyl chloride, 2-chloropropene and hydrogen chloride.

In the concentration column, around 99 % of the propylene fed to this distillation column is obtained at the distillate (stream 31), with a mass flowrate of 22,261 kg/h. The percentage mass composition of this distillate stream is the following: allyl chloride (30,25 %), 2-chloropropene (20,49 %) and propylene (48,89 %). The bottom stream of the concentration column (streams 30 and 44) has a total mass flowrate of 1.462,920 kg/h and contains the following chemicals: allyl chloride (93,19 %) and 2-chloropropene (6,73 %).

The adsorption filter separates propylene from the rest of the chemicals at a rate of 99,00 %, which is obtained at the top stream of this equipment (stream 34) in gaseous state with a mass flowrate of 2.273,19 kg/h. The bottom liquid stream of this filter (stream 35), which has a total mass flowrate of 115,670 kg/h, contains allyl chloride (24,53 %), 2-chloropropene (16,38 %),

propylene (19,85 %) and water (37,91 %). It's recommended to send this bottom liquid stream to a wastewater treatment system before dispose it in the environment.

Regarding the 2-chloropropene column, about 98,99 % of the 2-chloropropene fed to this distillation column is separated and obtained in the top stream (stream 46), with a mass flowrate of 97,482 kg/h. The top stream of the 2-chloropropene column is composed by 2-chloropropene (87,55 %) and allyl chloride (12,24 %), with traces of the rest of the chemicals, except water. This stream of chloroprene could be further purified to commercialize it as a byproduct with a higher purity. The bottom stream of the 2-chloropropene column (streams 45 and 47) contains allyl chloride with a purity of 99,86 % and a mass flowrate of 1.349,805 kg/h, with minor traces of 2-chloropropene and 2,3-dichloropropene.

Finally, in the allyl chloride column, about 1.336,307 kg/h of allyl chloride are obtained at the top stream (stream 48) with a purity of 99,92%, while the bottom stream of this column (stream 49, 14,279 kg/h) contains allyl chloride (94,53 %) and 2,3-dichloropropene (5,46 %) as the main products. About 99,00% of the allyl chloride fed to this distillation column is separated and obtained at the top stream.

3.2. Operating parameters of the main equipment

Below are shown various operating and design parameters calculated by ChemCAD[®] simulator for the main equipment involved in the simulation flowsheet.

Fired heater:

- Heat absorbed: 4.088,08 MJ/h.
- Reactor:
- Heat duty: - 2.199,23 MJ/h.

Waste heat boiler:

- Heat duty: 2.864,24 MJ/h.
- Log Mean Temperature Difference (LMTD): 206,97 °C.
- LMTD Correction factor: 0,898.
- Calculated overall heat transfer coefficient (U): 75,09 W/m².K.

Cooler 1:

- Heat duty: 1.040,36 MJ/h.
- LMTD: 67,32 °C.
- LMTD Correction factor: 0,926.
- Calculated U: 89,09 W/m².K.

Cooler 2:

- Heat duty: 2.471,39 MJ/h.
- LMTD: 35,84 °C.
- LMTD Correction factor: 0,50.
- Calculated U: 766,09 W/m².K.

Propylene Column

- Condenser duty: - 2.928,26 MJ/h.
- Reboiler duty: 3.103,19 MJ/h.
- Minimum stages: 4.
- Reflux ratio, minimum: 0,024.

Heater 1:

- Heat duty: 1.495,14 MJ/h.
- LMTD: 182,99 °C.
- LMTD Correction factor: 1,0.
- Calculated U: 26,70 W/m².K.

Cooler 3:

- Heat duty: 547,24 MJ/h.
- LMTD: 17,31 °C.
- LMTD Correction factor: 0,5.
- Calculated U: 250,88 W/m².K.

Concentration Column:

- Condenser duty: - 45,23 MJ/h.
- Reboiler duty: 90,79 MJ/h.
- Minimum stages: 5.
- Reflux ratio, minimum: 0,694.

Compressor 1 (Reciprocating):

- Theoretical power: 261,054 MJ/h.
- Calculated head: 12.163,5 m.
- Cp/Cv: 1,170.

