DESIGN SIMULATION PRODUCTION
BUTYL CHLORIDE FROM BUTANOL AND HIDROCHLORIC ACID
CAPACITY 25000 Ton/year

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INTRODUCTION

Background

Indonesia is a developing country which is currently intensively carrying out development in various sectors or fields, one of which is in the industrial sector, especially the chemical industry. One of the efforts to increase economic growth in connection with the increasing demand for chemicals in the country and also to meet foreign demand (exports) as well as the development of semi-finished materials (intermediates) and finished materials which are the driving factors for the construction of chemical industrial units is one of the only establishment of a butyl chloride plant.

Butyl chloride has an important function as a raw material or supporting material for industrial processes. Butyl chloride is a chemical compound used as a solvent and extractant. This liquid is mostly used for chromatography and spectrophotometry. Butyl chloride is also used as a pesticide because of its nature as an active ingredient for controlling worms (BNT, 2022). Butyl chloride can be used for ethylene polymerization and the synthesis of lauric acid in the formation of 2-butyl aluminum as butyl cellulose. Also as raw material for organometallic compounds, as an antihelmintic in veterinary medicine, and used as an ingredient in the preparation of the anti-oxidant tert-butyl venol and neohexyl chloride fragrance.

Domestic demand for butyl chloride is increasing by an average growth in butyl chloride imports in Indonesia of 6.86% in 2015 until 2019 with import values in 2019 reaching 8,565,857 kg (Comtrade, 2022). The increase of import value is because the functions of butyl chloride are very diverse, that the demand for butyl chloride will increase, so the establishment of a butyl chloride factory is a good alternative so that it can create new jobs for residents around the factory and from outside the area and increase local government revenue. The establishment of this plant is supported by the existence of a butanol and HCl factory in Indonesia where this material is the primary raw material in producing butyl chloride.

Process Selection

Butyl chloride with the molecular formula C4H9Cl can be produced by two processes

A. Butanol Hydrochlorination

The hydrochlorination process is a process in which halogen atoms derived from hydrochloric acid combine with an organic compound. In the manufacture of butyl chloride, the hydrochlorination process occurs by substitution reaction mechanism. Butyl chloride production from butanol and hydrochloric acid runs in the liquid–liquid phase. The reaction is as follows:

C4H9OH(l)	+	HCl(l)	$\longrightarrow$	C4H9Cl(l)	+	H2O
olefin		Hydrochloric Acid		Butyl Chloride		Water

The reaction between butanol and hydrochloric acid is an equilibrium reaction. This process operates at a temperature of 80oC and a pressure of 1 atm and molar ratio between butanol and hydrochloric acid is 1:1 to produce a conversion of 90% - 95% (Aijun, 2008).

B. Olefin Hydrochlorination

The process for making butyl chloride can use the technology of the olefin hydrochlorination process, where butyl chloride is produced by a substitution reaction between olefin and hydrochloric acid with the help of a boron trifluoride catalyst, the reaction that occurs is as follows:

C4H8(l)	+	HCl(l)	$\xrightarrow{\text{BF3}}$	C4H9Cl(l)
olefin		Hydrochloric Acid		Butyl Chloride

This reaction was carried out at RATB with a liquid-liquid phase and the olefin: catalyst ratio was 10:1 to 20:1, the pressure was 500 to 600 psia and the operating temperature was 100^{o}F and the resulting conversion was 84% (Axe, 1948).

The butyl chloride production process chosen is the best is Process A, which is the butanol hydrochlorination process with the reaction mechanism between butanol and hydrochloric acid because the operating conditions of the process are lower operating pressure, but produce a higher conversion than Process B or hydrochlorination olefin.

SPECIFICATIONS OF RAW MATERIALS AND PRODUCTS

Raw Material Specifications

A. Butanol

Molecular Formula	: C4H9OH
Purity	: 99.5%wt
Phase	: Liquid
Color	: Colorless
Impurities (H2O)	: 0.5%wt
Boiling point	: 117.7^{o}C
Solubility	: 7.7 g/100 g H_2O

(PT Petro Oxo Nusantara)

B. Hydrochloric Acid

Molecular Formula	: HCl
Purity	: 33%wt
Phase	: Liquid
Color	: Colorless
Impurities (H2O)	: 67%wt
Boiling point	: 84^{o}C
Solubility	: 63.3 g/100 g H_2O

(PT Asahimas Chemical)

