CL452 – Design Project

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Group 19

Production of Chloromethane

Final Report

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Chapter 1

INTRODUCTION

1.1 Properties of Chloromethane [1]

Chemical Formula	CH_3Cl
Molecular weight	50.49 g/mol
Chemical Safety	Flammable, Health hazard
Appearance and Odour	Colorless gas with a faint, sweet odour
Boiling Point	-23.7 °C
Melting Point	-97.6 °C
Density	0.911 g/ml at 25 °C (pressure > 1 atm)
Flash Point	-49.55 °C
Taste	Sweet

Table 1.1: Properties of Chloromethane

1.2 Uses of Chloromethane

Chloromethane, whose chemical formula is CH_3Cl, is a water-soluble gas colorless gas that has a faint, sweet odor. It is used as intermediates in many chemicals, but mostly, it is used in the manufacturing of silicones and which is later on used in the manufacturing of methylate silicon. It is also used in the manufacturing of agricultural chemicals such as pesticides and fumigants. It can be used in the production of adhesives and paint additives (additives are used for deforming, good flow, and leveling of paints). Earlier, chloromethane was also used as a refrigerant, but it is not used due to its toxic properties [1].

1.3 Uses of Side-products

Dimethyl ether

Dimethyl ether is generally prepared from methanol in the presence of acidic catalysts. It can be used as a substitute for CFCs. It is also used in personal care products as a propellant for aerosol sprays (hair spray, styling mousse/foam, self-tanner, hair dye, sunscreen, anti-aging treatment). In cold weather, it is used as a starter for gasoline engines of rocket propellant. It is used as Adhesives, sealant chemicals, Intermediates, Propellants, and blowing agents in industries [2].

1.4 Product Specifications [3]

Component	Specifications
Methyl Chloride	99.50 min wt%
Dimethyl ether	20 max ppm
Lower Boiling Compounds	250 max ppm
Higher Boiling Compounds	100 max ppm
Water	80 max ppm
Acidity	10 max, ppm as HCl
Nonvolatile residue	100 max ppm

Table 1.2: Product Specifications

Chapter 2

Market Survey

Chloromethane is mainly used as an intermediate in the production of silicone polymers. These polymers are one of the essential components in the construction sector. So, the need for urbanization leads to an increase in demand for chloromethane. Due to advancements in agriculture to improve crop production, there is an increase in demand for agricultural chemicals such as pesticides, fungicides, insecticides, herbicides, and fertilizers. The use of chloromethane as an intermediate in the production of agricultural chemicals boosts the production as well as consumption of chloromethane. Apart from construction and agricultural usage, it is also used in pharmaceutical, personal care products, automotive, and rubber industries for the production of methylcellulose, quaternary amines, tetramethyl lead, and butyl rubber, respectively.

2.1 Global Consumption Pattern

The pharmaceutical sector is dominated by the chloromethane market with a revenue share of 34%, followed by the construction sector with 15%, and the paint & coatings sector with 13%.
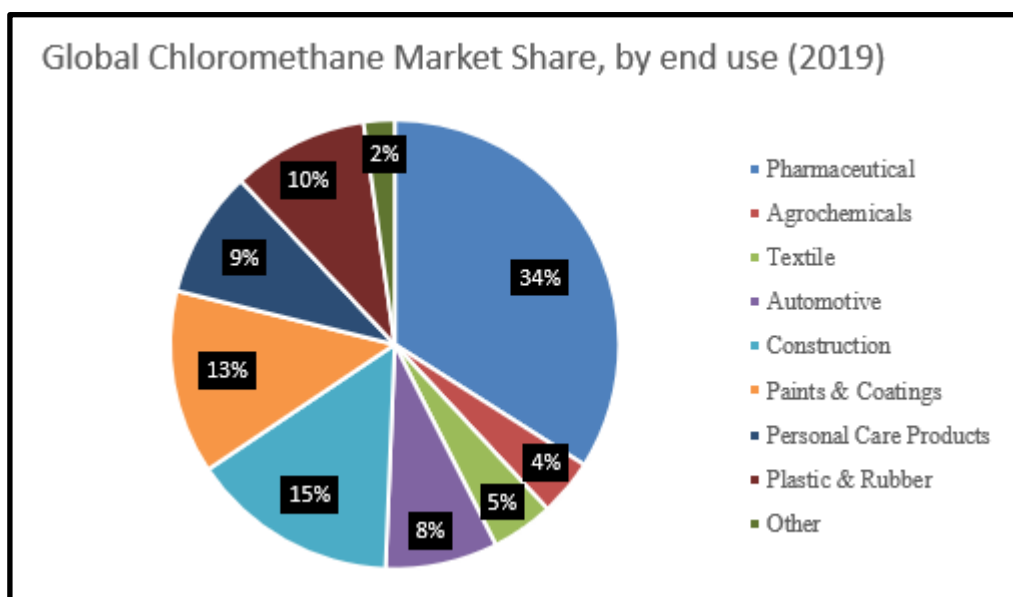
Figure 2.1: Global Chloromethane Consumption, sector-wise analysis

According to Pharma World Magazine, the pharmaceutical sector is anticipated to grow from 1.2 trillion USD in 2018 to over 1.5 trillion USD in 2023. Asia-Pacific region is expected to register the fastest CAGR of 5.3% from 2020 to 2027. It is estimated to be the largest regional market over the upcoming years [4].
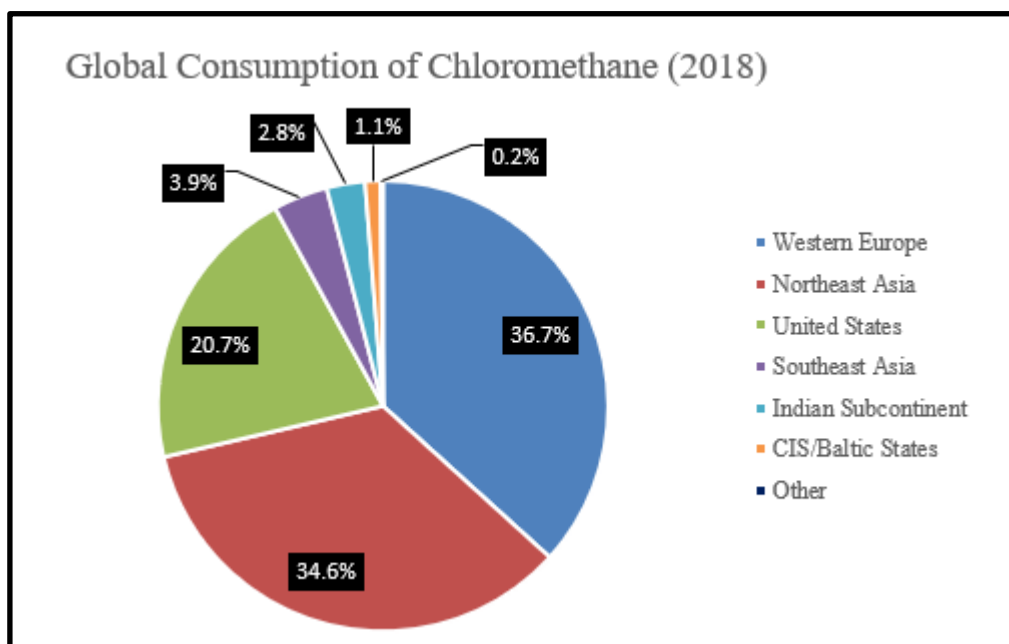
Figure 2.2: Global Chloromethane Consumption, the region-wise analysis

In 2018, Western Europe accounted for the largest consuming region of chloromethane, followed by Northeast Asia and the United States [5].

2.2 Indian Market Scenario [6]
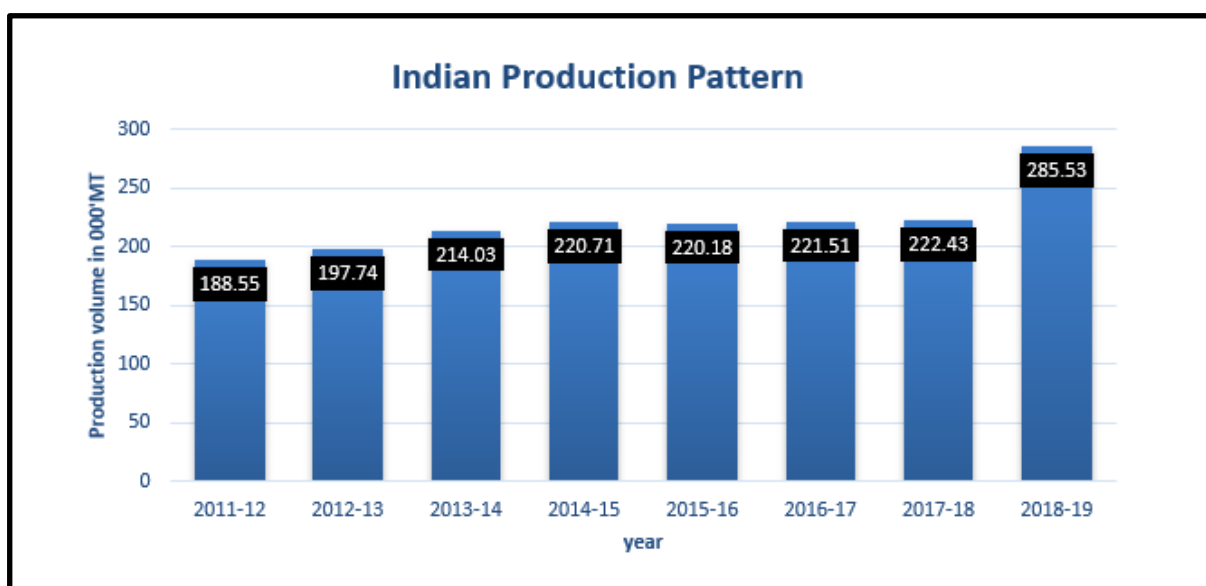
Figure 2.3: Indian Chloromethane Production Volume from 2011-2019
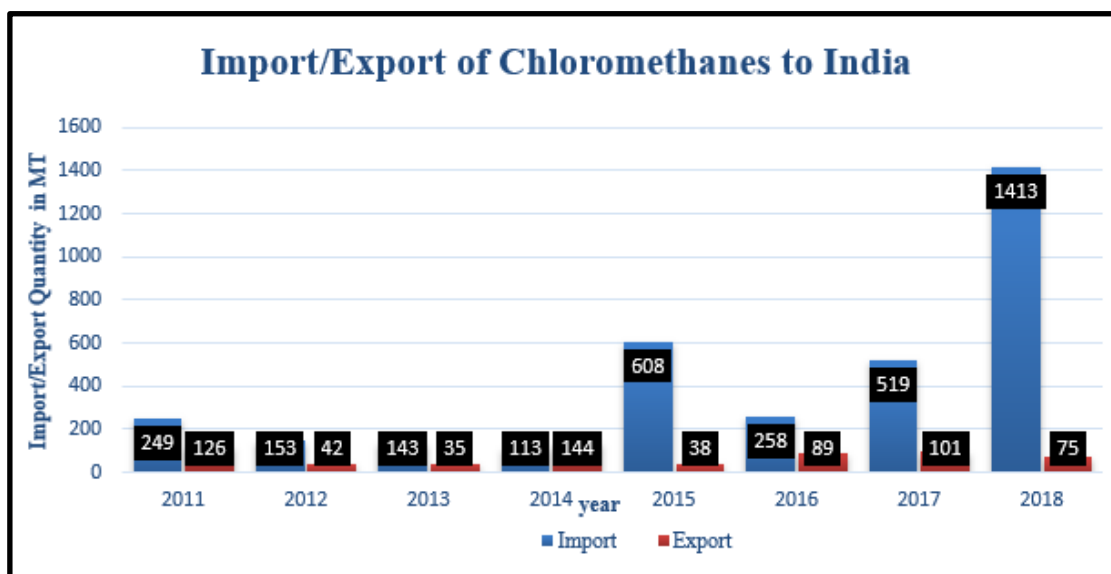
Figure 2.4: Import/Export of Chloromethane to India

2.3 Top Market Producers [7], [8]

The chloromethane market is a highly consolidated market. It is dominated by very few major players and is unlike the fragmented market, where very few dominant companies function in a competitive market.