Cooler 4:

- Heat duty: 247,496 MJ/h.
- LMTD: 14,29 °C.
- LMTD Correction factor: 0,5.
- Calculated U: 192,33 W/m².K.

Compressor 1 (Centrifugal):

- Theoretical power: 85,95 MJ/h.
- Calculated head: 4.081,07 m.
- Cp/Cv: 1,251.

Condenser:

- Heat duty: 809,42 MJ/h.
- LMTD: 34,76 °C.
- LMTD Correction factor: 0,718.
- Calculated U: 180,01 W/m².K.

2-Chloropropene Column:

- Condenser duty: - 76,92 MJ/h.
- Reboiler duty: 108,71 MJ/h.
- Minimum stages: 17.
- Reflux ratio, minimum: 14,888.

Allyl Chloride Column:

- Condenser duty: - 944,20 MJ/h.
- Reboiler duty: 967,78 MJ/h.
- Minimum stages: 9
- Reflux ratio, minimum: 0,408.

According to the results shown above, the calculated value of the heat absorbed for the fired heater ($\sim 4,1$ GJ/h) is within the range reported by [13] of 0,5 to 21 GJ/h and the range reported by [9] of 4,0 – 5,4 GJ/h for this type of fired heater. Likewise, the calculated value of the heat duty for the fluidized bed reactor ($- 2.199,23$ MJ/h) is close to the value reported by [9] of $- 2.188$ MJ/h.

In this study, we selected a shell and tube heat exchanger to simulate the waste heat boiler, thus the results of the operating parameters obtained for this type of equipment are similar to those described for typical heat exchangers, not specifically boilers. The value of the calculated heat duty for the waste heat boiler ($2.864,24$ MJ/h) is very similar to that reported by [9] of 2.850 MJ/h, while the calculated value for the overall heat transfer coefficient ($75,09$ W/m².K) is within the range reported by [14] of 30-100 W/m².K.

The Cooler 1 had a value for the heat duty of $1.040,36$ MJ/h, which is comparable to the value of the heat duty stated by [9] of 1.025 MJ/h, while the value of the calculated overall heat transfer coefficient for this heat exchanger ($89,09$ W/m².K) is within the range reported by [14] of 20-300 W/m².K.

Regarding the Cooler 2, the value of the heat duty was of $2.471,39$ MJ/h (comparable to the range reported by [9] for the heat duty), while the calculated overall heat transfer coefficient had a value of $766,09$ W/m².K, which is within the range reported by [14] of 700-1,000 W/m².K for condensers.

The Heater 1 had a heat duty of $1.495,14$ MJ/h (analogous to the range reported by [9] for the heat duty) and a calculated overall heat transfer coefficient of $26,70$ W/m².K, which is below the range reported by [14] of 30-300 W/m².K.

Concerning the Cooler 3, the heat duty was of $547,24$ MJ/h, while the calculated overall heat transfer coefficient was of $250,88$ W/m².K, which is within the range of 250-750 W/m².K reported by [14].

The Cooler 4 had a heat duty of $247,496$ MJ/h and a calculated overall heat transfer coefficient of $192,33$ W/m².K, which is between the range reported by [14] of 20-300 W/m².K.

Finally, the Condenser had a heat duty of $809,42$ MJ/h (similar to the range stated by [9] for the heat duty of a condenser) and a calculated value for the overall heat transfer coefficient of $180,01$ W/m².K, which is below the range reported by [14] of 700-1.000 W/m².K.

In this case, the waste heat boiler had the highest value of the heat duty, which is due to the fact that is in this heat exchanger where water is vaporized to produce saturated steam using the hot gaseous mixture exiting the reactor as the heating agent, while the Cooler 4 had the lowest value of the heat duty because this heat exchanger cools down the gaseous pressurized propylene stream coming from the reciprocating compressor from $99,7$ °C to 40 °C using cooling water at 30 °C. With respect to the calculated value of the overall heat transfer coefficient, the Cooler 2 and Heater 1 had the highest and lowest values of this parameter, respectively.

