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Design of a Distillation Column for the Separation of Refrigerants from Natural Gas Chlorination

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Abstract.

The design of a plug distillation column for the separation of refrigerants from natural gas chlorination, was aimed at achieving high purity volume percent of Methyl Chloride (CH_3Cl) and Methylene Chloride (Ch_2Cl_2) as desired products. The distillation column was simulated using Aspen HYSYS software at a temperature of 50^0C and 10atm Pressure. The composition of the refrigerants coming into the distillation column are Methyl chloride ***192.41mol/sec,*** *Methylene Chloride* ***80.17 mol/sec****, Chloroform* ***32.07mol/sec****, Tetra Chloromethane* ***16.04mol/sec*** *after the chlorination of 200,000 metric tonnes per year of Natural gas. The distillation column operating parameters were set and distillation column sizing was done to determine Column height, Column diameter, tray spacing, tray volume, tray thickness and weir height. From the results obtained, high pressure operation of the distillation column favours the separation of the refrigerants. HYSYS simulation of this distillation column design is found to improve both engineering, Safety and energy efficiency of the overall system of separation.*

Keywords: Natural gas, Aspen HYSYS, Distillation Column, Refrigerants, Separation

1. Introduction

Distillation is one of the separation techniques where a mixture of two or more liquid or vapour substances is separated into its component fractions of desired purity by the application and removal of heat (Tham, 1997). Distillation is one of the oldest unit operation processes and due to its usefulness, it is also one of the most important operation in the chemical and petroleum industry. This separation method is also called fractional distillation. Though distillation had been practiced for many centuries, it was not known until 1957 when the first technical publication on distillation was developed. Distillation process is an energy consuming process requiring huge amounts of energy for both heating and cooling. It has been estimated that about half of plants operating costs are from distillation (Lee, 2019).

The principle of the separation in distillation processes is to vaporize the more volatile component. The pure component is collected from the top of the column in its simplest form (binary mixture). The distillation of liquid or vapor mixtures is dependent on the differences in the volatility of the components. Separation is easier and high purity is obtained if the relative volatilities of components in the mixture are large. (Richardson, 2007). From previous researchers, the mixture of refrigerants is condensed while unreacted methane is recycled to the mixing chamber. As all the chlorine was reacted with the methane, so that little or no chlorine remains in the reaction gases. Crude methyl chloride was distilled under pressure to yield pure Methyl chloride and Dichloromethane chloride of refrigerant grade. Approximately 85 – 90% of the condensate distils between -23 to -

25^0C at atmospheric pressure to give a yield of methyl chloride of about 80% based on the amount of chlorine fed. (Boswell & McLaughlin, 2011). The desire is to achieve high purity methyl chloride using Aspen HYSIS to simulate the column at elevated pressure and raise the relative volatility of the various components in the mixture. The research focuses on achieving high purity yield. The Chlorinated Methane products were feed into a distillation column where, methyl chloride and methylene dichloride were separated by a fractionating column. The top product methyl chloride was removed from the top since it is more volatile

2. Materials and Methods

2.1 Materials

The materials required in this research are considered based on several factor including engineering, safety and economics. Plug flow reactor was used for the chlorination of natural gas; Aspen HYSYS, which is a steady state simulation software, was utilized to simulate the Plug Flow reactor. Feed Composition, feed operating condition and process flow diagram were also included.

2.2. Methods

The following methods were considered,

i. Material and energy balance for the production process
ii. Kinetics of the reaction and model development
iii. Simulation of the reactor using Aspen HYSYS
iv. Generate results of the production process
v. Specification and sizing of the reactor.

2.3. Design Assumptions

The following assumptions were made for the development of the design models:

i. A steady state distillation process
ii. The feed stream comprises of four components.
iii. Liquid and vapor flow rates are constants for all trays
iv. Methyl chloride is light key component and methylene chloride is the heavy key component
v. No heat loss as the column is properly lagged
vi. Overhead product is condensed in a total condenser.