Company	Location	Production Capacity (TPA)
Dow Chemical	Louisiana (US)	350,000
Vulcan Materials	Kansas (US)	205,000
Ineos Chlor	Runcorn (UK)	150,000
Asahi Glass Co. Ltd.	Japan	85,000
Tokuyama Corporation	Tokuyama (Japan)	60,000
Solvay SA	Italy	50,000
(All plants in China)	China	400,000
(All plants in India)	India	90,000

Table 2.1: Top Producers in the Global Market

Company	Location	Production Capacity (TPA)
Gujarat Alkalies and Chemicals Private Limited (GACL)	Gujarat	40,000
Chemplast Sanmar Limited	Chennai, Tamil Nadu	34,580
Gujarat Fluorochemicals Limited	Gujarat	---

Table 2.2: Top Producers in Indian Market

2.4 Price Trends [6]

The price of chloromethane increased during the early decade of the 2010s. In the latter half, the prices of chloromethane lowered. This may be the result of an increase in the production of chloromethane, better technology in production or increased competition, etc.
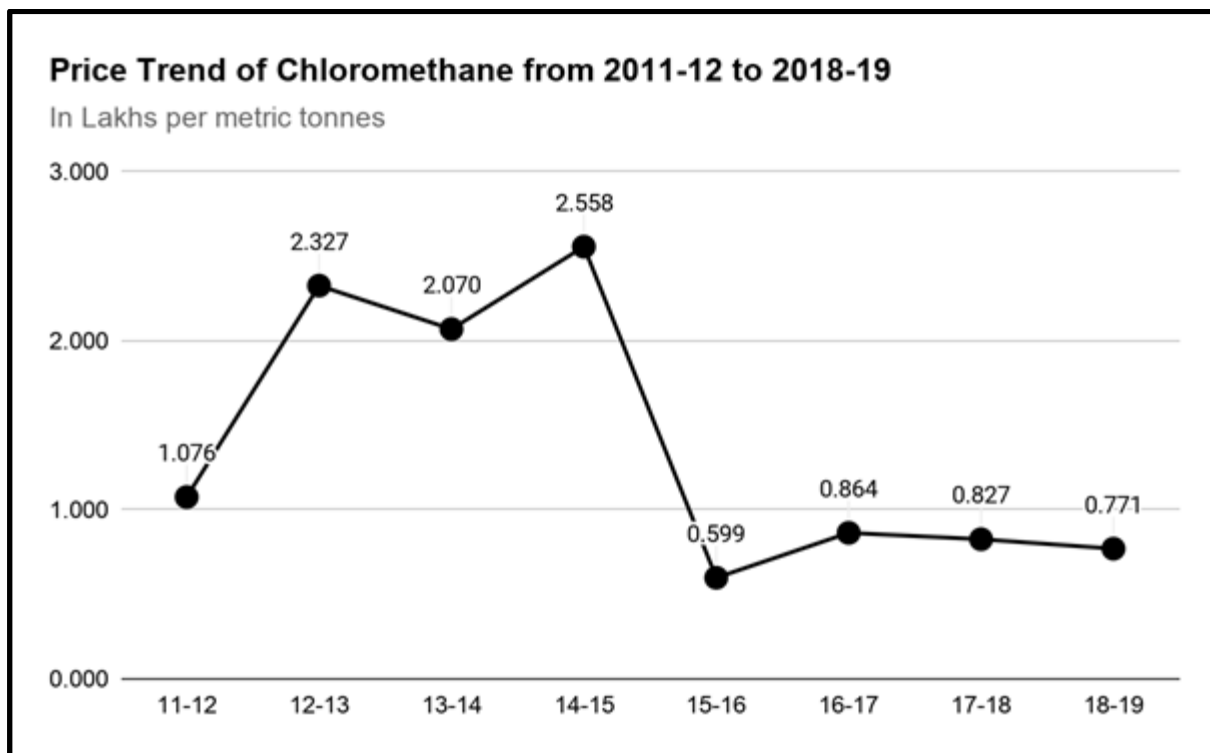
Figure 2.5: Price Trend of Chloromethane from 2011 to 2019

2.5 Technology Providers

- Dow Chemical
- Vulcan Materials
- PPG Industries

2.6 Location Selection for New Plant [8], [9]

The factors used to select the location of any plant are market, availability of raw material, land, utilities, and labor, environmental regulations, political and strategic factors, etc.

Reasons for selecting Visakhapatnam-Kakinada belt, Andhra Pradesh:

- Proximity to the 3 ports, including Visakhapatnam Port, for importing the raw material and exporting the final product (especially to the Asia-Pacific region)
- Well established industrial belt with great connectivity to the rest of the world via roadways, railways, and waterways

- Availability of cheap and skilled labor
- High and growing local demand
- Favourable policies by the Indian government and business friendly environment in Andhra Pradesh
- Availability and easy access to utilities like power, water

Based on the above-mentioned factors, the final location for the Chloromethane plant was selected to be Visakhapatnam, Andhra Pradesh, India.

2.7 Proposed Capacity of New Plant

There is rising demand for chloromethane in Asia-Pacific region as well as the domestic market. India has the highest CAGR for the chloromethane market in the world, led by growth in pharmaceutical, agrochemical and construction sectors. The domestic demand itself is touching 3,00,000 MTPA. The global market which is around 17,00,000 MTPA presently is supposed to grow by 30-40% by 2027. Considering all these factors, we have chosen the capacity to be 1,00,000 MTPA for our plant. This quantity will also give us the advantage of scale (~6% of global production).

Chapter 3

PRODUCTION PROCESS

3.1 Routes for production of Monochloromethane [10]

Route 1: Hydrochlorination of methanol

Main Reaction

$$P: 5 \text{ bar}, T: 280\ ^\circ C - 350\ ^\circ C$$
$$CH_3OH\ (g) + HCl\ (g) \ \text{----------------->} \ CH_3Cl\ (g) + H_2O\ (g)$$
$$\text{ɣ-aluminum oxide}$$

Side Reaction

$$2CH_3OH\ (g) \ \text{---------->} \ (CH_3)_2O\ (g) + H_2O\ (g)$$
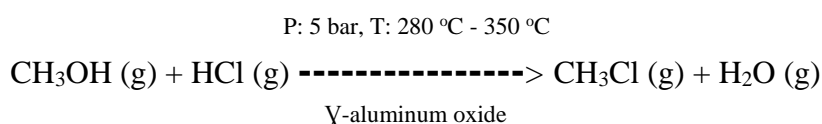
Sulfuric Acid Treatment

$$CH_3OH\ (g) + HCl\ (g) \ \text{----------------->} \ CH_3Cl\ (g) + H_2O\ (g)$$

This is a catalytic method that is done at 3-6 bar pressure and 280-350 °C temperature. This route has a purity of 96-99% of monochloromethane, with the major byproduct dimethyl ether ranging from 0.2- 1%. Excess HCl gives a purer product. The catalyst used is ɣ-aluminum oxide, doped with O2 for better results, lesser byproducts, and improved catalyst life. High purity raw materials can also be used to prolong catalyst life.

Route 2: Chlorination of methane

$$CH_4\ (g) + Cl_2\ (g) \ \text{---------->} \ CH_3Cl\ (g) + HCl\ (g)$$

This route has a low yield. Apart from HCl, this method also produces higher derivatives such as dichloromethane and trichloromethane as byproducts.

Route 3: Liquid phase hydrochlorination

This route starts with Methanol + 70% Zinc Chloride. The reaction is 130 °C - 150 °C at modest pressure. It has Low yield and energy-intensive. It is troublesome to use zinc chloride owing to its corrosive nature.

Comparison of above routes

Route 1	Route 2	Route 3
High yield	Low yield	Low yield
Environmentally friendly	Environmentally unfriendly	Environmentally unfriendly
Uses troublesome HCl	Troublesome to dispose of HCl	$ZnCl_2$ is corrosive and hard to handle

Table 3.1: Comparison of possible routes for Chloromethane Production

After analyzing the above routes based on yield, environmental effects, and considering the availability of methanol at a low price, the convenience to store and transport, and low cost of HCl, Route 1 is finalized. This route also utilizes hydrogen chloride, whose disposal is difficult, rather than producing it.

3.2 Process Flow Diagram

The following process flow diagram was drawn using Draw.io (online flowsheet drawing tool) [33].
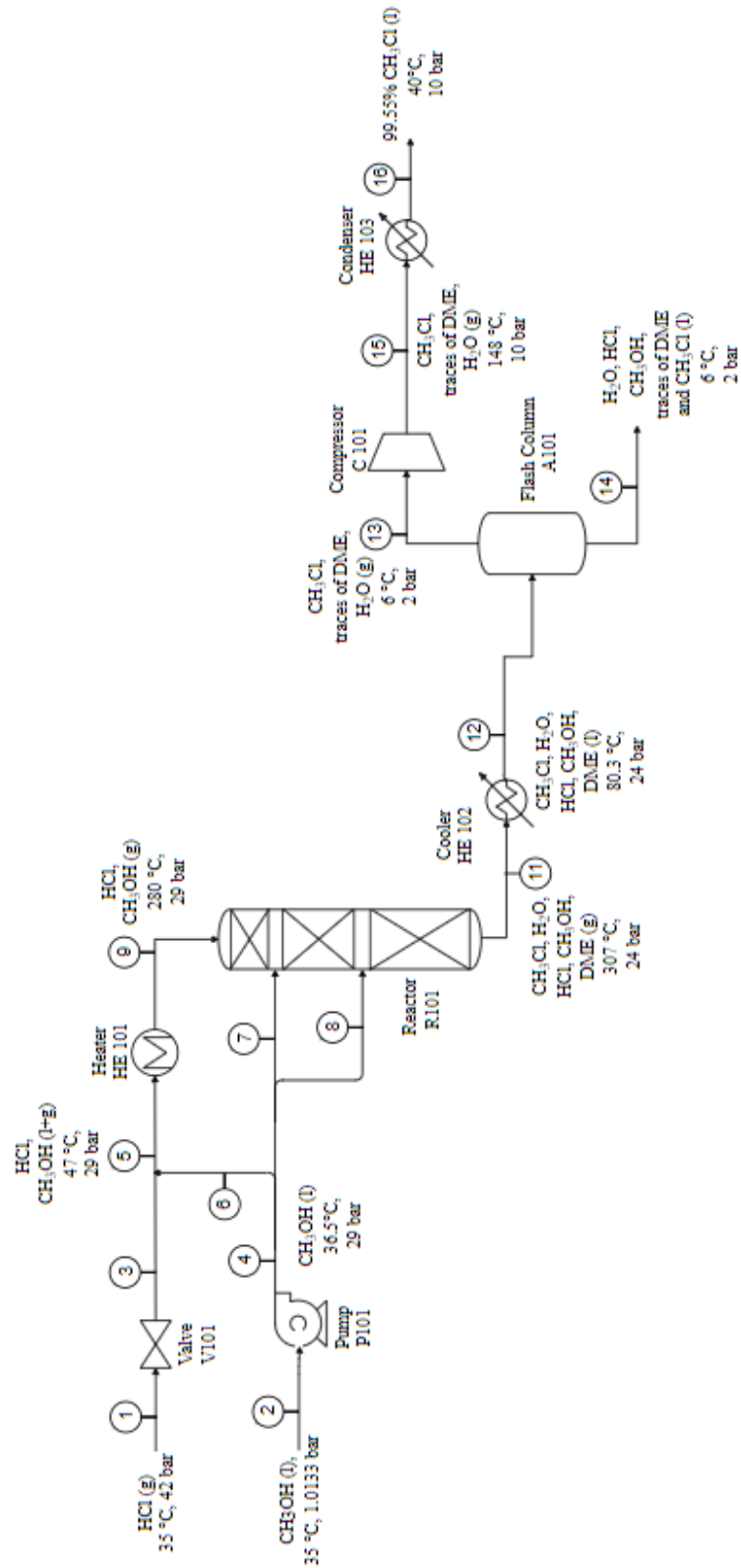
3.2.1 Process Description

- The raw material, stream 1, containing hydrogen chloride gas is passed through a valve V101 to reduce the pressure to 29 bar. Similarly, the methanol feed at 1 bar is pressurized to 29 bar using pump P101. The hydrogen gas stream (stream 2) is mixed with 46% splitted methanol feed (stream 6).
- The heater HE101 is used to increase the temperature of mixed steam (stream 5) to 280 ^{o}C. Then the heated stream 9 is sent to the first bed of reactor R101, where 87% of conversion of methanol takes place. Then, the heated stream is quenched using a 33% splitted methanol stream (stream 7) and sent to the second bed, where the 94% of conversion of methanol takes place. Then, the outlet stream from the second bed is further quenched using a 21% methanol stream (stream 8) and a third bed, where 99% of methanol takes place.
- The gaseous crude product stream (stream 11) from reactor R101 is sent to cooler HE102 to decrease the temperature to 80.3 ^{o}C.
- Then the cooled stream 12 at pressure 24 bar and 80.3 ^{o}C is sent to the flash vessel, where it is flashed at 2 bar and 6 ^{o}C.
- The main outlet gas stream (stream 13) containing a large amount of methyl chloride is collected at top of the flash vessel, while the liquid aqueous HCl stream (stream 14) separated from the stream 13 is collected at the bottom of the vessel.
- The gas stream (stream 13) is sent to compressor C101, where it is compressed to 10 bar.
- Finally, the 99.55% pure chloromethane stream is condensed through the condenser HE103 to 40 ^{o}C.
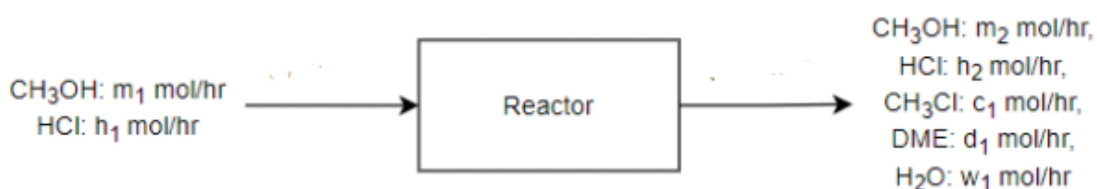
Chapter 4

Mass Balance

The manual mass balance was done based on the first version of PFD (as shown in Chapter 3 above). Based on rising demand in the Asia-Pacific region as well as the domestic market, the capacity of the plant was finalized to 1,00,000 MTPA.