Product Specifications

A. Butyl Chloride

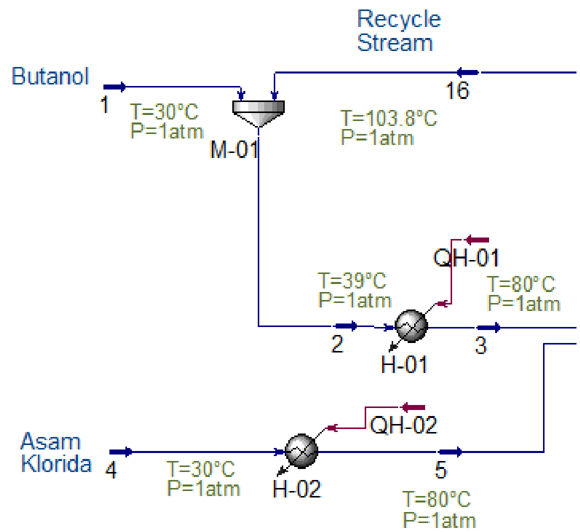
Molecular Formula	: C4H9Cl
Purity	: 99.5% by weight
Phase	: Liquid
Color	: Colorless
Impurity	: 0.5% wt
Boiling point	: 78^{o}C
Solubility	: 0.11 g/100 g H_2O

(Haihang Industry Co., LTD)

SIMULATION PROCESS

Process Details

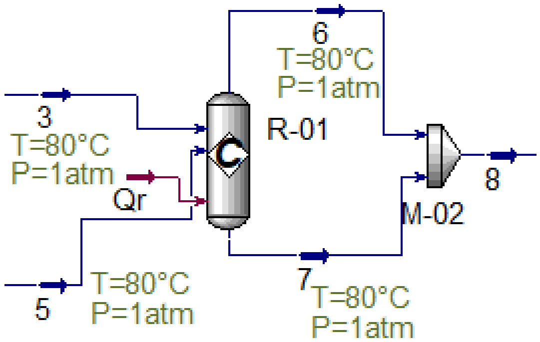
A. Raw Material Preparation Stage



The process of preparing raw materials at this factory begins with flowing butanol and hydrochloric acid from a storage tank which is stored at the same conditions, namely a temperature of 30ºC and a pressure of 1 atm. Butanol from the storage tank enters the mixer (M-01) together with the output recycle stream under the distillation tower (MD-01) which before entering into the reactor is heated to a temperature of 80oC with heater 1 (H-01). Meanwhile, hydrochloric acid from the storage tank enters the heater (H-02) to increase the temperature to 80oC which then enters the reactor (R-01). The composition of each stream at the raw material preparation stage can be seen in the following table,

	17	1	2	4
1-Butanol	0.7317	0.9601	0.9334	0.0000
HCl	0.0000	0.0000	0.0000	0.1887
1-ClC4	0.2115	0.0000	0.0247	0.0000
H2O	0.0569	0.0399	0.0419	0.8113

B. Reaction Stage



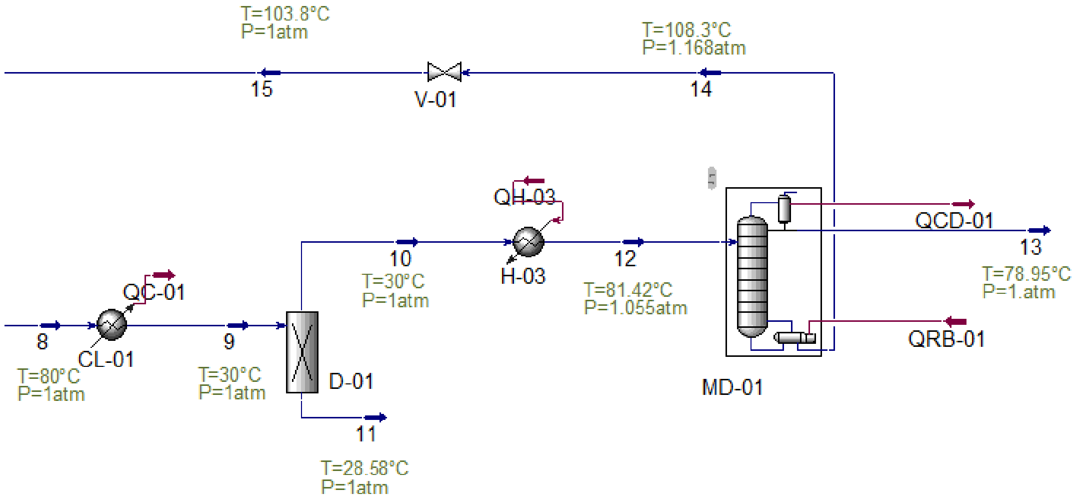
Materials that have been heated, both butanol mixed with recycle flow and hydrochloric acid enter the reactor (R-01) simultaneously. Inside the reactor the following reactions occur:

$C_4H_9OH(l)$	+	$HCl(l)$	$\longrightarrow$	$C_4H_9Cl(l)$	+	H_2O
olefin		Hydrochloric Acid		Butyl Chloride		Water

The reaction occurs isothermically at 80oC to produce a butanol conversion of 90%. The following data composition involved in the reaction stage,

	3	5	7	6	8
1-Butanol	0.9334	0.0000	0.0148	0.0250	0.0154
HCl	0.0000	0.1887	0.0016	0.3266	0.0194
1-ClC4	0.0247	0.0000	0.1378	0.2190	0.1423
H2O	0.0419	0.8113	0.8458	0.4294	0.8230

C. Product Separation and Purification Stage



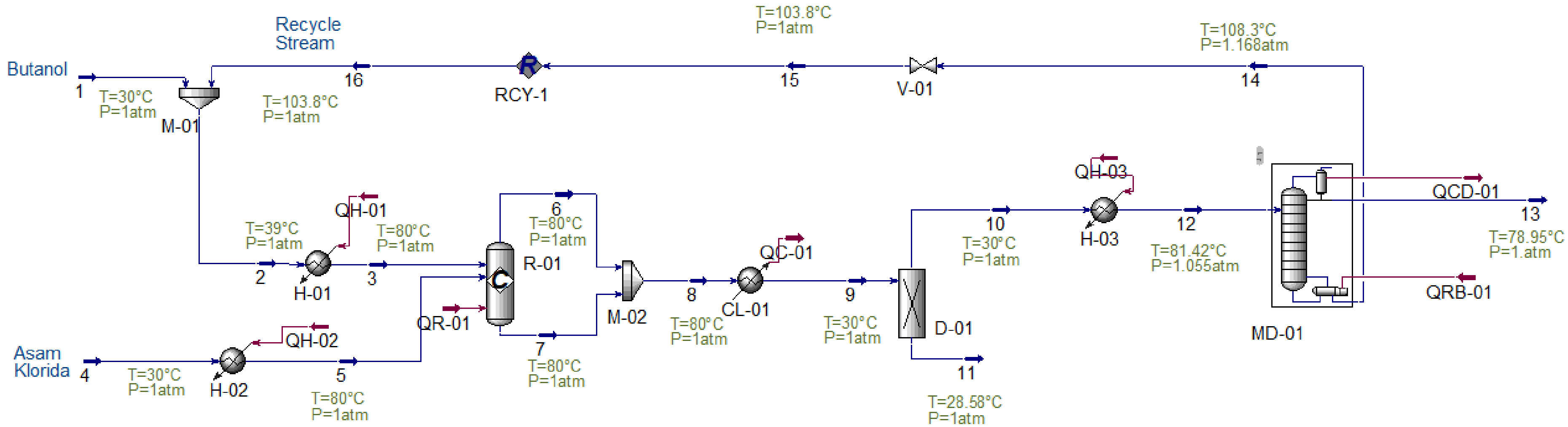
The output product of the reactor still contains unreacted raw material compounds, for this reason it is necessary to separate it, the separation is carried out using a decanter (D-01). Based on the differences in the solubility of the substance and its density, the decanter is carried out at a temperature of 30oC for this reason a cooler (C-01) is needed to cool the output product of the reactor (R-01). The output of the decanter (D-01) is the heavy phase and the light phase, the heavy phase goes to the waste treatment unit (UPL), while the light phase goes to the distillation tower (MD-01).

Light phase pass through heater 3 (H-03) so that the MD-01 feed condition is saturated to facilitate the distillation process. The upper output of the distillation tower is butyl chloride product with a purity of 99.5% by weight, while the lower output is non-volatile butyl chloride, reusable butanol and water which later goes to M-01 to be mixed with butanol from the storage tank. The composition at the separation and purification stage can be seen in the following table,

	9	11	12	13	14	15
1-Butanol	0.0154	0.0889	0.0013	0.0889	0.0012	0.7315
HCl	0.0194	0.0000	0.0231	0.0000	0.0000	0.0000
1-ClC4	0.1423	0.8864	0.0002	0.8864	0.9785	0.2115
H2O	0.8230	0.0246	0.9753	0.0246	0.0202	0.0569

Process Flow Diagrams**Hysys**

The following is a flowchart of the process for making butyl chloride from butanol and hydrochloric acid using hysys software.