2.4. Material Balance for the Distillation Column.

The general conservation equations for one-dimensional is written as follows:

$$\begin{bmatrix} rate\ of\ accumulation \\ of\ materials \\ within\ a\ controlled\ volume \end{bmatrix} = \begin{bmatrix} rate\ of\ inflo \\ of\ material \\ into\ a\ controlled \end{bmatrix}$$

$$\begin{bmatrix} rate\ of\ outflow \\ of\ materials\ in \\ controlled\ volume \end{bmatrix} \pm \begin{bmatrix} rate\ of\ depletion \\ of\ material\ due \\ to\ chemical\ reaction \end{bmatrix} \quad (1)$$

2.4.1 Model development for the Distillation Column

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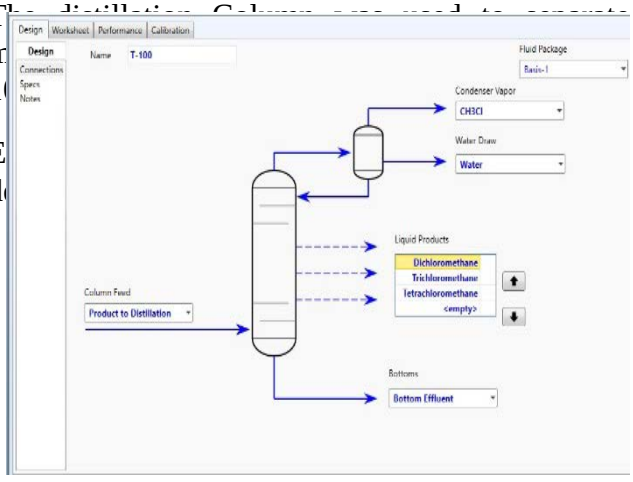


Fig.1: Schematic Diagram for a distillation column

This figure depicts the schematic of the distillation column. The chlorinated methane from a reactor was fed to the column at elevated temperature and pressure. The distillate contains majorly mono chloromethane and the bottom product a combination of di, tri and tetrachloromethane

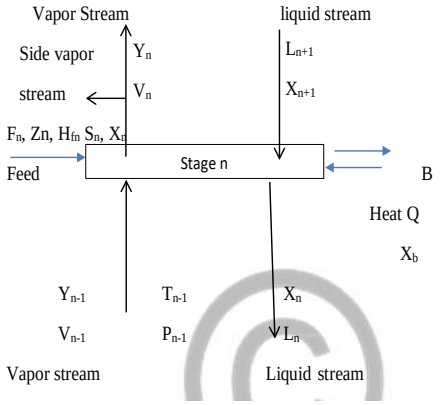


Fig 2. Multicomponent distillation Column diagram for stage n (Feed)

Y_n = The concentration of Vapor leaving tray n

X_n = The concentration of liquid leaving tray n

Y_{n-1} = The concentration of Vapor entering tray n

X_{n+1}=The concentration of Liquid entering tray n

V_n= Stream of vapor mol/hr leaving plate n

V_{n-1}= Stream of vapor mol/hr entering plate n

L_{n+1}=Stream of liquid mol/hr entering plate n

L_n = Stream of liquid leaving plate n

F= Feed flow rate

D = Flow rate of distillate

Q = Heat flow into plate n

Z_n = Mole fraction of component in the feed stream

Total material balance on the rectifying section

At steady state, there is neither accumulation nor depletion,

Rate of accumulation of material within the plate n (kg/s) = 0

Rate of flow of material into the plate n (kg/s) = $L_{n+1} + V_{n-1} + F$

Rate of flow of material out of plate n (kg/s) = $V_n + L_n$

Rate of depletion due to chemical reaction (kg/s) = 0

Substituting the values into equation 1 gives

$$L_{n+1} + V_{n-1} + F = V_n + L_n \quad (2)$$

Equation 2 is total material balance.

Component material balance,

Considering the component balance,

Rate of accumulation of component material within plate n (kg/s) = 0

Rate of flow of material into plate n (kg/s) = $L_{n+1}X_{n+1} + V_{n-1}Y_{n-1} + F_{zn}$

Rate of flow of material out of plate n (kg/s) = $V_nY_n + L_nX_n$

Rate of depletion due to chemical reaction (kg/s) = 0

Substituting the values into equation 1 gives,

$L_{n+1}X_{n+1}+ V_{n-1}Y_{n-1} +F_{zn} = V_nY_n +L_nX_n$ (3)

$X_{n+1}= \frac{V_{nY_n}+L_nX_n-V_{n-1}Y_{n-1}+F_{zn}}{L_{n+1}}$ (4)

Equation 4 represents the operating line equation for rectifying section.