We assumed no wastage of product chloromethane from effluent streams. The conversion of the main reaction (hydrochlorination of methanol) was assumed to be 99%, while the yield of the process to be 98% on the basis of methanol. Using this information, the required mass flow rate of chloromethane was calculated. Excess HCl feed is assumed to be 1.15 times the chloromethane moles.

4.1 Sample Calculations

4.1.1 Reactor (R101)

The hydrogen chloride-containing raw material stream 1 is pressure released from 42 bar to 29 bar and is combined with part of the methanol feed that has been pumped up to 29 bar. The HE 101 heater is used to boost the temperature to 280 °C. The hot pressurized stream is then sent to the R101 reactor running adiabatically, where the main reaction (methanol hydrochlorination) takes place. The temperature is controlled by injecting the rest of the methanol into the reactor with interstage feeds and at 37 °C. A conversion of about 99% of methanol was achieved.

CH₃OH: m_1 mol/hr
HCl: h_1 mol/hr → **Reactor** → CH₃OH: m_2 mol/hr, HCl: h_2 mol/hr, CH₃Cl: c_1 mol/hr, DME: d_1 mol/hr, H₂O: w_1 mol/hr

Main Reaction

$$CH_3OH (g) \; + \; HCl (g) \; \text{------------------->} \; CH_3Cl (g) \; + \; H_2O (g)$$

	CH_3OH	HCl	CH_3Cl	H_2O
Initial number of moles	m_1	h_1	0	0
No. of moles after reaction	$(m_1 - 0.99m_1)$	$(h_1 - 0.99m_1)$	$0.99m_1$	$0.99m_1$

Side Reaction

$$2\,CH_3OH (g) \; \text{--------------------->} \; (CH_3)_2O(g) \; + \; H_2O (g)$$

	CH_3OH	$(CH_3)_2O$	H_2O
Initial number of moles	m_1	0	0

No. of moles after reaction $(m_1 - 2d_1)$ d_1 d_1

$d_1 = 0.2/100*[(m_1 - 0.99m_1)+(h_1 - 0.99m_1)+0.99m_1+0.99m_1+(m_1 - 2d_1) + d_1+d_1]$
$d_1 = 0.2/100*[m_1 + h_1]$

Now, Based on the plant capacity and operating period, we get,

m_1 = 8,082.44 kg/hr = 252.26 kmol/hr, and h_1 = 1.15*m_1 = 290.46 kmol/hr = 10,601.89 kg/hr
So, $d_1 = 0.2/100*[m_1 + h_1]$ = 0.2/100*542.72 = 1.08 kmol/hr

Thus, mass flow rate of DME = 49.96 kg/hr,
Similarly, For water, $w_1 = 0.99m_1 + d_1$ = 2511.14 kmol/hr = 4520.46 kg/hr

Also, For residual methanol, $m_2 = m_1 - 0.99m_1 - 2d_1$ = 0.36 kmol/hr = 11.32 kg/hr
Residual HCl, $h_2 = h_1 - 0.99m_1$ = 40.73 kmol/hr = 1475.05 kg/hr
And chloromethane flow rate, $c_1 = 0.99m_1$ = 249.74 kmol/hr = 12627.55 kg/hr

4.1.2 Flash Column

The flash vessel is used to separate the Chloromethane from the product stream. The stream is cooled to 80 °C and the flash vessel drops the pressure from 29 bar to 2 bar, and is operated at 6 °C. The bulk of the chloromethane goes through the top as vapour along with small quantities of water and DME as impurities, while a major portion of water and other side products are removed from the bottoms as dissolved liquid. We assume that CH3Cl will separate out as vapur, while almost all of the remaining components come out from the bottoms owing to the high solubility in water.

CH3CI = 12627 kg/hr

CH3CI = 12627.55 kg/hr
CH3OH = 11.32 kg/hr
HCl = 1475.05 kg/hr
H20 = 4520.46 kg/hr
DME = 49.96 kg/hr

Flash Vessel

Temperature= 6C
Pressure = 2 bar

CH3CI = 0.55 kg/hr
CH3OH = 11.32 kg/hr
HCl = 1475.05 kg/hr
H20 = 4520.46 kg/hr
DME = 49.96 kg/hr
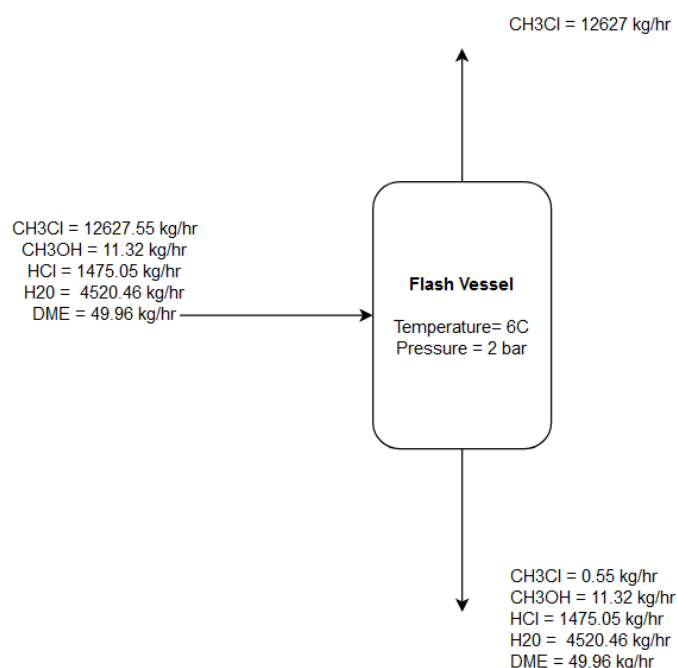
4.2 Equipment Selection

Possible Reactors [13]

- Fixed Bed Reactor
- Shell and Tube Reactor (calandria)
- Fluidized Bed Reactor

Reactor selected- Fixed Bed Reactor with interstage feed inlet

Reason for selection

- The reaction is exothermic, and it helps in efficiently controlling the temperature
- The reactor can be operated adiabatically, while the feed itself acts as coolant
- The large tube diameter reduces pressure loss
- We can customize its design according to our needs

Heat Exchangers [15]

Type of Heat Exchanger	Pressure Limit	Temperature Limit	Cost
Plate	~20 bar	~230 ^{0}C	Low
Shell and Tube	~100 bar	~550 ^{0}C	Moderate
Finned Tube	~70 bar	~1000 ^{0}C	High

Table 4.2: Comparison of different types of Heat Exchangers

As per our requirement of the temperature range of 280-350 ^{o}C and pressure of 5 bar most suitable heat exchangers are Shell and Tube. Shell and tube heat exchangers are also not much costly, so we can use them in our reaction.

Chapter 5

Aspen Flowsheet Simulation

We used ASPEN Plus to simulate the process plant. The reason for using ASPEN is that it has relevant thermodynamics packages that work well for gas-liquid interactions like chloromethane and water in the simulations.

5.1 Property Method and Flowsheet Development

5.1.1 Property Method

The ELEC-NRTL model is used for the simulation of the flowsheet to consider the ion-ion interactions in the solutions state at pressure less than 10 atm as the ELEC-NRTL model cannot be used at higher pressures (greater than 10 atm). So, SRK model is used at higher pressures (greater than 10 atm), as it is recommended at higher pressures[28].

5.1.2 Flowsheet Development

Two streams S-1 and S-2 with the raw materials HCl and CH_3OH are adjusted to appropriate pressure and temperature. They are fed into the reactor and they react to produce CH_3Cl, dimethyl ether and water. The output stream S-7 also contains unreacted methanol and HCl. The crude product stream is passed through the separation system to obtain the final product stream S-13 containing 99.55% pure chloromethane.

a. **Valve**– Adiabatic valve is simulated to reduce the pressure of HCl gas feed to 29 bar.
b. **Pump** – Pump is used to increase the pressure of the methanol feed stream to 29 bar.
c. **Splitter**- The splitter is used to split the methanol feed into 0.46 (S-6), 0.33 (S-7), and 0.21 (S-8).
d. **Mixer** - The mixer B-3 is used to combine the raw material input streams S-3 containing HCl gas and S-4 containing splitted methanol feed.
e. **Heater**- The heater is used to raise the temperature of the raw material mixture before entering the reactor to achieve the required process conditions.
f. **Catalytic Reactor**- The RStoic reactor is used. The inlet of the reactor contains methanol and HCl to complete the simulation in aspen. However, the detailed simulation of the reactor is carried out in the matlab to consider the differential pressure drop and temperature changes. The RStoic reactor requires the conversion of each reaction, i.e. the main reaction and side reaction. The outlet temperature of the reactor is 307 ℃, while the outlet pressure is 24 bar.
g. **Cooler**- The gaseous crude product stream from the catalytic reactor is cooled from 307 ℃ to 80.3 ℃.
h. **Flash Separation**- The flash separator aims to remove the majority of water from the crude product stream. The crude product stream from the cooler is sent to the flash separator B-7, which is operated at 6 ℃ and 2 bar pressure. These operating conditions were obtained from sensitivity analysis.

i. **Compressor-** The vapour outlet from the flash vessel is compressed to 10 bar using an isentropic compressor.
j. **Condenser-** The condenser is used to condense the gaseous product stream from the compressor to 40 °C.

5.2 Aspen Simulation

5.2.1 Aspen Simulation Diagram

Figure 5.1: Aspen Simulation Flowsheet

5.2.2 Aspen Simulation Blocks description

1. B-1 - Valve which reduces the pressure of hydrogen chloride gas feed to 29 bar
2. B-2 - Pump which pressurizes the methanol feed to 29 bar
3. B-3 - Mixer which mixes both hydrogen chloride gas feed with splitted methanol stream and sent to heater
4. B-4 - Splitter which splits the methanol feed stream into 0.46 (S-6), 0.33 (S-7), and 0.21 (S-8)
5. B-5 - Heater which heats the mixed reactant stream and sent to reactor
6. B-6 - Reactor which converts reactants to chloromethane and water
7. B-7 - Cooler which cools the crude product stream to 80.3 °C and sent to flash column
8. B-9 - Flash Column which removes the most of water content from crude product stream
9. B-11 - Compressors which compresses the gas to 10 bar
10. B-12 - Condenser which condenses the gas into liquid at 40 °C and 10 bar

5.2.3 Aspen Simulation Stream description

1. S-1 - Pure Hydrogen Chloride feed present at 35 °C and 42 bar pressure.
2. S-2 - It is the feed containing methanol as the raw material and is present at 35 °C and 1 bar pressure.
3. S-3 - Gas phase stream S-2 is passed through the valve to reduce the pressure to 29 bar. The stream S-3 is present at 29 bar and 17.4 °C.
4. S-4 - Liquid stream S-2 is passed through the pump to pressurize it. S-4 is present at 29 bar pressure.
5. S-5 - Streams S-3 and S-4 mix to get the stream S-5.
6. S-6, S-7 and S-8 - Stream S-4 splitted into 0.46 (S-6), 0.33 (S-7), and 0.21 (S-8)
7. S-9 - Stream S-9 is a heated stream present at 280 °C, 29 bar and fed to the reactor.
8. S-11 - It is output stream from the reactor
9. S-12 - The stream S-11 is cooled to 80.3 °C and it is sent to the flash separator B-7
10. S-13 - Main output gas stream from B-7 containing large amounts of methyl chloride.
11. S-14 - Stream which gets separated from S-13 taking off water (majorly)
12. S-15 - Methyl chloride rich-stream S-13 is compressed to form S-15 at 10 bar
13. S-16 - The final product condensed stream containing 99.55% chloromethane

5.2.3 Aspen Simulation Stream Results

Stream No.	CH$_3$OH (kg/h)	HCl (kg/h)	CH$_3$Cl (kg/h)	H$_2$O (kg/h)	CH$_3$OCH$_3$ (kg/h)	Total (kg/h)	T (^{0}C)	P (bar)	Phase
1	0	9294.80	0	0	0	9294.8	35	42	v
2	8082.4	0	0	0	0	8082.4	35	1	l
3	0	9294.8	0	0	0	9294.8	16.48	29	v
4	8082.4	0	0	0	0	8082.4	36.5	29	l
5	3717.9	9294.8	0	0	0	13012.7	47.02	29	v, l
6	3717.9	0	0	0	0	3717.9	36.5	29	l
7	2667.2	0	0	0	0	2667.2	36.5	29	l
8	1697.3	0	0	0	0	1697.3	36.5	29	l
9	3717.9	9294.8	0	0	0	13012.7	280	29	v
11	12.1	189.8	12607.8	4518.1	49.4	17377.2	307	24	v
12	12.1	189.8	12607.8	4518.1	49.4	17377.2	80.3	24	l
13	0.5	0.00	12550.7	21	35.3	12607.6	6	2	v
14	11.6	189.8	57.1	4497.1	14.1	4769.7	6	2	l
15	0.5	0.00	12550.7	21.1	35.3	12607.6	145.8	10	v
16	0.5	0.00	12550.7	21.1	35.3	12607.6	40	10	l