Mass Balance Table and Operating Conditions

Parameter	1	2	3	4	5	6	7	8
Temperature (°C)	30	39.04	80	30	80	80	80	80
Pressure(atm)	1	1	1	1	1	1	1	1
Vapor Fraction	0	0	0	0.19	0.3526	1	0	0.0549
Mass Flow (kg/h)	3055	3477	3477	5255	5255	670.9	8061	8732
Component Flow Rate (kg/h)								
Butanol	3024874	3330184	3330184	0	0	29.7171	303.3012	333.0184
Hydrochloric Acid	0	0	0	1681609	1681609	191.2809	16.0347	207.3156
Butyl Chloride	0	110.1924	110.1924	0	0	325.6453	3527577	3853223
Water	30,554	36.3234	36.3234	3573,419	3573,419	124.2636	4213.92	4338.183

Parameter	9	10	11	12	13	14	15	16
Temperature (°C)	30	30	28.58	81.42	78.95	108.3	103.8	103.8
Pressure(atm)	1	1	1	1,055	1	1.168	1	1
Vapor Fraction	0.0074	0	0.0178	0	0	0	0.0252	0.0252
Mass Flow (kg/h)	8732	4178	4554	4178	3757	421.3	421.3	421.3
Component Flow Rate (kg/h)								
Butanol	333.0184	309.0411	23.9773	309.0411	3.7311	305.31	305.31	305.31
Hydrochloric Acid	207.3156	0	207.3156	0	0	0	0	0
Butyl Chloride	3853223	3848213	5.0092	3848213	3738004	110.2092	110.2092	110.2092
Water	4338.183	20.8233	4317.36	20.8233	15.0526	5.7707	5.7707	5.7707

TOOL SPECIFICATIONS

Main tools

A. Reactor (R-01)

Function : Reacting butanol and hydrochloric acid

Amount :1

Reaction :C4H9OH(l) + HCl(l) -> C4H9Cl(l) + H2O(l)

Conversion :90%

Operating conditions

Pressure :1 atm

Temperature :80oC

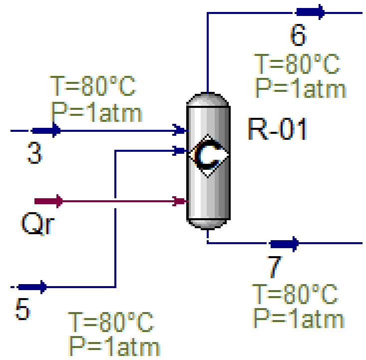
Tank Dimensions

Form : Vertical Cylinder

Volume : 27.71 m3

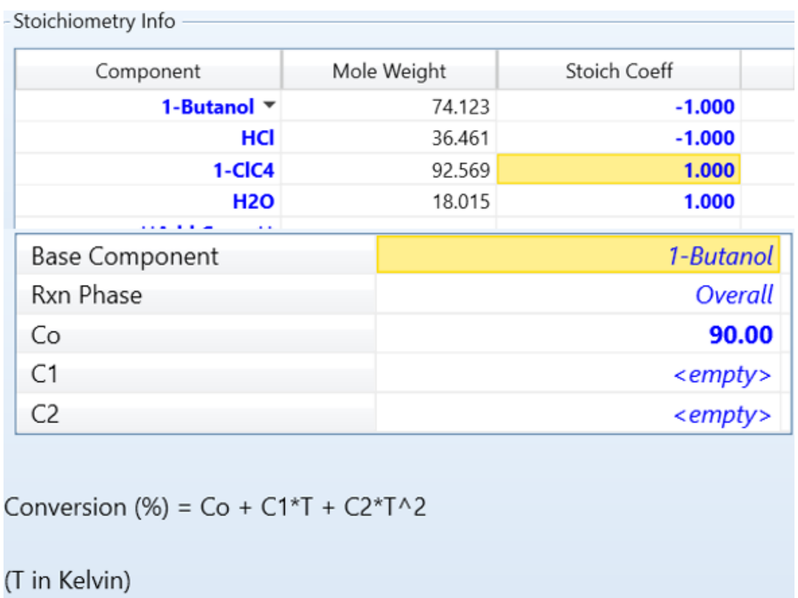
Diameter : 2.8m3

Tall : 4.5m3



Process Simulation

1. Stoichiometric equations and conversion equations



Stoichiometry Info

Component	Mole Weight	Stoich Coeff
1-Butanol	74.123	-1.000
HCl	36.461	-1.000
1-ClC4	92.569	1.000
H2O	18.015	1.000