Regarding to the compressors, the reciprocating compressor had a value of the theoretical power of $261,054$ MJ/h ($\sim 72,52$ kW), which is between the range reported by [15] of 7,5 kW - 9 MW for reciprocating compressors, while the centrifugal compressor had a value of $85,95$ MJ/h ($\sim 23,87$ kW) for the theoretical power, which is below the range reported by [15] of 75-97 MW for centrifugal compressors. Lastly, the values of the calculated head were $12.163,5$ m and $4.081,07$ m for the reciprocating and centrifugal compressor, respectively.

The Propylene Column had a condenser duty of $- 2.928,26$ MJ/h, a reboiler duty of $3.103,19$ MJ/h and will require 4 stages minimum with a minimum reflux ratio of 0,024. The condenser duty and the reboiler duty for the Concentration Column were $- 45,23$ MJ/h and $90,79$ MJ/h,

respectively, while it will require 5 stages minimum and a minimum reflux ratio of 0,694. In case of the 2-Chloropropene Column, the condenser duty and the reboiler duty were - 76,92 MJ/h and 108,71 MJ/h respectively, while the value for the minimum stages was 17 with a minimum reflux ratio of 14,888. Finally, the Allyl Chloride Column had a condenser duty of - 944,20 MJ/h, a reboiler duty of 967,78 MJ/h, 9 minimum stages and a minimum reflux ratio of 0,408.

3.3. Required flowrate of utilities

ChemCAD® simulator presents an option to calculate the flowrate of utilities (i.e. cooling water, steam, etc.) to achieve a predetermined heat exchange duty in heat exchangers. In this study we utilized this option to know the mass flowrate of the utilities selected, which were cooling water (30 °C, 3 bar), steam (162 °C, 6,5 bar), chilled water (2 °C, 3 bar) and propylene (- 62 °C, 0,5 bar), in order to heat/cool a particular process stream. Figure 3 shows the calculated flowrate of each utility selected in this study.

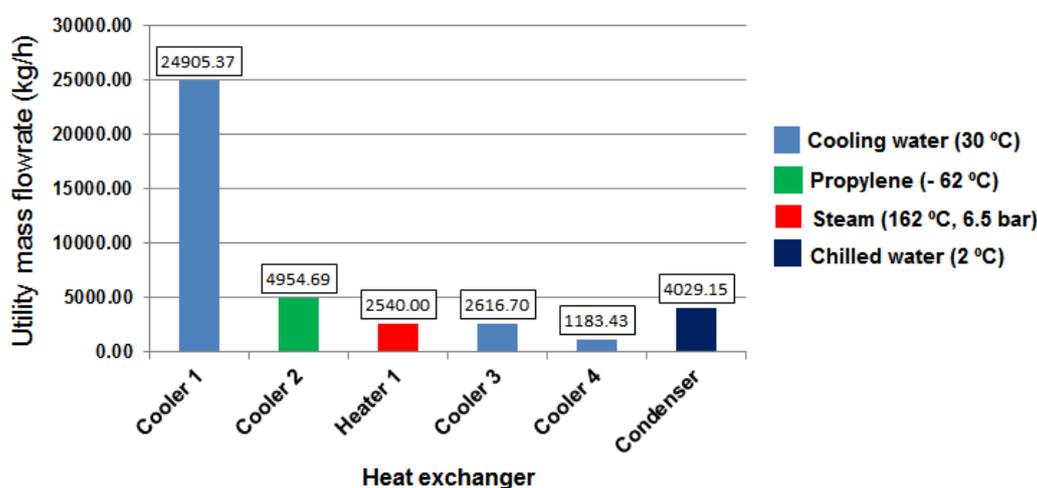


Figure 3. Calculated flowrate of each utility selected in this study.