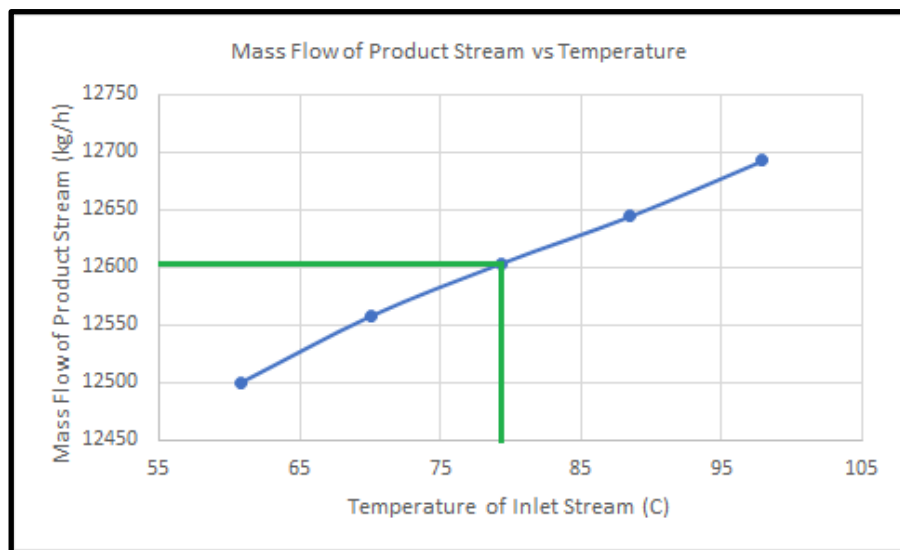Table 5.1: Mass Balance and Composition of streams

Chapter 6

Parametric Analysis

6.1 Flash Vessel

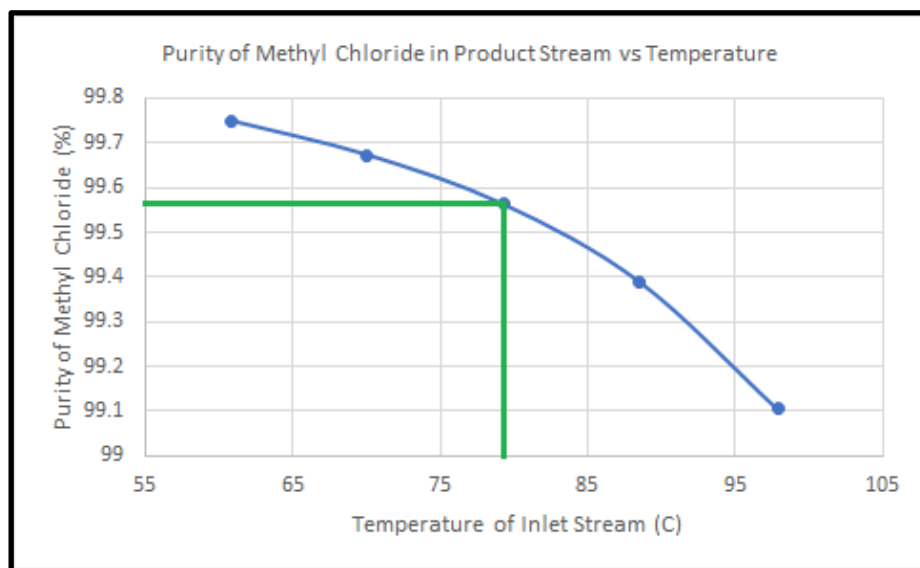The major operating parameters are the temperature of inlet stream, and pressure drop across the flash vessel.

6.1.1 Temperature

The effect of temperature (of inlet stream) variation on the total mass flowrate of the product stream (vapour outlet) is shown as follows:

The effect of temperature (of inlet stream) variation on the purity of methyl chloride in the product stream (vapour outlet) is shown as follows:

We observed that the mass flow rate of the product stream as well as the amount of methyl chloride separated out decreases with an increase in temperature of inlet stream, but the purity of methyl chloride in the product stream decreases. To get a minimum purity of 99.5%, the temperature we get is 80.3 C. Also, the mass flowrate is 12608 kg/h. So, the optimum temperature from the parametric analysis is 80.3 C.

6.1.2 Pressure Drop

We considered the purity of methyl chloride as well as the total mass flowrate of the product stream in sensitivity analysis by varying the pressure drop across the flash vessel.

The effect of variation in the pressure drop on the total mass flowrate of the product stream (vapour outlet) is shown as follows:
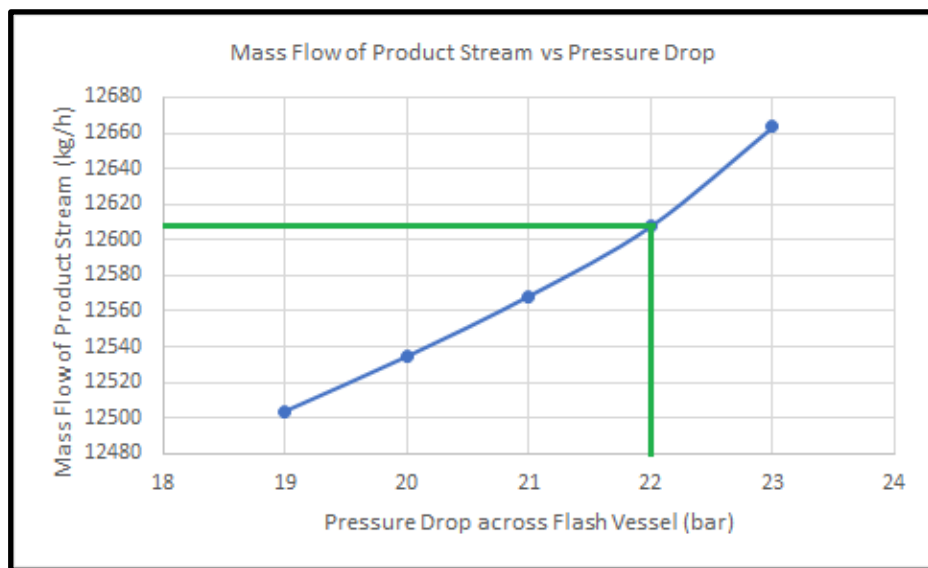
The effect of variation in the pressure drop on the purity of methyl chloride in the product stream (vapour outlet) is shown as follows:

24
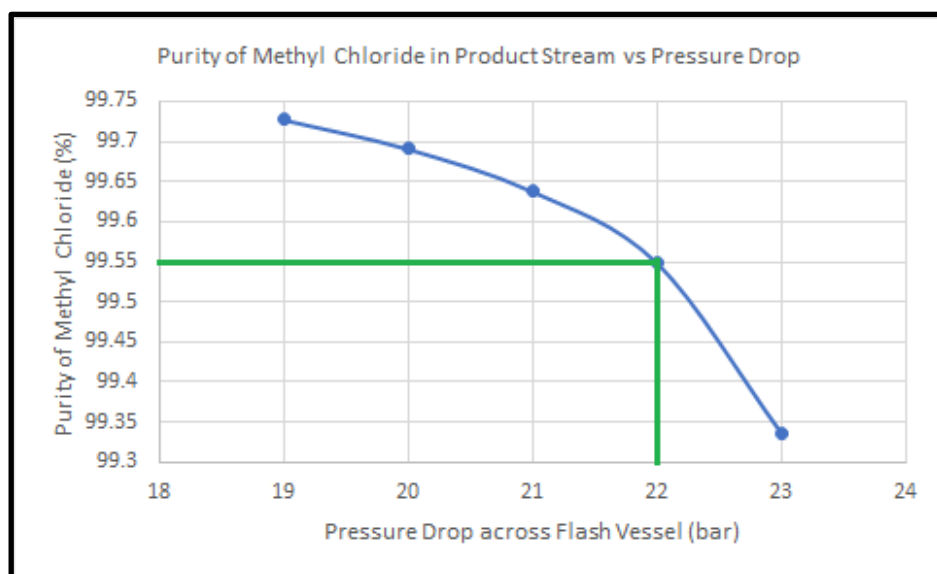
On observing both above plots, we found that the purity of methyl chloride decreases with increase in the pressure drop across the flash vessel, while the mass flow rate of the product stream increases as operating pressure increases. The minimum required purity of methyl chloride is 99.5%. So, the pressure drop of 22 bar is decided (which gives 99.55% purity).

Chapter 7

Equipment Sizing and Costing

7.1 Equipment sizing

7.1.1 Reactor [18,21]

Height	1.4 m
Internal Diameter	30 cm
Wall Thickness	7.93 mm
Enclosure Shape	Hemispherical
MOC	Carbon Steel (Monel lined)

Table 7.1: Dimensions of Reactor

The reactor is used to perform the hydrochlorination reaction of methanol. γ-alumina is used as the catalyst during the process.

Our reaction has high conversion. But, it is highly exothermic. So, we want to control the temperature from rising significantly (otherwise it can affect conversion and the reactor may even explode). We have opted to use a packed bed reactor and sending the feed in splits.

For getting the height and diameter for desired performance, we wrote a code (given in appendix). The results are summarised in the above table (detailed discussion will be done in chapter 9).

For thickness:

Design Pressure, $P = \max(29*1.1, 29+2) \sim 32$ bar
$t = PD_o/(2(S_a*E-0.6*P)) = 32*30*10/(2(82*1+0.4*32)) \sim 5.99$ mm
milling tolerance = 12.5%
$t_m = 5.99/(1-0.125) = 6.85$ mm
recommended (next commercially available) thickness = 7.93 mm
Outer diameter = 31.6 cm
Hemispherical enclosures would require lesser thickness than the cylindrical body, but considering the worst condition for safety reasons, the enclosure thickness is also 7.93 mm.

7.1.2 Heat Exchangers

i. Heat Exchangers- Type Selection [22]

Heat Exchanger	Pressure Limit	Temperature Limit	Cost
Plate	~20 bar	~230 °C	Low
Shell and Tube	~100 bar	~550 °C	Moderate
Finned Tube	~70 bar	~1000 °C	High

Table 7.2: Types of heat exchanger

Based on our operating conditions, cost and industrial application, we have selected a shell and tube heat exchanger.

ii. Heat Exchangers- MOC [23]

The materials of construction selected for all heat exchangers is carbon steel. But, as there are corrosive compounds such HCl and CH_3Cl along with moisture on the process side, so the monel lining is provided from the inner surface of the heat exchangers to protect them from corrosion.

iii. Heat Exchangers- Sizing [24]

There are a total of three heat-exchangers we are using for evaporation, cooling and condensation purposes. The heat exchanger HE101 is a heater, which is used for preheating raw material. The heat exchanger HE102 is cooler, which is cooling crude product stream coming out of the reactor. While the heat exchanger HE103 is used for condensing the final product of 99.55% chloromethane. We assumed the overall heat transfer area from a range of values and found some approximate figures for the area required form heat transfer. The summary of all results of heat exchanger sizing are as follows:

Block ID	Fluid stream			Utility			Heat Duty	LMTD (Counter-current flow)	Total Heat Transfer Area Required
	Comp.	In (°C)	Out (°C)	Comp.	In (°C)	Out (°C)	kW		m²
B-4	HCl, CH_3OH	47	280	Oil	360	90	2305.4	59.6	128.94

B-7	H_2O, HCl, CH_3Cl	307	80.3	Oil	40	270	4810.2	38.4	415.21
B-10	CH_3Cl	147.4	40	Chilled Water	20	90	1659.5	35.5	77.97

Table 7.3: Heat exchanger sizing

7.1.3 Pumps [16]

The process plant has a pump which is used to feed liquid methanol into the mixer. Methanol at 35 °C and 1 bar pressure is fed at a flow rate of 10.38 m³/h into the pump. Since methanol is a non-corrosive fluid and is flowing at ambient temperature, material of construction (MOC) of the pump is chosen to be carbon steel.

$$W_P = \frac{\Delta P}{\rho} + g\Delta z + \frac{\Delta P_f}{\rho}$$

Flow rate = 2.247 kg/s; Pressure difference = 28 bar; Density of liquid = 792 kg/m3

Hence, we get pump work as WP = 3.67 kJ/kg.

Power required = WP * Flow Rate/pump efficiency(assumed to be 0.43) = 19.2 kW

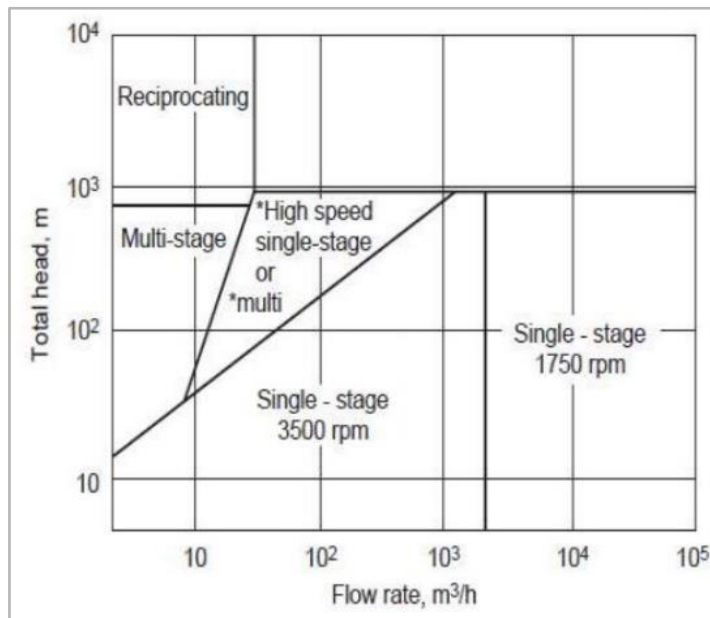Based on figure 7.1, we use a multi-stage centrifugal pump for our process.