Net flow rates

D is the distillate in mol/sec which is the difference between the flow rates of the streams entering and leaving the top of the column.

$D= V_{n-1}-L_n$ (5)

Material balance of component A which is methyl chloride gives,

$D_{XD} = V_{n-1}Y_{n-1} -L_nX_n$ (6)

D_{XD} is the net flow rate of component A in the rectifying section of the column.

2.4.2 Stripping Section Vapor Flow Rate

The flow rate of vapor at the stripping section is the flow rate of vapor from the bottom to the top of the feed plate and it is obtained as follows.

Rate of accumulation of material within the plate n (kg/s) = 0

Rate of flow of material into plate n (kg/s) = L_{n+1}

Rate of flow material out of plate n = Y_n +B

Rate of depletion due to chemical reaction (kg/s) =0

Substituting into equation 1 gives,

$0 = L_{n+1}- (Y_n + B) – 0$ (7)

$Y_n = L_{n+1} –B$ (8)

Where;
Y_n =The flow rate of vapor out of plate n

L_{n+1} =The flow rate of liquid in plate n

B =The flow rate of bottom product

The desire is to set limit on two key components CH_3Cl and CH_2Cl_2. In this case they are adjacent keys since they are adjacent in listing in order of volatility.

In order to use cooling water as a cooling medium in the overhead condenser, the separation of the refrigerants will be carried out at 10 atm Pressure and 50^{o}C Temperature

2.5 Overall material balance for distillation Column

$F= D+W$ (9)

$F_{xf} = D_{xD}+W_{xw}$ (10)

Where;

F= The feed flow rate

D= The molar flow rate of Distillate

W= The molar flow rate of Residue

X_D = The mole fraction of more volatile component in Distillate

X_W= The mole fraction of more volatile component in Residue

X_F = The mole fraction of more volatile component in feed

Relative volatility Calculation

Where **α**= relative volatility

$\alpha_{top} = P_{vi} / P_{VHK}$ (11)

Where,

P_{vi}= vapour pressure of distillate (in this case CH_3Cl which is the light key component)

P_{VHK} = Vapour pressure of the heavy key component CH_2Cl_2

Mechanical Design

The Mechanical design will determine the shell thickness, weight and other mechanical parameters of a vessel or equipment.

i. The Diameter of the column (Dc) = 0.5 m
ii. The material of construction for the shell is Stainless steel 18 Cr/8Ni unsterilized (304)
iii. Vessel Operating pressure is 10atm = 10.1325 bar
iv. Assuming the column is designed for 10% above the normal operating pressure. So, the design pressure will be 1.1 × 10.1325 = 11.14575 bar = 1.114575 N/mm^2

Theoretical Stages of the Distillation Column

Feskey's method will be used to calculate the theoretical number of stages of the distillation column, N_m

$$N_m = \frac{log\left[\left(\frac{X_{LK}}{X_{HK}}\right)_d \left(\frac{X_{HK}}{X_{LK}}\right)_b\right]}{log \propto_{LK}} \quad (12)$$

Where,

$\propto_{LK}$= Average relative volatility of light key with respect to heavy key

$(X_{LK}, X_{HK})_d$ = The mole fraction of light key and heavy key in distillate respectively.

$(X_{LK}, X_{HK})_b$ = The mole fraction of light key and heavy key in residue respectively

(Coulson and Richardson, Vol 6, 2008)

Using Underwood method,

$$\Sigma \frac{\alpha i x i f}{\alpha i - \vartheta} = 1 - q \quad (13)$$

where,

αi = Average relative volatility of the components

xif = Mole fraction of the components in feed

For minimum Reflux Ratio,

$$\Sigma \frac{\alpha i x i d}{\alpha i - \vartheta} = R_m + 1 \quad (14)$$

Gilliland's correlation for actual number of trays;

$$f(N) = \frac{N - N_m}{N+1} = 1 - exp\left[\left(\frac{1 + 54.4\Psi}{11 + 117.2\Psi}\right)\left(\frac{\Psi - 1}{\Psi^{0.5}}\right)\right] \quad (15)$$