As described in Figure 3, Cooler 1 needs the highest mass flowrate of cooling water with 24.905,37 kg/h, which is due to the fact that in this exchanger the hot gaseous mixture stream coming from the waste heat boiler is cooled from 200 °C to 50 °C (having a temperature difference of 150 °C), thus requiring a high amount of cooling water to carry out this cooling service. On the other hand, Cooler 4 requires the lowest mass flowrate of cooling water (1.183,43 kg/h) since this heat exchanger cools the propylene gaseous stream coming from the reciprocating compressor from 100 °C to 40 °C, with a temperature difference of only 60 °C. Heater 1 requires a steam mass flowrate of 2.540 kg/h, which could be classified as adequate [9], Cooler 2 requires a propylene mass flowrate of 4.954,69 kg/h, which can be classified as relatively high because this exchanger condenses the gaseous stream exiting the Cooler 1 from 50 °C to -50 °C (temperature difference of 100 °C), thus requiring this high mass flowrate of propylene to obtain a condensed liquid stream containing the allyl chloride, the chlorinated hydrocarbon derivatives as well as the unreacted propylene. Finally, the Condenser requires a chilled water mass flowrate of 4.029,15 kg/h, which can be classified as acceptable because this heat exchanger carries out the condensation of the gaseous pressurized propylene stream from 78 °C to 45 °C, thus obtaining liquid propylene at the heat exchanger outlet.

3.4. Heat curves

Figure 4 presents the heat curves of each shell and tube heat exchanger employed in the simulation study.