Figure 7.1: Total head vs Flow rate (for pump)

7.1.4 Compressor [16]

A compressor is used in our process plant to compress the stream coming out of the flash vessel, containing primarily methyl chloride. We use a two-stage compressor with a flow rate of 2815 m^3 /h and discharge pressure of 10 bar.
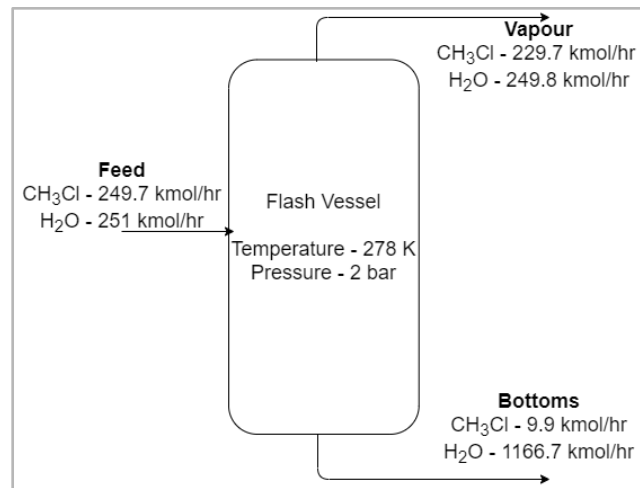
$$W = P_1 V_1 \frac{n}{n-1}[(\frac{P_2}{P_1})^{\frac{n-1}{n}} - 1]$$

Assuming 72% isentropic efficiency of the compressor and a compression ratio of 2.282, a total power of 407 kW is required for the compressor to operate.

Since methyl chloride becomes corrosive in presence of water, MOC of the compressor is chosen to be stainless steel.

7.1.5 Flash Vessel

Flashing devices are widely used in a variety of industries because of their ability to distinguish vapours from liquids. They can also be used to extract light vapours and gases from stream lines. Since the density of the vapour stream is much higher than the mass of the liquid stream, the flash vessel measurement is performed with a vertical vessel. We chose an L/D ratio of 4 out of a range of 3-5. To make the equations simpler, the very small components are neglected. Some of the values are estimated, while others are obtained from Aspen.

$F_{LV} = (W_L/W_V)*sqrt(\rho_V/\rho_L) = 0.0662$

$K_{drum} = e^{\wedge}(-1.8774*ln(F_{LV})^0 -0.8146*ln(F_{LV})^1 -0.1871*ln(F_{LV})^2 -0.0145*ln(F_{LV})^3 - 0.001*ln(F_{LV})^4) = 0.4704$ ft/s

$u_{perm} = K_{drum} *sqrt((\rho_L- \rho_V) / \rho_V) = 7.07$ ft/s = 2.8 m/s

$Area_e$ = Mass flow of Vapour / ($u_{perm} * \rho_V$) = 0.362 m^2

D = 0.68 m

L = 4*D = 2.72 m

We went with an Length / Diameter ratio = 4 to maintain a vertical vessel design. And this approach was chosen to go with a preliminary costing and sizing [32]

$P_{operating} = max(P+2\ bar,\ P*1.1\ bar) = 4\ bar$

$MOC = Carbon\ steel\ ;\ S_a = 118MPa\ (17,100psi)\ at\ T=55F$

$Weld\ joint\ efficiency\ E = 0.85$

$t_{regulation} = P_{operating}*D_I/(2*(S_a*E+0.4*P_{operating}))$ ..... internal diameter from codes

$t_{regulation} = 1.35\ mm$

$t_{recommended} = 4.7625mm$ or 0.1875 in from commercially available sheets

7.2 Equipment Costing

7.2.1 Reactor [18,19]

The reactor has following specifications:

Height	1.4 m
Internal Diameter	30 cm
Wall Thickness	7.93 mm
Enclosure Shape	Hemispherical
MOC	Carbon Steel (Monel lining)

Table 7.4: Dimension of Reactor

The cost was found using the procedure and data in Peters et al [16] for carbon steel in 2002 .Then it was adjusted for Chemical Engg. Plant Cost Index[17] for year 2019.

Cost index in 2002 = 390.4 and Cost index in 2019 = 607.5

CS density = 7840 kg/m^3

Weight of shell and headers = Density* Volume =

7840*(3.14*(30/100)*(7.93/1000)*1.4+2*(1/2)*(4*3.14*(15/100)^2*(7.93/1000)))   ~ 96.75 kg

Assuming 15 % increase in this weight from nozzles, manholes, etc.., total weight = 96.75*1.15 ~111.26 kg

Cost, in year 2002 = 147*(111.26$^{0.66}$)= $ 3295.4
Cost in 2019=3295.4*607.5/390.4 ~ $ 5127.9

7.2.2 Heat Exchangers [25]

The purchased cost is calculated with the help of following formula

$$C_P \text{ (in \$)= } F_P*F_M*F_L*C_B$$

Pressure factor: F_p= 0.9803+0.018*(P/100)+0.0017*(P/100)^2
Note: The pressure factor is based on the shell-side pressure, P in psig.
Materials of Construction factor: F_m= a+(A/100)^b
a= 0 and b= 0 for Carbon steel shell and tube HE
So, F_m= 1
Base cost: C_B= exp{11.551-0.9186*[ln(A)]+0.09790*[ln(A)]^2}   for U-tube HE
Note: In all above cases, A is area in ft^2,and C_p is for year 2013.
We considered carbon steel shells and tubes for the heat exchanger and considered 0.05 mm thickness of monel lining to protect the inner surface of the heat exchangers from corrosion.

Block ID	Area (m^2)	Purchased Cost ($) in year 2013	Purchased Cost ($) in year 2019	Purchased cost ($) including corrosion layer (0.05 mm thickness)[30, 31]
B-4	128.94	25,670	27,503	41,119
B-7	415.21	52,547	56,300	100,146
B-10	77.97	19,933	21,357	29,590

*Purchased cost for year 2019 computed using Chemical Engineering Plant Cost Index

7.2.3 Pumps [18,19]

The capacity factor of the pump required is 8.3 and the pressure change during pumping is 28 bar. The cost for the pumps is determined from figure 7.2. It shows the costing of a centrifugal pump with a motor for the year 2002.

Cost index in 2002 = 390.4 and Cost index in 2019 = 607.5

From the graph of Jan 2002, Purchased Cost of pump was $ 4500. Adjusting for Jan 2019, we get the purchased cost as $ 7700.
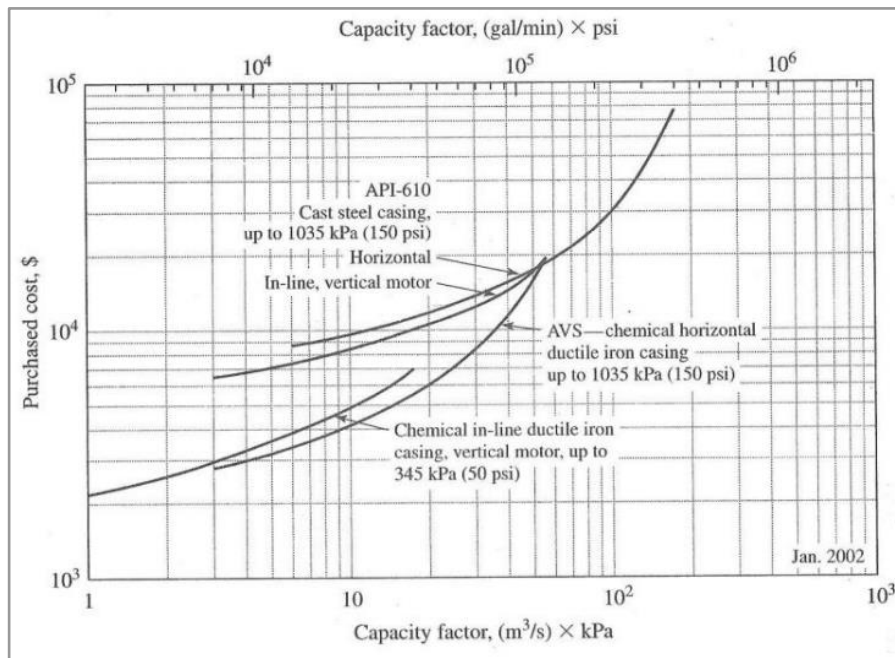
Figure 7.2: Purchased cost vs capacity factor for pump

7.2.4 Compressor [18,19]

The power required for the centrifugal compressor is 407 kW. The MOC for the compressor is stainless steel with material adjustment factor of 2.5. From figure 7.3, for centrifugal motor and stainless steel,
Purchased Cost = $ 2.5x10^5
Adjusting for year (2019), Purchased Cost = $ 10.7x10^5
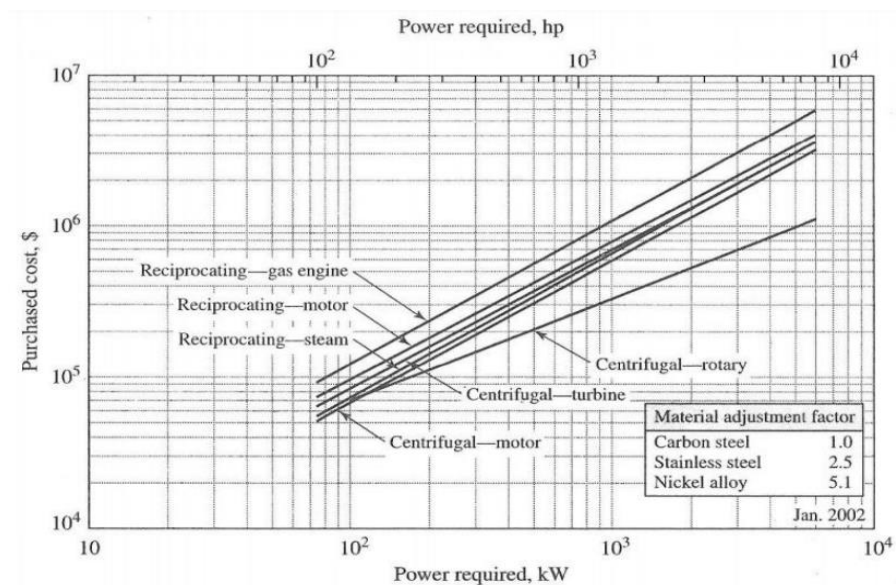
Figure 7.3 Purchased cost vs power required for compressor

7.2.5 Flash Vessel [26]

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The flash vessel has a diameter of 6.8 and length 2.72m or 2.23 ft and 8.9 ft. Hence the volume of the vessel is 324.9 gallon. The pressure and temperature are 29 psi and 43 °F respectively.

Cost from chart = $ 9,500

Adjusting for year (2019), Purchased Cost = $ 14,800

Design Basis:
1st Quarter 1998 Dollars
Shell Material: A515
(Carbon Steel Plates for pressure vessels for intermediate and higher temperature service)
Design Temperature: 650 °F
Design Pressure: 15 psig and 150 psig
Diameter: 2.5 – 8 feet
Length: 2.7 – 13.3 feet
Total Weight: 1,000 –7,100 pounds

Figure 7.4: Purchased cost vs capacity for flash vessel [26]

Chapter 8

Plant Economics

8.1 Major Equipment Costing

We can see from the data that the majority of equipment costing is coming from the compressor and the heat exchanger. The cost of all the equipments are as follows:-

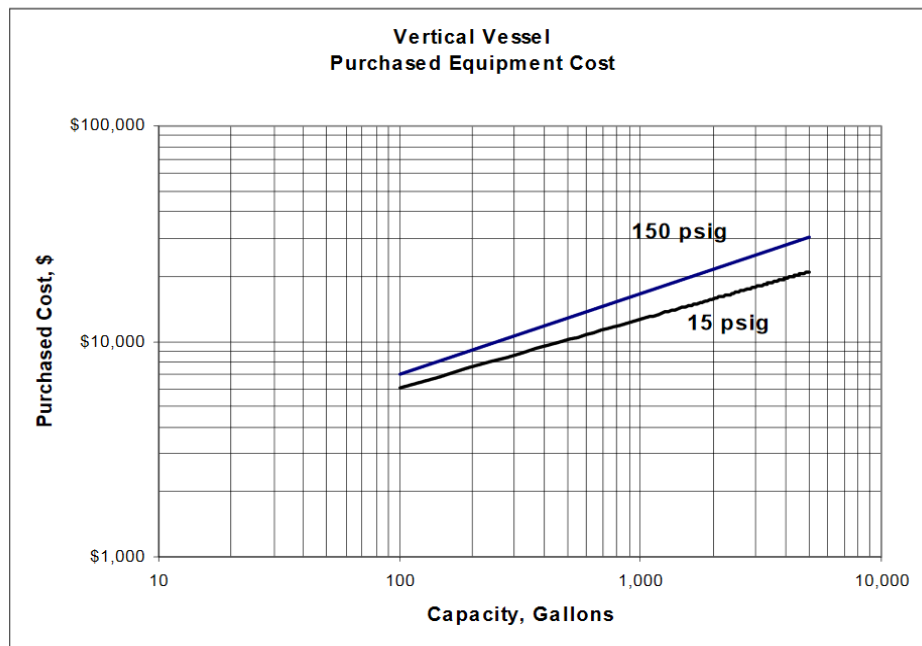| Equipment	Purchased Cost (x10^3 USD)
Reactor	5.1
Compressor	972.6
Pump	7.0
Flash Column	14.8
Heat Exchanger	250.6
Total (inc. freight charges)	1375.1

Table 8.1: Cost of equipments

8.2 Capital Investment [16]

There are two types of cost in capital investment, first is direct cost and the other is indirect cost. The direct cost consists of equipment cost, property cost etc. while the indirect cost consists of construction expense, legal cost etc. Equipment cost constitutes the largest share of investment capital.