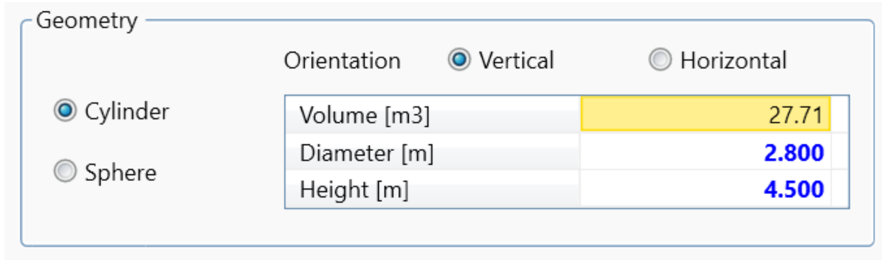
Base Component	1-Butanol
Rxn Phase	Overall
Co	90.00
C1	<empty>
C2	<empty>

Conversion (%) = Co + C1*T + C2*T^2

(T in Kelvin)

The stoichiometric input is the components and their stoichiometric coefficients and the conversion obtained is 90% based on research conducted by Aijun (2008).

2. Reactor shape and size



The shape of the reactor is a vertical cylinder with a diameter of 2.8 m and a height of 4.5 m so that a volume of 27.71 m3 is obtained.

3. operating conditions

Name	3	5	7	6	QR-01
Vapour	0.0000	0.3526	0.0000	1.0000	<empty>
Temperature [C]	**80.00**	**80.00**	**80.00**	80.00	<empty>
Pressure [atm]	**1.000**	**1.000**	1.000	1.000	<empty>
Molar Flow [kgmole/h]	48.13	244.5	276.5	16.06	<empty>
Mass Flow [kg/h]	3477	5255	8061	670.9	<empty>
Std Ideal Liq Vol Flow [m3/h]	4.252	5.513	8.574	0.7464	<empty>
Molar Enthalpy [kJ/kgmole]	-3.100e+005	-2.380e+005	-2.654e+005	-1.699e+005	<empty>
Molar Entropy [kJ/kgmole-C]	95.90	77.69	41.99	192.6	<empty>
Heat Flow [kJ/h]	-1.492e+007	-5.820e+007	-7.339e+007	-2.729e+006	-2.996e+006

The reactor runs isothermically with exothermic reaction properties so that there is heat coming out of the reactor.

B. Decanter (D-01)

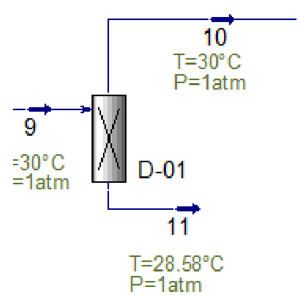
Function : Separating components based on the solubility and density of each component of the solution

Amount : 1

operating conditions

Pressure : 1 atm

Temperature : 30°C



Process Simulation

1. operating conditions

Name	9	10	11
Vapour	0.0074	0.0000	0.0178
Temperature [C]	30.00	30.00	28.58
Pressure [atm]	0.9901	1.000	1.000
Molar Flow [kgmole/h]	292.6	46.90	245.7
Mass Flow [kg/h]	8732	4178	4554
Std Ideal Liq Vol Flow [m3/h]	9.320	4.721	4.599
Molar Enthalpy [kJ/kgmole]	-2.660e+005	-1.913e+005	-2.802e+005
Molar Entropy [kJ/kgmole-C]	30.63	102.7	12.52
Heat Flow [kJ/h]	-7.783e+007	-8.971e+006	-6.886e+007

The decanter runs adiabatically with the set light phase temperature of 30^{o}C resulting in a decrease in the heavy phase temperature of 28.58^{o}C.

2. Separation fractions in the heavy and light phases

Components	Basis	Type	10	11
1-Butanol	Mass	*FeedFrac. to Products*	0.9280	7.200e-002
HCl	Mass	*FeedFrac. to Products*	0.0000	1.000
1-ClC4	Mass	*FeedFrac. to Products*	0.9987	1.300e-003
H2O	Mass	*FeedFrac. to Products*	4.800e-003	0.9952

Fraction data based on the solubility of the substance. The heavy phase, namely current 11, is soluble in water, while the light phase, namely current 10, is insoluble in water.