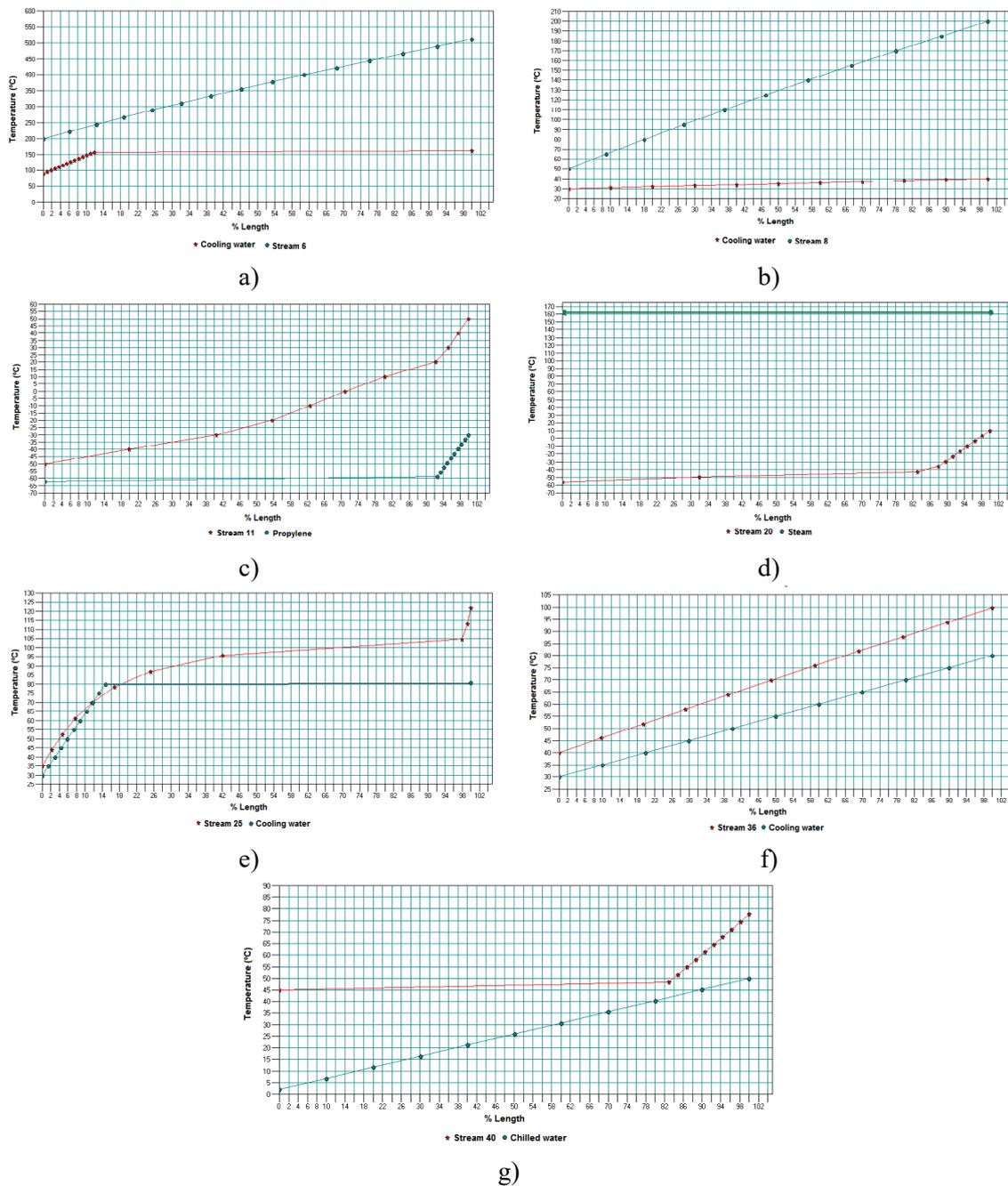


Figure 4. Heat curves of each shell and tube heat exchanger employed in the simulation study, corresponding specifically to a: Waste heat boiler, b: Cooler 1, c: Cooler 2, d: Heater 1, e: Cooler 3, f: Cooler 4, g: Condenser.

Figure 4a) shows that a change of pattern occurs for the cooling water at the 12 % length and 162 °C, thus indicating that a phase change takes place from liquid to vapor, thus obtaining saturated steam, while the heat curve of Stream 6 (hot gaseous mixture exiting the reactor) has a linear trend, indicating that this stream cools down from 511 °C to 200 °C without phase change.

Regarding the heat curve obtained for the Cooler 1 (Figure 4b) both the Cooling water stream and Stream 8 (cooled gaseous stream coming from the waste heat boiler) don't undergo phase change, which is indicated by the linear tendency of the two heat curves.

Concerning the heat curve of Cooler 2 (Figure 4c), both the Propylene stream and Stream 11 (cooled gaseous stream coming from the Cooler 1) experience phase change. In the case of the Propylene stream, it shows a linear trend from $-62\text{ }^{\circ}\text{C}$ to $-58\text{ }^{\circ}\text{C}$ of temperature and from 0 % to 93 % length, to then be subjected to a phase change verified by the pattern change of its heat curve (an increasing linear trend) until reaching $-30\text{ }^{\circ}\text{C}$ (the outlet temperature). This phase change is confirmed by checking the vapor mole fraction of both the inlet and outlet streams for Propylene stream in the simulation flowsheet, where the inlet stream has a vapor fraction of 0,00 (liquid) while the vapor fraction of the outlet stream is 1,00 (vapor). That is, the Propylene stream is vaporized. For the heat curve of Stream 11, it undergoes sensible heat until reaching $20\text{ }^{\circ}\text{C}$ and 92% length of the heat exchanger, to then experience phase change from this point to the outlet temperature of this stream ($-30\text{ }^{\circ}\text{C}$), which is corroborated by the change of pattern of the heat curve, thus obtaining a liquid stream at the outlet. This phase change is proved by checking the vapor mole fraction of both the inlet and outlet streams of Stream 11 in the simulation flowsheet, where the inlet stream presents a vapor mole fraction of 1,00 (vapor) and the outlet stream has a vapor mole fraction of 0,00 (liquid), i.e., Stream 11 undergoes condensation.

In the case of the heat curve of Heater 1 (Figure 4d), the Stream 20 suffers phase change taking into account the pattern of its heat curve. Specifically, this stream is heated without phase change (sensible heat) from $-56\text{ }^{\circ}\text{C}$ to $-43\text{ }^{\circ}\text{C}$ and 83 % length, to then undergo a phase change, which is demonstrated by the increasing linear trend occurring from 88 % length and $-36\text{ }^{\circ}\text{C}$ approximately, to the final length of the heat exchanger and the outlet temperature ($10\text{ }^{\circ}\text{C}$). This is corroborated by checking the vapor mole fraction of this stream in the simulation flowsheet, where it is 0,09 at the inlet (two phase vapor-liquid flow) and 1,00 (vapor) at the outlet of this heat exchanger, i.e., Stream 20 vaporizes. On the other hand, the Steam stream doesn't experience phase change (i.e. condensation), which is verified by the constant linear trend of its heat curve at the temperature of $162\text{ }^{\circ}\text{C}$.