	Component	Selected % of FCI	Normalised % of FCI	Cost (Mn USD)
	Purchased Equipment	27	20.6	1.4
	Purchase Equipment Installation	10	7.6	0.5
	Instrumentation and Controls	7	5.3	0.4
	Piping	10	7.6	0.5
	Electrical Systems	6	4.6	0.3
	Buildings	10	7.6	0.5
	Yard Improvements	3	2.3	0.2
	Service Facilities	19	14.5	1.0
Direct Costs	Land	1	0.8	0.1

	Engineering & Supervision	12	9.2	0.6
	Construction Expenses	11	8.4	0.6
	Legal Expenses	2	1.5	0.1
	Contractor's Fee	3	2.3	0.2
Indirect Costs	Contingency	10	7.6	0.5

Table 8.2 : Direct and indirect costs

Fixed Capital Investment (FCI)	USD 6.7 Mn
Working Capital Investment (15% of TCI)	USD 1.2 Mn
Total Capital Investment (TCI)	USD 7.8 Mn
TCI (adjusted for India)	INR 37.2 Cr

8.3 Raw Material Cost & Revenue

Raw material cost contributes to about 50% of the total production cost. We have taken the approximate cost of the raw material according to our required quantity.

Material	Quantity (MT)	Cost (INR/MT)	Annual Cost (Cr INR)
Methanol	64716	22400	144.96
Hydrogen Chloride	74420	72000	535.82
Catalyst	0.015	1095000	0.002
Total raw material cost/yr (inc. freight charges)			**748.87**

Table 8.3 : Raw material cost

Revenue:

Methyl Chloride production: 1,00,000 MT/yr

Price: INR 1,82,500/ MT

Revenue = 100000*182500 = INR 1825 Cr

8.4 Total Production Cost [16]

Components	selected % of production cost	normalised %	Annual Cost (INR cr)
Raw materials	50	42.0	₹748.87
Operating Labour	5	4.2	₹74.89
Supervisory Labour	0.75	0.6	₹11.23
Utility	15	12.6	₹224.66
Repair & Maintenance	7	5.9	₹104.84
Operating Supplies	1.05	0.9	₹15.73
Laboratory Charge	0.75	0.6	₹11.23
Patents & Royalties	3	2.5	₹44.93
Fixed Charges	15	12.6	₹224.66
Plant Overhead Costs	7.65	6.4	₹114.58
Administrative Costs	0.75	0.6	₹11.23
Distribution & Marketing	8	6.7	₹119.82
R&D	5	4.2	₹74.89

Table 8.4: Production cost

Total Production cost /year = INR 1781.56 Cr

From the following pie chart, we can see that raw materials, utilities, fixed charges contribute the most to production cost followed by marketing and distribution.
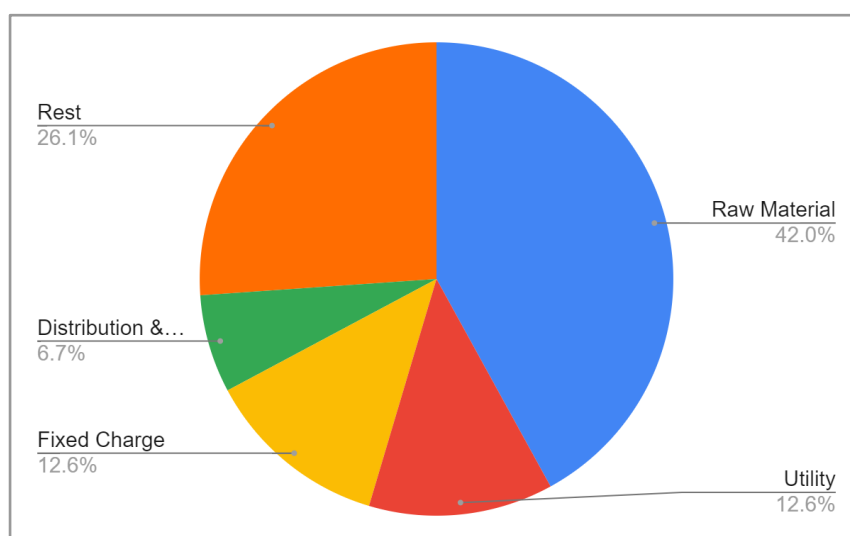

Figure 8.1: Contribution to production cost

8.5 Payback Period

Certain assumptions are made in calculating the revenue like the cost of product and raw material does not vary during the years and we have also assumed the depreciation to be linear.

	Crore INR
Depreciable FCI	31.34
Annual Depreciation	3.13
Gross Profit	40.31
Net Profit	27.00
Interest on TCI	29.80

Table 8.5: Payback period

Assuming 70% production capacity in 1st year, service life of 10 years, 8 % interest rate and using the below formula, we get a payback period to be 2.3 years.

Payout period including interest = (Depreciable FCI + Interest on TCI during service life)
(Avg profit/yr + Avg depreciation/yr)

= 2.3 years

Chapter 9

Detailed Design: Chemical Reactor

9.1 Model Selection and Reactor Configuration

The chemical reactor used for the hydrochlorination of methanol is a packed bed reactor. We need to control the temperature of the reactor. Packed bed reactor can be very effective for this. Therefore, we choose it. It consists of three beds in which the catalyst is present. The mixture of HCl and 46% splitted methanol feed enters from the top of the reactor. The other two splitted methanol streams (33% and 21%) are sent into the reactor as interstage feeds, which are used for quenching and thus maintain the temperature of the reactor.
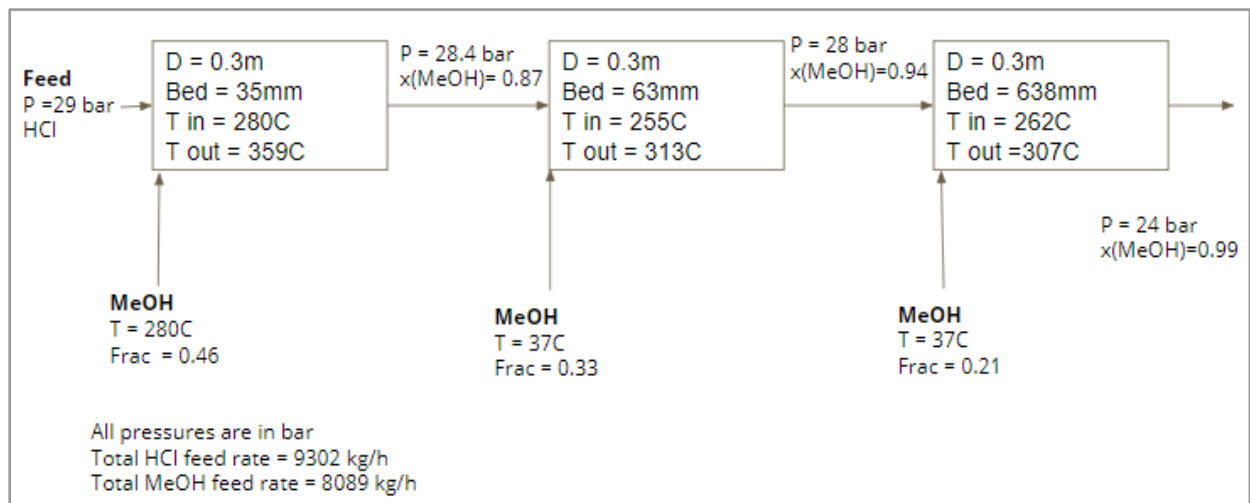

Figure 9.1: Reactor Schematics

The following figure shows the temperature at the inlet and outlet of each bed inside the reactor. We can see that the temperature increases due to reaction in the bed and we use further cooling to lower down the temperature before the feed goes into the next reactor.
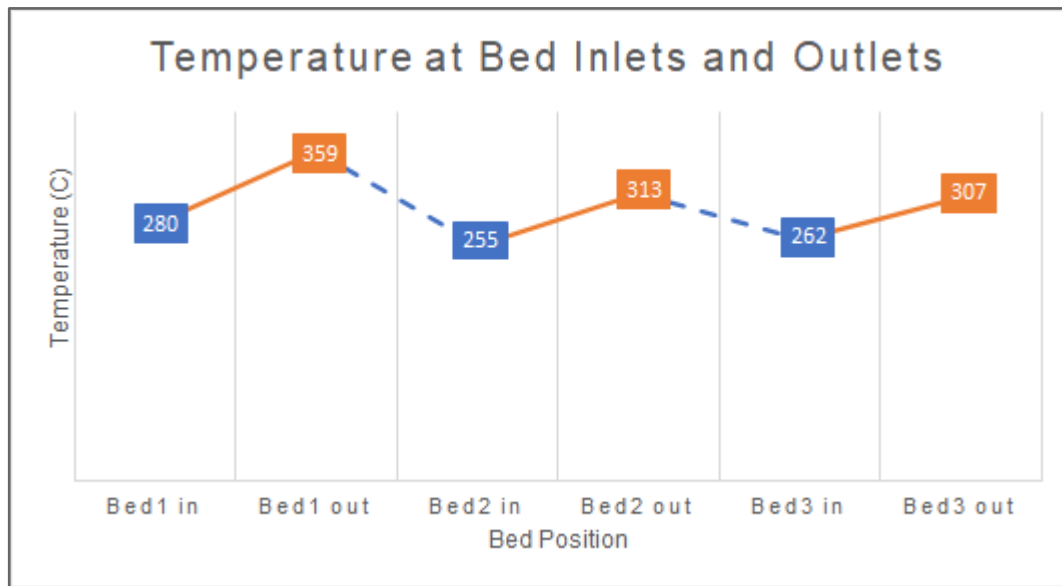
Figure 9.2 Temperature at inlet and outlet of each bed

9.2 Reactor Calculations:

9.2.1 Reaction Kinetics:

We used the following equations to find the pressure drop as well as temperature profile and conversion in a packed reactor. For this purpose, we used matlab to simulate the pressure, temperature profile through a packed bed reactor. We used a power law model to get the reaction kinetics.

Ergun equation:

$$\frac{dp}{dz} = -\frac{G(1-\emptyset)}{\rho D_p \emptyset^3}\left[\frac{150(1-\emptyset)\mu}{D_p} + 1.75G\right]$$

Kinetics:

$$r = -kP_{MeOH}P_{HCl}$$

The Ergun equation was used to calculate the pressure drop across the reactor configuration as a function of length of reactor. Rate kinetics and performance equations were used to evaluate further parameters of the reactor. The temperature change taking place across each bed after the reaction was also calculated using the Temperature equation mentioned below. These gave an approximation of the parameters which was further verified through Aspen simulation.

Performance Equation:

$$F_{A0}\frac{dX}{dW} = -r$$

Temperature:

$$T = \frac{X[-\Delta H^\circ_{Rx}(T_R)] + \Sigma \Theta_i C_{P_i} T_0 + X \Delta C_P T_R}{[\Sigma \Theta_i C_{P_i} + X \Delta C_P]}$$

The appendix A1 consists of the reactor code used to find the temperature variation as the feed passes through each bed.

9.2.2 Reactor Thickness

As there are pressure variations in the reactor, we considered the maximum operating pressure to get the worst operating pressure, which further we used in the design calculations.

Design Pressure, P = max(29*1.1,29+2) ~ 32 bar
t = PDo/(2(S$_a$*E-0.6*P)) = 32*30*10/(2(82*1+0.4*32)) ~ 5.99 mm
milling tolerance = 12.5%
t$_m$ = 5.99/(1-0.125) = 6.85 mm
recommended (next commercially available) thickness = 7.93 mm
Outer diameter = 31.6 cm

Hemispherical enclosures would require lesser thickness than the cylindrical body, but considering the worst condition for safety reasons, the enclosure thickness is also 7.93 mm

9.2.3 Nozzle and Reinforcement Plate

We considered following points in designing of nozzles and reinforcement plate:

- Used maximum pressure in reactor for enclosure thickness calculation
- The nozzle protruding area as well as weldment area are negligible
- We are using 50 mm NB nozzles with schedule no. 80
- Effect of catalyst weight to pressure exerted on wall is negligible
- We are using total four nozzles: 1 inlet, 1 outlet and 2 for methanol interstage feed
- Nozzle MOC: Carbon steel with inside monel lining

Sample calculations to reinforcement plate thickness:

Nozzle Outlet Diameter (do)= 60.3 mm,

Nozzle thickness (t)= 5.54 mm

Nozzle Inner diameter (di)= do-2*t= 49.22 mm

As we are using monel lining, so, corrosion tolerance, c = 0.

Diameter of opening on last day of operation= di+2*c= 49.22 mm

Area lost (AL)= (di+2*c)*Treg= 221.35 mm^2

Area available with vessel ($A_A{}^1$)= (di+2*c)*(T-Treg-c-Mt*T)= 120.78 mm^2

Here, Mt= m*T/100

Area available with vessel ($A_A{}^2$)= 2*H_1*(t-treg-c-mt*t)= 11.57 mm^2

Here, H_1= ((di+c)*(t-c))^0.5= 16.51 mm, mt = m*t/100

Area deficit (AD)= AL - ($A_A{}^1$ +$A_A{}^2$)= 89.59 mm^2 > 0 So, there is requirement of reinforcement plate of thickness, t_p= AD/(d+2*c)= 1.49 mm

$t_{p,reg}$= 1.70 mm

So, we considered the next available commercially available plate thickness, which is 4.76 mm.