Where,

$$\Psi = \frac{R - R_m}{R+1} \quad (16)$$

Actual Reflux Ratio

The rule of thumb is:

R = (1.2 ------- 1.5) R_m (17)

Kirkbride equation is used to calculate the feed tray location,

$$log\left(\frac{N_r}{N_s}\right) = 0.206 log\left[\left(\frac{W}{D}\right)\left(\frac{x_{HK}}{x_{LK}}\right)_f \left(\frac{x_{bLK}}{x_{dHK}}\right)^2\right] \quad (18)$$

Where Nr = number of stages above the feed

Ns = number of stages below the feed

Column diameter, (Dc)

$$Dc = \sqrt{\frac{4 \times A}{\pi}} \quad (20)$$

Where,

Dc = The diameter. A=Area

Column Area,

$$A_c = \frac{\pi D_c^2}{4} \quad (21)$$

Downcomer Area, (A_d)

The Downcomer area (Ad) is 12% of the column area (Ac):
Net Area, An = Ac - Ad (22)

Active Area, Aa = Ac - 2Ad (23)

Column Height

The height of the distillation column can be deduced using;

$$H_c = (N - 1) \times H_s + \Delta H + \text{t.} \quad (24)$$

where,

N= The number of plates (stages) required in the column

H_s = Tray spacing

ΔH = The distance of liquid holdup and vapour disengagement

t= thickness of plate(shell)

Shell Thickness

$$e = \frac{P_i D_i}{2f - P_i} \quad (25)$$

Where:

e = Column minimum shell thickness

P_i= The design pressure

D_i= Diameter of the distillation column

f =The design stress = from literature at 100ºC the design stress is 140 N/mm^2

Weight of the distillation Column

To find the weight of the shell we use,

$$Weight\ of\ Vessel = 240 \times C_v \times D_m \times (H_v + 0.8 \times D_m) \times t \quad (26)$$

Where,

C_v: =Factor accounts for the weight of the nozzle, for distillation columns = 1.15

H_v= The height of the distillation column

t= shell thickness.

D_m= Diameter of the column plus the shell thickness

Head Design

A Torispherical head is selected.

$$\text{Thickness of the head } (t_h) = \frac{P\ x\ R_c\ x\ C_s}{2fj + P(C_c - 0.2)} \quad (27)$$

Where,

Cs = The stress concentration factor for torispherical heads = $\frac{1}{4}(3 + \sqrt{\frac{R_C}{R_k}})$

R_C = The crown radius,

R_k =The knuckle radius.

2.6. Design Basis/Input Parameters

The data shown in Table 1 are the general input data and defined parameters for the distillation Column.

Table 1. Design Parameters

Parameters	Values
Pressure of Column	10atm (1013KPa)
Temperature	323 K
Feed flow rate	320.69 mol/s

Table 2. Relative Volatility of refrigerants at different temperature

Components	α_{top} $_{(47.2\ ^0C)}$	$\alpha_{bottom(120\ ^0C)}$	$\alpha_{average}=(\alpha_{top} x\ \alpha_{bottom})^{1/2}$
CH_3Cl (LK)	9.1	8.7443	8.92
CH_2Cl_2 (HK)	1	1	1
$CHCl_3$	0.5818	0.6241	0.6026
CCL_4	0.2364	0.50	0.3438

Table 3. Vapour pressure (atm) of Refrigerants at different temperature from literature

	Temperature	
Components	**47.2 ^oC**	**120 ^oC**
CH_3Cl	10atm	69.08 atm
CH_2Cl_2	1.1 atm	7.90 atm
$CHCl_3$	0.64 atm	4.93 atm
CCL_4	0.26 atm	3.95 atm