C. Distillation Tower (MD-01)

Function : Purify butyl chloride from butanol and water

Amount : 1

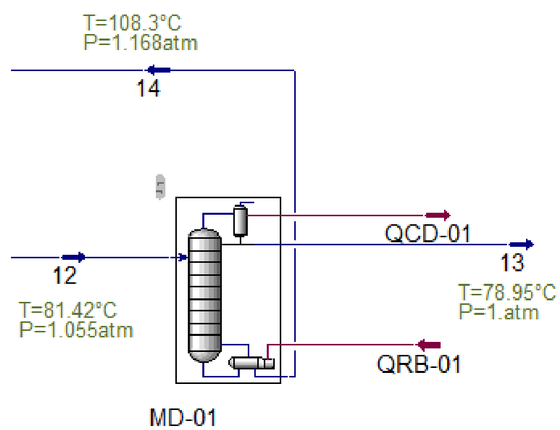
operating conditions

Pressure

- Bait : 1055 atm
- Condenser : 1 atm
- *Reboilers* : 1168 atm

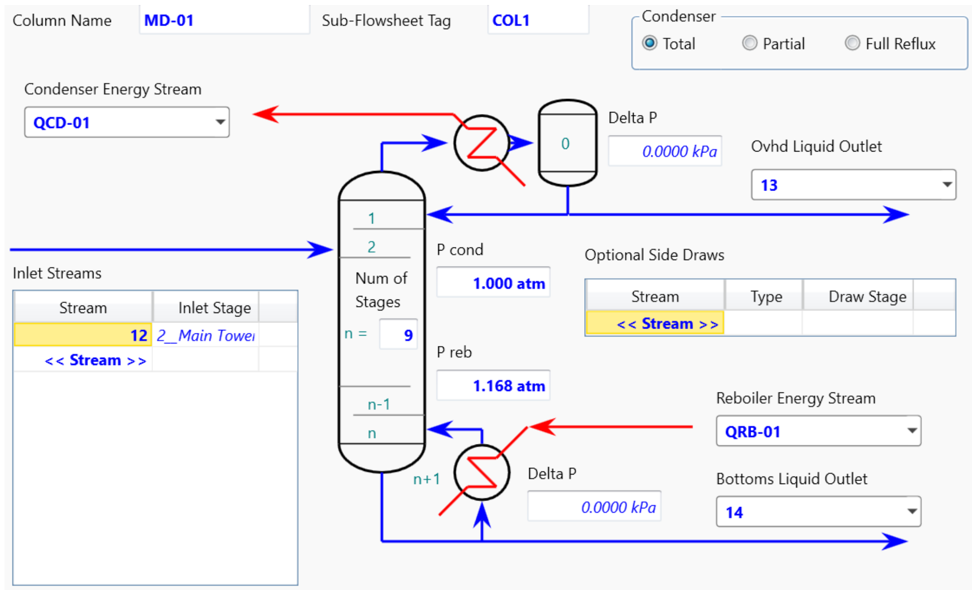
Temperature

- Bait : 81.42^{o}C
- Condenser : 78.95^{o}C
- *Reboilers* : 108.3^{o}C



Process Simulation

1. Pressure on condenser and reboiler



The input data is the number of stage 9 with inlet stage 2 and the total condenser type condenser with a condenser pressure of 1 atm, and a reboiler pressure of 1,168 atm.

2. The purity setting is 99.5% by weight

	Specified Value	Current Value	Wt. Error	Active	Estimate	Current
Reflux Ratio	5.000	5.000	0.0000	☑	☑	☑
Distillate Rate	<empty>	41.27	<empty>	☐	☑	☐
Reflux Rate	<empty>	206.3	<empty>	☐	☑	☐
Btms Prod Rate	<empty>	5.630	<empty>	☐	☑	☐
Comp Fraction	0.9950	0.9950	0.0000	☑	☑	☑

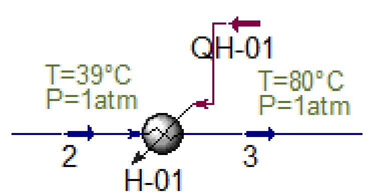
MD simulation monitoring, namely the reflux ratio 5 and the upper component fraction, namely 99.5%wt butyl chloride.