9.2.4 Flange, Gasket and Bolts [19]

There are two flange joints in the reactor. In the upper flange joint region, the vessel has an internal diameter of 330 mm and in the lower flange joint region, the inner diameter of the vessel is 290 mm.

Doing a calculation for the upper flange joint region:

Inner diameter of vessel (Di) = 330 mm

Inner diameter of gasket (Gi) = Di +50 mm = 380 mm

Assuming gasket to be flat metal jacketed asbestos filled made of Stainless Steel, m = 3.75 and y = 62 N/mm^2 [19]

$$\left(\frac{G_o}{G_i}\right) = \sqrt{\frac{y - mP}{y - (m+1)P}}$$

From the above relation between Gi and Go, 'y' is the yield stress, 'm' is the gasket factor, 'P' is the design pressure, we get Outer diameter of gasket (Go) = 402 mm

Actual width of gasket (N) = 11.24 mm

Assuming the flange and gasket are raised-faced, effective width (b) = N/2 = 5.62 mm

Force experienced by the bolt (F) = 822.8 kN

We get $S_a{}^{bolt}$ = 110 MPa for Carbon steel at T>350 C [20]. Using this, the total bolt root area to bear the process force (A) = F / $S_a{}^{bolt}$ = 7480 mm^2

We choose a configuration of 12 bolts, each with a nominal diameter of 35 mm.

Wrench clearance = 2.5 * d_n = 87.5 mm

So, Maximum number of bolts (N_B^{max}) = 16

Maximum spacing between adjacent bolts (B_s^{max}) = 210 mm

So, Minimum number of bolts (N_B^{min}) = 8

Performing similar calculation for lower flange joint, we get the results for appropriate nominal bolt size and number of bolts as summarised in the below table:

	Di (mm)	Gi (mm)	Go (mm)	A (mm2)	Number of bolts	Nominal bolt size (mm)
Upper flanged joint	330	380	402.49	7480.00	12	35
Lower flanged joint	290	340	360.12	5988.15	12	32

Table 9.1: Flanges and bolts

9.3 Mechanical Design of Reactor

The mechanical design of the reactor bed is such that it has 3 beds sandwiched between layers of Ceramic balls of varying diameters. These layers help in proper mixing and redistribution of the fluid. Internal monel lining is used to prevent the reactor from corrosion.

The catalyst pellets are embedded in a monel lined lattice bed. This can be seen in the image below
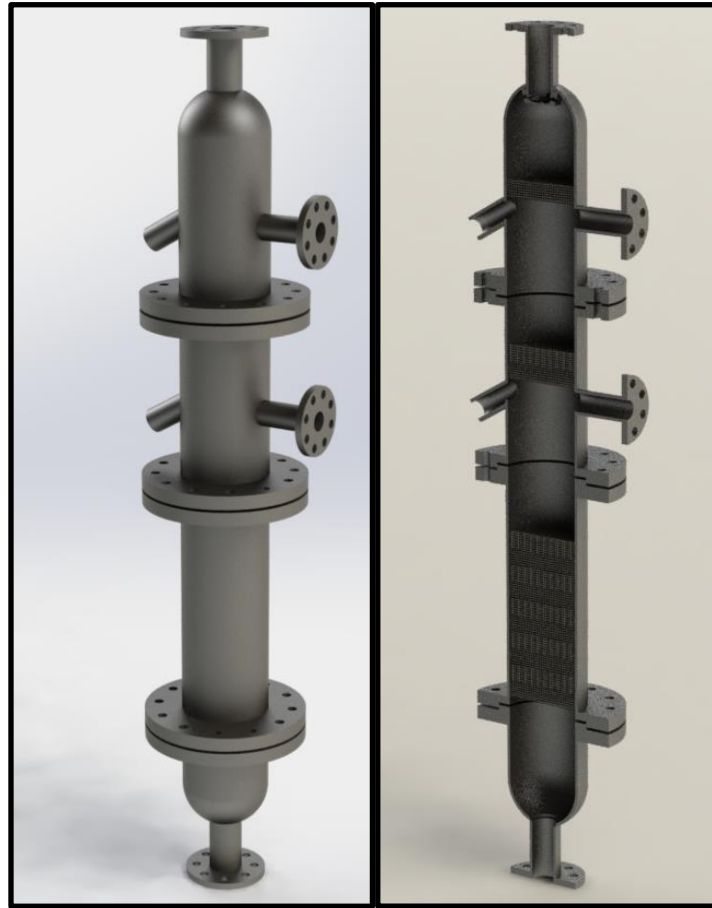
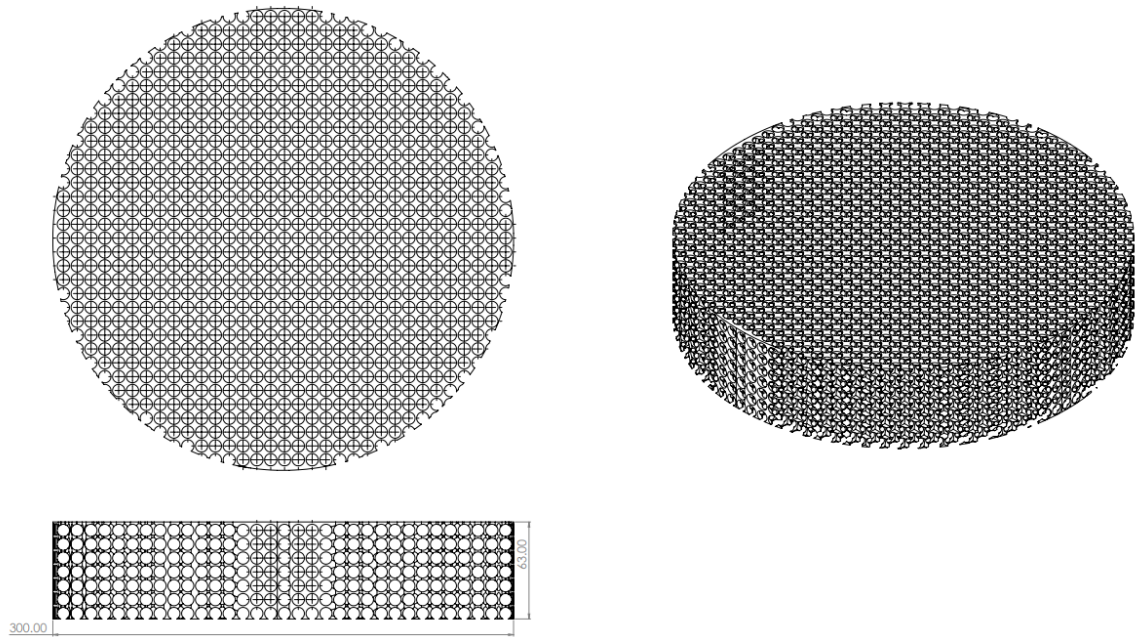Figure 9.3: 3D model: outside view, cross sectional view of Reactor

Figure 9.4: Schematic of the second catalyst bed
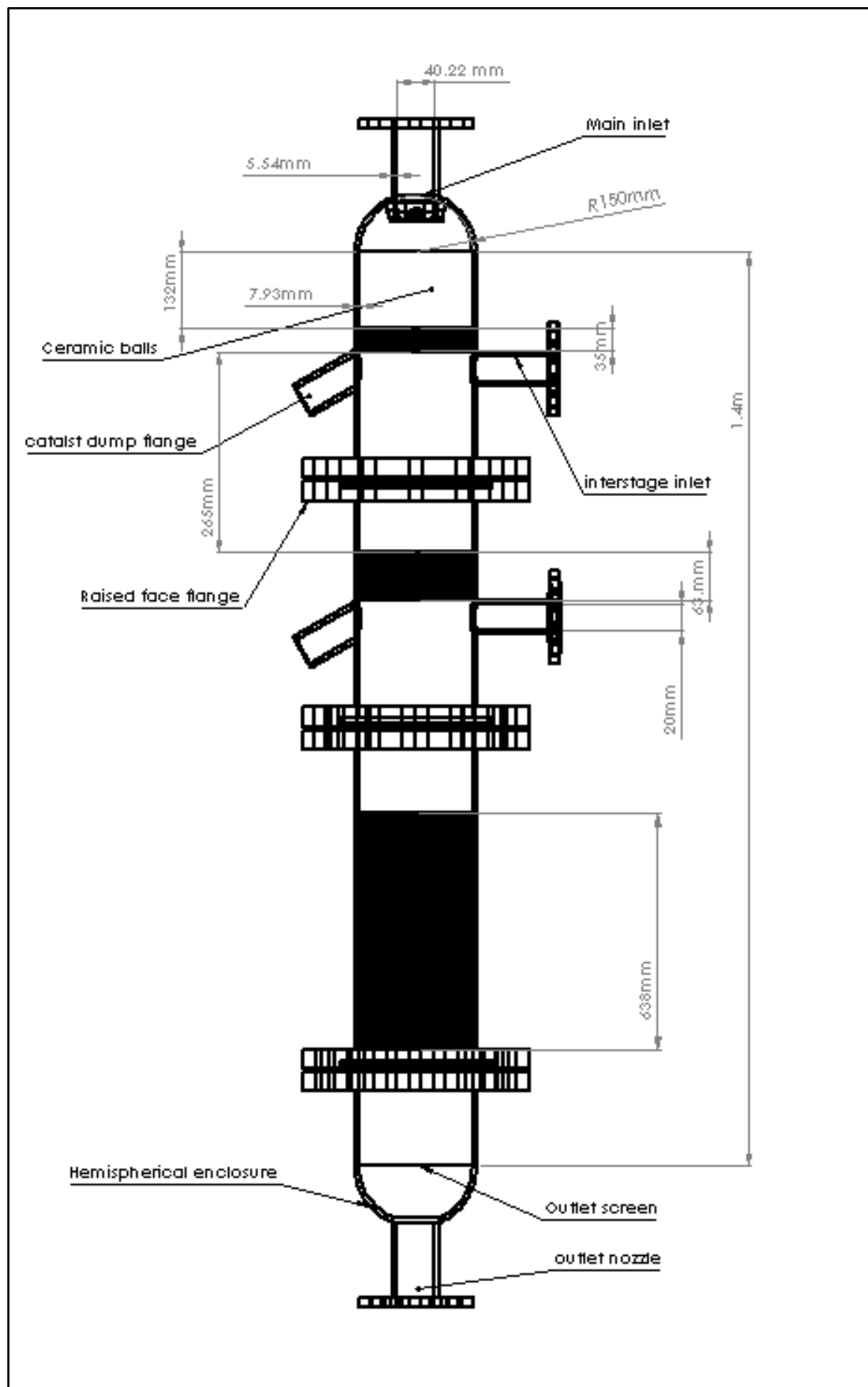
Figure 9.5:Cross Sectional Front View Engineering Drawing of the Reactor (not to scale)

Chapter 10

Environmental Impact and Assessment

10.1 Identification of Waste Streams

We identified there are three sources of waste are as follows:

Waste	Source	Components
Wastewater	Flash liquid outlet	HCl, H_2O, CO_2
Flue gas emission	Boiler and heating furnace	CO_2, CO, NOx, SO_2
Solid waste (in 2 years)	Catalyst	Al_2O_3

Table 10.1: Pollutants and source

10.2 Potential Pollutants and their Hazardous Impact[27]

Waste	Components	Hazardous Impact
Wastewater	HCl	Increased in acidity of soil disables some organisms from growing, thus disturbs the food chain
	CH_3Cl	Ozone Formation and Depletion, Global Warming Impacts
Flue gas emission	CO_2	Major Greenhouse gas causes climate change, thus contributes in temperature rise
	CO	Causes headache, weakness, dizziness, shortness in breathing
	NOx	Smog formation, acid rain
	SO_2	React in atmosphere to form aerosol, which can contribute to outbreak of haze
Solid waste	Al_2O_3	Alumina dust can cause irritation in the respiratory system, eyes