3. RESULTS AND DISCUSSION

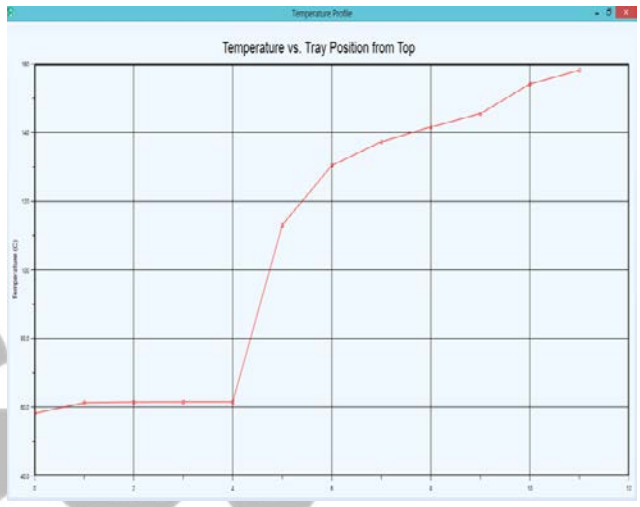
Table 4. Summary of Feed and Distillate flow rate.

	Feed		Distillate		Residue	
Components	**mol%**	**mol/s**	**mol%**	**mol/s**	**mol%**	**mol/s**
CH_3Cl	60	192.41	99	191.13	1	1.28
CH_2Cl_2	25	80.17	1	1.93	61.3	78.24
$CHCl_3$	10	32.07	-	-	25.1	32.07
CCL_4	5	16.04	-	-	12.6	16.04
Total	**100**	**320.69**	**100**	**193.06**	**100**	**127.63**

Table2 shows the Feed flow rate of Methyl chloride as **192.41mol/sec**, Methylene Chloride= **80.17 mol/sec**, Chloroform =**32.07mol/sec**, Tetra chloromethane =**16.04 mol/sec**

99% of pure methyl chloride was recovered after distillation.

Fig 3. Plot of Temperature vs tray position



Shows the Temperature vs Tray position from top. The graph shows the uneven distribution of the temperature across the distillation column.

Fig 4. Plot of molar flow of feed vs tray

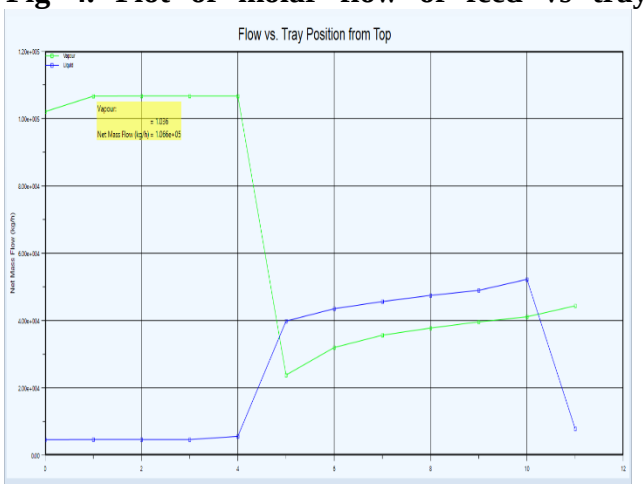


Fig 4 Shows the flow of liquid and vapour at the various stages in the column

The shows that the flow at the top plates have higher vapour concentration than the plates at the bottom plates which represent the behaviour of the system as usually obtained in distillation columns. More liquid in the base of the distillation column with low methyl chloride concentration is expected at the bottom plates. However, the figure shows a relatively steady flow rate of vapour across the column

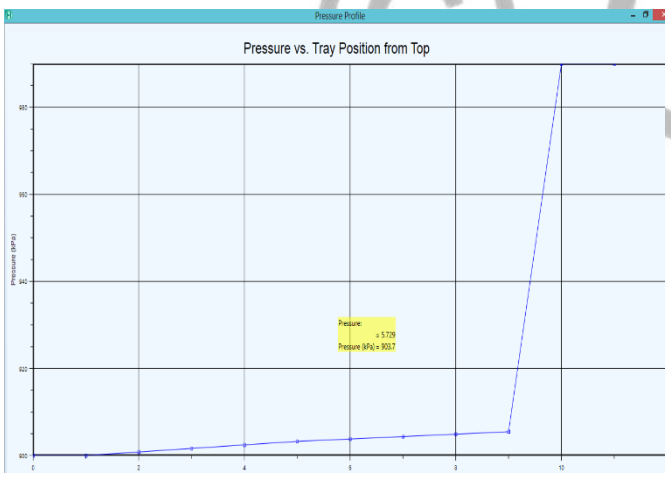


Fig 5. Plot of Pressure vs tray position

This Figure shows a constant pressure being maintained at the various stages. It clearly shows that the recovery of high purity methyl chloride from other chloromethane is achievable at high pressure within the distillation column. In this simulation, a pressure of 1013kpa was maintained. Though negligible dropped in pressure is observed.