Support tools

A. *Heater*1 (H-01)

Function : Heat the butanol output of mixer 1 to input the reactor to a temperature of 80°C

Heat load : 4,019 x 105 kJ/h



Simulation process

3. Heater operating conditions 1

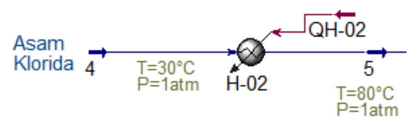
Name	2	3	QH-01
Vapour	0.0000	0.0000	<empty>
Temperature [C]	39.04	80.00	<empty>
Pressure [atm]	1.000	1.000	<empty>
Molar Flow [kgmole/h]	48.13	48.13	<empty>
Mass Flow [kg/h]	3477	3477	<empty>
Std Ideal Liq Vol Flow [m3/h]	4.252	4.252	<empty>
Molar Enthalpy [kJ/kgmole]	-3.184e+005	-3.100e+005	<empty>
Molar Entropy [kJ/kgmole-C]	53.66	95.90	<empty>
Heat Flow [kJ/h]	-1.533e+007	-1.492e+007	4.019e+005

The heater 1 output temperature input is 80^{o}C with a constant pressure of 1 atm so that the required heat is obtained.

B. *Heater*2 (H-02)

Function : Heating HCl from the storage tank to 80^{o}C for reactor input

Heat load : 2,416 x 106 kJ/h



Simulation process

1. Heater operating conditions 2

Name	4	5	QH-02
Vapour	0.1920	0.3526	<empty>
Temperature [C]	30.00	80.00	<empty>
Pressure [atm]	1.000	1.000	<empty>
Molar Flow [kgmole/h]	244.5	244.5	<empty>
Mass Flow [kg/h]	5255	5255	<empty>
Std Ideal Liq Vol Flow [m3/h]	5.513	5.513	<empty>
Molar Enthalpy [kJ/kgmole]	-2.479e+005	-2.380e+005	<empty>
Molar Entropy [kJ/kgmole-C]	47.49	77.69	<empty>
Heat Flow [kJ/h]	-6.062e+007	-5.820e+007	2.421e+006

The heater 2 output temperature input is 80oC with a constant pressure of 1 atm so that the required heat is obtained.

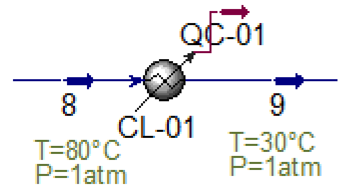
C. *Cooler*1(CL-01)

Function : Cooling the reactor outlet solution to 30oC before entering the decanter

Cooling load : 1,717 x 106 kJ/h

Simulation process

1. Heater cooler operating conditions 1



Name	8	9	QC-01
Vapour	0.0549	0.0074	<empty>
Temperature [C]	80.00	30.00	<empty>
Pressure [atm]	1.000	0.9901	<empty>
Molar Flow [kgmole/h]	292.6	292.6	<empty>
Mass Flow [kg/h]	8732	8732	<empty>
Std Ideal Liq Vol Flow [m3/h]	9.320	9.320	<empty>
Molar Enthalpy [kJ/kgmole]	-2.601e+005	-2.660e+005	<empty>
Molar Entropy [kJ/kgmole-C]	50.25	30.63	<empty>
Heat Flow [kJ/h]	-7.612e+007	-7.783e+007	1.717e+006

Cooler 1 output temperature input is 30°C so that the required cooling load is obtained.

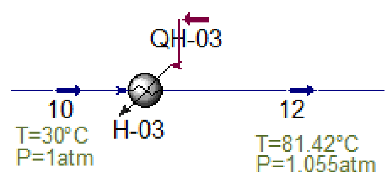
D. *Heater*3 (H-03)

Function :Heat the top outlet temperature or the light phase outside the decanter to a temperature of 81.42°C

Heat load :3,763 x 105 kJ/h

Simulation process

1. Heater operating conditions 3



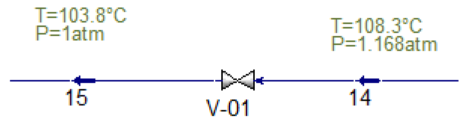
Name	10	12	QH-03
Vapour	0.0000	0.0000	<empty>
Temperature [C]	30.00	81.42	<empty>
Pressure [atm]	1.000	1.055	<empty>
Molar Flow [kgmole/h]	46.90	46.90	<empty>
Mass Flow [kg/h]	4178	4178	<empty>
Std Ideal Liq Vol Flow [m3/h]	4.721	4.721	<empty>
Molar Enthalpy [kJ/kgmole]	-1.913e+005	-1.833e+005	<empty>
Molar Entropy [kJ/kgmole-C]	102.7	141.3	<empty>
Heat Flow [kJ/h]	-8.971e+006	-8.595e+006	3.763e+005

The heater 3 output temperature input is 81.42oC with a pressure of 1,055 atm or a pressure drop of 0,055 atm so that the required heat is obtained.