The heat curve of Cooler 3 (Figure 4e) displays two phase changes for both the Cooling water stream and Stream 25. The Cooling water stream is heated under sensible heat from $30\text{ }^{\circ}\text{C}$ to $80\text{ }^{\circ}\text{C}$ and 15% length approximately, to then undergo phase change (condensation) at this point, showed by the change of pattern of its heat curve, thus obtaining a vapor stream at the outlet. The Stream 25 is cooled under sensible heat from $122\text{ }^{\circ}\text{C}$ until reaching a point of $104\text{ }^{\circ}\text{C}$ and 98 % length, and then suffers phase change (condensation) demonstrated by the decreasing curved trend of its heat curve. This is verified by checking the vapor mole fraction of both the inlet and outlet streams of this stream in the simulation flowsheet, where the vapor mole fraction has value of 1,00 (vapor) at the inlet and a value of 0,00 (liquid) at the outlet, i.e. condensation occurs.

In relation to the heat curve for Cooler 4 (Figure 4f), both the Stream 36 and the Cooling water streams don't experience phase change, which is certified by the linear trend of both heat curves. That is, the Cooling water stream is heated from $30\text{ }^{\circ}\text{C}$ to $80\text{ }^{\circ}\text{C}$ without evaporation, while the Stream 36 is cooled from 100 to $40\text{ }^{\circ}\text{C}$ without condensation.

Finally, the heat curve obtained for the Condenser (Figure 4g) shows that the Stream 40 goes through cooling without phase change from $78\text{ }^{\circ}\text{C}$ to $48\text{ }^{\circ}\text{C}$ and 83 % length approximately; to then go through phase change from this point until reaching the outlet temperature ($45\text{ }^{\circ}\text{C}$). This is validated by checking the vapor mole fraction of both the inlet and outlet streams of this stream in the simulation flowsheet, where the inlet stream has a vapor

mole fraction of 1,00 (vapor) while the vapor mole fraction of the outlet stream is 0,00 (liquid), thus occurring condensation. In case of the heat curve obtained for the Chilled water, its linear trend indicates that this stream doesn't undergo phase change, i.e. it's heated from 2 °C to 50 °C without vaporization.

4. CONCLUSIONS

An innovative ChemCAD® simulation model was obtained in this study in order to conceptually design an allyl chloride production process by the propylene chlorination route. By means of the simulation results, the temperature, pressure, vapor mole fraction, enthalpy and mass flowrate of the intermediate and final streams were known, as well as various important operating and design parameters of the main equipment included in the simulation flowsheet. Likewise, the required flowrate of utilities and the heat curves of all the shell and tube heat exchangers employed in the production process were also determined. Allyl chloride is obtained at the distillate of the last distillation column with a flowrate and purity of 1.336,307 kg/h and 99,92 %, respectively, while 2.273,189 kg/h of pure liquid propylene, 2.218,202 kg/h of an aqueous solution of HCl 32,4 % wt. %, and 97,482 kg/h of 2-Chloropropene with a purity of 87,55 % are also generated as byproduct in the simulated process. The ChemCAD® simulation model obtained in this work could be used for future optimization studies, throughput increment assessments, and sensitivity analysis. The results of this simulation study, mostly the mass and energy balances and the equipment design and operating parameters, can be successfully applied and implemented at industrial scale due to its reliability, scalability, operability and consistency, in order to erect the proposed commercial-scale allyl chloride production plant. It's recommended carrying out further calculation and simulation analyses to determine several important financial indicators such as net present value, internal rate of return, payback time, return of investment, unit production cost, annual operating costs and others, to verify the economic feasibility and viability of this chemical engineering design project.

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