Fig 6. Distillation Column tray Sizing

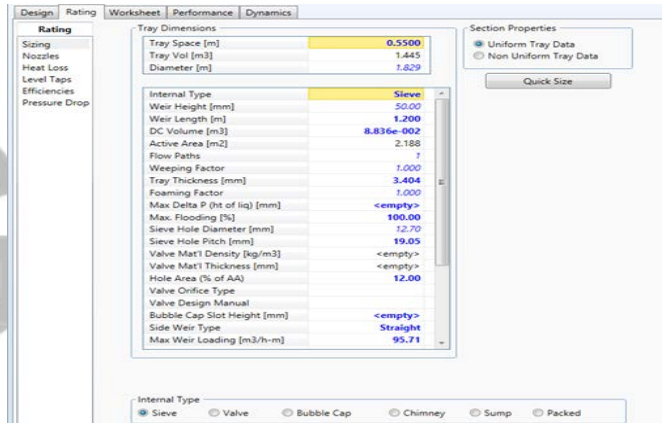


Fig 7. Summary of Distillation Column Result

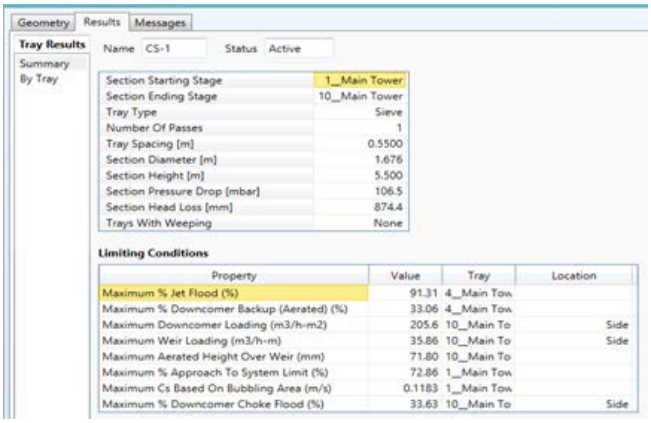


Fig 6 and 7 Show the distillation column sizing result obtained using Aspen HYSYS. The column geometry, internals results are shown

Table 5. Comparison between Aspen HYSYS simulation and Theoretical data of the distillation column sizing

Parameters	Theoretical results	HYSYS Simulation	% Deviations
Column diameter(m)	0.5m	1.676m	70.17
Column height	6.005m	5.50m	8.4
Plate thickness (mm)	5mm	3.404mm	31.9
No of holes on plate	745	668	10.34
Weir length	1.05m	1.2m	12.5
Tray spacing	0.5m	0.55m	9.1
Column area	1.96m^2	2.188m^2	10.4
Hole Area	0.196m^2	0.21886m^2	10.4
Weir Height	50mm	50.mm	0
No of trays	12	10	16.67

The values obtained shows the distillation column specification nccessary to separate the multicomponent refrigerants at the design parameter to give desired purity

Fig 8. Percentage of product recovered after distillation

Fig 8 Shows the percentage of the pure methyl chloride recovered at after distillation 99.99% methyl chloride was recovered at the design condition. The simulation condition gives a high purity methyl chloride

4. Conclusion

The design of a distillation column for the separation of refrigerants from natural gas Chlorination was achieved using Aspen HYSYS software to simulate the separation process and a high purity yield of refrigerants (methyl Chloride and dimethyl chloride) which are the desired products for this research were obtained in a safe manner.

Pressure, Temperatures and Flow rate) were maintained at their desired set points to ensure no external disturbances affect the system negatively.

Comparing theoretical and HYSYS simulation results shows that Aspen HYSY gives,

i. High yield of refrigerants at the given design parameters
ii. Improve efficiency of the overall production process
iii. Improves safety and reliability of the plant

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