E. Valve 1 (V-01)

Function : Lower the yield pressure at the bottom of the distillation tower (MD-01) to recycle together with the butanol from the storage tank on mixer 1 (M-01).

Simulation process



1. Valve operating conditions 1

Name	14	15
Vapour	0.0000	0.0252
Temperature [C]	108.3	103.8
Pressure [atm]	1.168	1.000
Molar Flow [kgmole/h]	5.630	5.630
Mass Flow [kg/h]	421.3	421.3
Std Ideal Liq Vol Flow [m3/h]	0.5047	0.5047
Molar Enthalpy [kJ/kgmole]	-2.763e+005	-2.763e+005
Molar Entropy [kJ/kgmole-C]	132.2	129.9
Heat Flow [kJ/h]	-1.555e+006	-1.555e+006

The output vale input is 1 atm so it can be mixed with butanol feed in mixer 1 (M-01).

UTILITY SYSTEM

The utility for making butyl chloride as much as 3757 kg/h 99.5%wt from butanol and hydrochloric acid uses the following utilities

	Energy			Greenhouse Gases			Energy Cost Savings		ΔTmin [C]	Status
	Current [kJ/h]	Target [kJ/h]	Saving Potential [kJ/h]	Current [kg/h]	Target [kg/h]	Reduction Potential [kg/h]	Cost/Yr	%		
LP Steam	9.891E+06	7.836E+06	2.055E+06	552.8	438	114.8	34,224	20.77	**10.0**	
Total Hot Utilities	**9.891E+06**	**7.836E+06**	**2.055E+06**	**552.8**	**438**	**114.8**	**34,224**	**20.77**		
Cooling Water	1.139E+07	2.799E+05	1.111E+07	636.6	15.64	620.9	20,690	97.54	**5.0**	
Air	0	9.055E+06	-9.055E+06	0	506.1	-506.1	-79	N/A	**10.0**	
Total Cold Utilities	**1.139E+07**	**9.335E+06**	**2.055E+06**	**636.6**	**521.7**	**114.8**	**20,611**	**97.17**		

The details of the types of utilities used are as follows

Unit Operation	Energy Stream	Utilities Type	Process Stream Temperatures [C]		Utility Temperatures [C]	
			Inlet	Outlet	Inlet	Outlet
R-01@Main	QR-01@Main	*Cooling Water*	80.0	80.0	20.0	25.0
H-01@Main	QH-01@Main	*LP Steam*	39.0	80.0	125.0	124.0
H-02@Main	QH-02@Main	*LP Steam*	30.0	80.0	125.0	124.0
CL-01@Main	QC-01@Main	*Cooling Water*	80.0	30.0	20.0	25.0
H-03@Main	QH-03@Main	*LP Steam*	30.0	81.4	125.0	124.0
Condenser@COL1	CMD@COL1	*Cooling Water*	79.2	79.0	20.0	25.0
Reboiler@COL1	RMD@COL1	*LP Steam*	98.6	108.3	125.0	124.0

The calculation of the energy flow for each tool along with the mass flow rate for the utility used is as follows

Tool	Energy kJ/h		*utilities*Mass Flow Rate (kg/h)	*utilities*type
	Inputs	output		
R-01		2,996 x 106	1,432 x 105	*cooling*water
H-01	4,019 x 105		183	LP Steam
H-02	2,421 x 106		1102	LP Steam
CL-01		1,717 x 106	8,210 x 104	*cooling*water
H-03	3,763 x 105		171.3	LP Steam
CD-01		6,677 x 106	3,192 x 105	*cooling*water
RB-01	6,691 x 106		3046	LP Steam

So that the total LP steam utility used is 4502.3 kg/h with an energy of 9.89 x 106 and the cooling water utility used is 5.45 x 105 with an energy of 1.14x107.

CONCLUSION

1. The reaction of forming butyl chloride with 3055 kg/d of butanol as raw material, 3477 kg/h of hydrochloric acid produces 99.5% wt butyl chloride of 3757 kg/d.
2. The tools used in this process are:
   a. *Mixers*2 pieces
   b. Reactor 1 piece
   c. *decanter*1 piece
   d. Distillation tower 1 piece
   e. *Heater*3 pieces
   f. *Cooler*1 piece
   g. *Valves*1 piece
3. The process can use the LP steam utility as much as 4502.3 kg/h with an energy of 9.89 x 106 kJ/h and cooling water of 5.45 x 105 kg/h with an energy absorbed of 1.14 x 107.

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