Table : 10.2: Pollutant and their harmful impact

10.3 Wastewater Treatment

Overall flow sheet for wastewater treatment

```
                        ┌──────────────┐        ┌──────────┐
Efflue  ──►│Sedimentati │         │ Collecting │──────►│ To sea   │
nt              │on Tank     │         │ section    │        └──────────┘
                └────┬───────┘         └─────▲──────┘
                     │                       │
                ┌────▼───────┐         ┌─────┴──────┐
                │ Aerobic    │         │ Grit       │
                │ bacterial  │         │ collecting │
                └────┬───────┘         └─────▲──────┘
                     │                       │
                ┌────▼───────┐         ┌─────┴──────┐
                │ Organic    │         │ Limestone  │
                │ biomass    │         │ bed tank   │
                └────┬───────┘         └─────▲──────┘
                     │                       │
                     └──────────►┌───────────┴──────┐◄──────┐
                                 │ Mixing tank      │
                                 └──────────────────┘
```
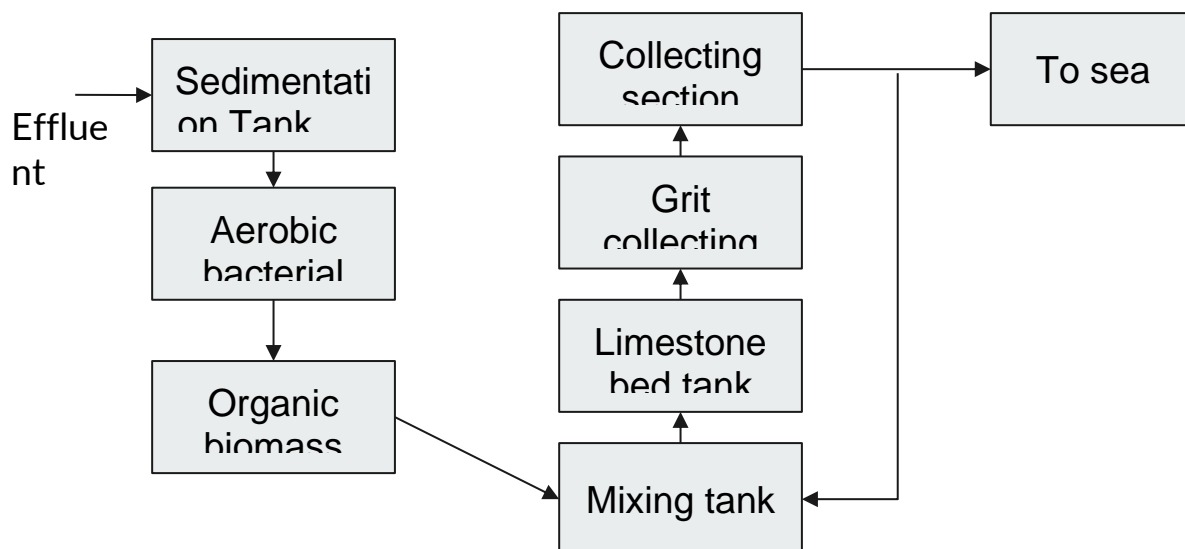
Figure 10.1: Overall Schematic

The effluent coming out from the system is the water generated as a byproduct. The major sources of pollutants in them are solid suspensions from powdered catalysts, DME from side reactions, unreacted methanol, HCl, and some quantities of Chloromethane. This contains Solid, organic, and acidic waste to be treated.

```
             ┌──────────────┐   ┌──────────────┐   ┌──────────────┐
Efflue ─►│ Sedimentat   │──►│ Aerobic      │──►│ Biomass      │───►
nt             │ ion Tank     │   │ treatment    │   │ Screening    │    To
               └──────┬───────┘   └──────▲───────┘   └──────┬───────┘    Mixin
                      │                  │                  │            g
                      ▼                  │                  ▼            tank
                   Solid               Air                Bioma
                   Sedime                                 ss
                   nts
```
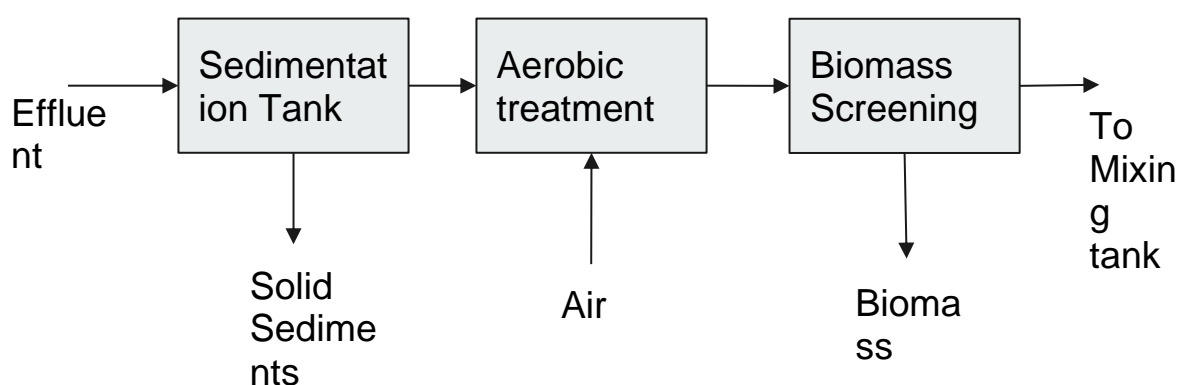
Figure 10.2: Sedimentation and Organic treatment system Schematic

The effluent stream is collected in a sedimentation tank, after providing enough travel distance to remove the suspended particles, it is then sent to an aerated tank containing aerobic bacteria. The bacteria there will eat up the organic components such as DME, and

chloromethane. Then this is passed an organic screener that would remove the dead bacterial biomass. Now it is sent to the acid neutralization.
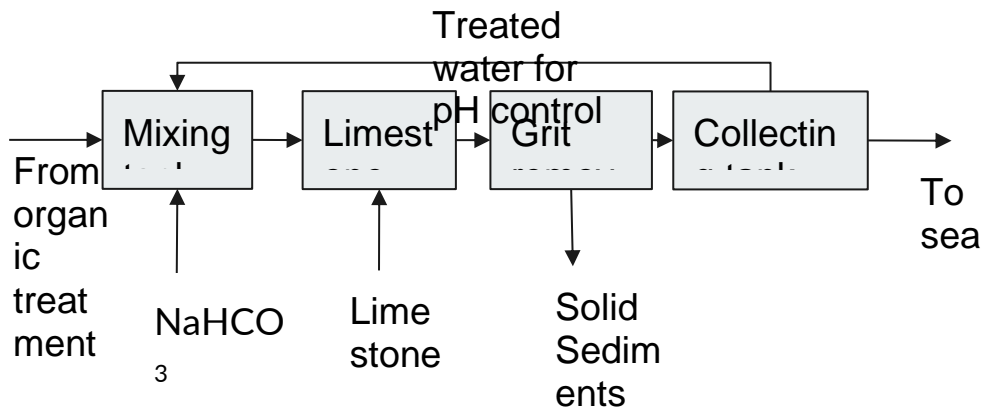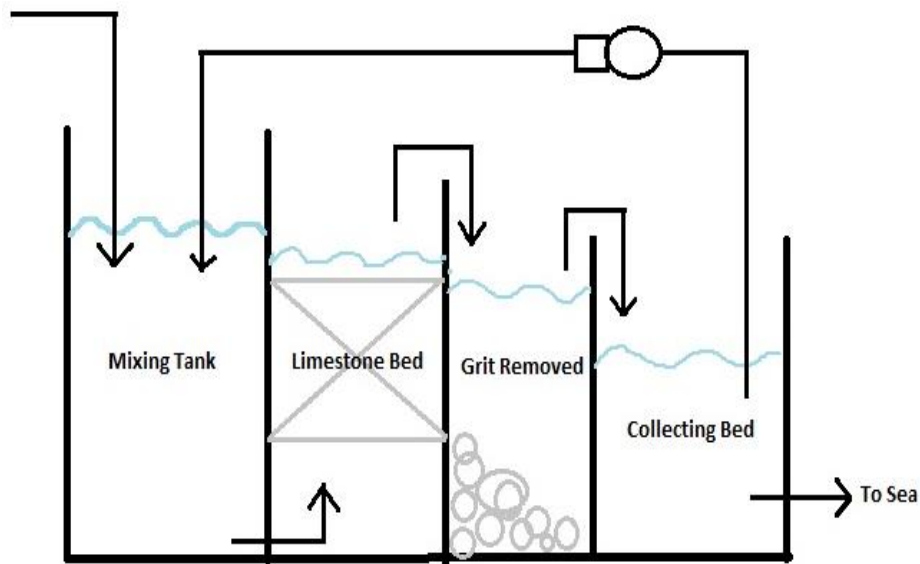

10.3: Acid Neutralization Schematics

Figure 10.4: Acid neutralization

The pH of the effluent stream is 0.4, it has to be brought up to at least 6.5 .Now the effluent is collected in a mixing tank, where treated water is added to control the pH of the fluid before entering the limestone bed. $NaHCO_3$ is added to further control the pH, this becomes much more important in case of any plant failure. The effluent once reached the limestone tank, will be neutralised. But this brings in further solid suspension. A secondary sedimentation tank removes them, and this treated stream is further collected in a collecting tank. Water from here is used for diluting the effluent in the mixing tank. The water from the collecting tank is disposed of into the sea.

Wastewater standards:

Parameter	Industry standards
pH	6.5-8.5
BOD	40 mg/L
Temperature	Does not exceed 7 C above ambient temperature of water bodies

Pollutant	8 hours (µg/l)	15 min (µg/l)
CH_3Cl	105	210

Table 10.3: Industry standards of wastewater

10.4 Flue Gas Emission [33,34,35,36]

We are using natural gas as fuel. The requirement is summarised below

Energy Required	2.4 MW
Calorific Value of NG	32.6 MJ/m³
Natural Gas Flow Rate Required	265 m³/h

For estimation of carbon dioxide and water vapor in the stack gas, we have assumed

Assumptions for calculations:
1) NG is methane
2) Complete combustion
3) 10% Excess Air

$$CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2O$$

we get,

Flue Gas	Flow Rate (kmol/h)
Oxygen	2.2

Nitrogen	92.8
Carbon Dioxide	11.2
Water Vapour	22.4

Table 10.4: Flue gas and flow rate

For NOx, SO₂, CO emission, we have estimated it using data found in [35,36] where natural gas was used as fuel:

(Note: PM are negligible to be considered for natural gas)

Pollutant	Standard Limit (mg/m^3)	Flue Gas (mg/m^3)
NOx	250	224
SO2	50	30
CO	100	95

Table 10.5: Comparison of pollutants with standard limits

So, our emissions are within limits required by CPCB.

Some Control Techniques (if required):

- Selective catalytic Reduction
- Wet Scrubber
- Selective non-catalytic reduction
- Catalytic Combustion

10.4.1 Ambient Concentration of gases

The average wind speed in the Visakhapatnam-Kakinada belt was found to be 5m/s. Considering daytime isolation conditions, we took the stability class to be C.

Surface wind speed (m/s) at 10m height	Daytime insolation			Night-time conditions	
	Strong	Moderate	Slight	Thinly overcast	High Cloudiness
<2	A	A-B	B		
2-3	A-B	B	C	E	F
3-4	B	B-C	C	D	E
4-6	C	C-D	D	D	D
>6	C	D	D	D	D

Table 10.6 Pasquill Stability Meteorological Conditions

Considering a stack height of 30m for our plant, we used the Plume Dispersion model for continuous release of gases.
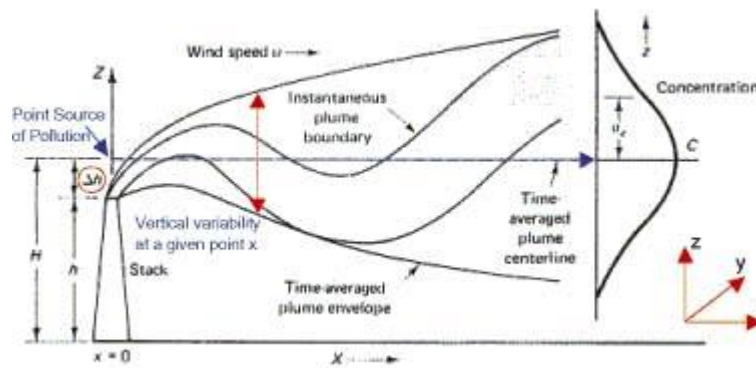

Figure 10.5 Plume Dispersion from ground source (continuous release)[29]

Pasquill-Gifford Stability class	σ_y (m)	σ_z(m)
A	$0.493x^{0.88}$	$0.087x^{1.10}$
B	$0.337x^{0.88}$	$0.135x^{0.95}$
C	$0.195x^{0.90}$	$0.112x^{0.91}$
D	$0.128x^{0.90}$	$0.093x^{0.85}$
E	$0.09x^{0.91}$	$0.082x^{0.82}$
F	$0.067x^{0.90}$	$0.057x^{0.80}$

Table 10.7 Equations for Pasquill-Gifford Dispersion Coefficients for Plume Dispersion (x = distance downwind from source)

The formula for steady state continuous plume dispersion is:

$$C(x, y, z) = \frac{G_V}{2\pi\sigma_y\sigma_z u}\left[\exp\left(\frac{-y^2}{2\sigma_y^2}\right)\right]\left[\exp\left\{\frac{-(z-H)^2}{2\sigma_z^2}\right\} + \exp\left\{\frac{-(z+H)^2}{2\sigma_z^2}\right\}\right]$$

Where x,y,z = distance from the source, m (x = downwind distance, y = crosswind distance, z = vertical distance) C = concentration (kg/m3) at location x, y, z; G_V = vapour emission rate (kg/s); H = height of source above ground level plus plume rise (m); σ_y, σ_z = dispersion coefficients (m), function of distance downwind, u = wind velocity (m/s)

We found the concentration of pollutants at a distance of 1000 m. The data along with the standard concentration according to the government norms is summarised below:

Pollutant	Annual (µg/m^3)	24 hours (µg/m^3)	Current level (µg/m^3)
NOx	40	80	26
SO2	50	80	4

Table 10.8 Comparison of pollutants with corresponding standards

The ambient concentration of the pollutants was well below the standard levels. So the plant follows the CPCB guidelines.

10.5 Catalyst

Alumina dust can cause irritation in the respiratory system and it can also cause irritation in eyes. The cement industry is known as one of the main industries where vast quantities of spent solid waste catalyst can be used as an additive or as raw materials in the manufacture of tile mixtures. In addition to cement production, building materials (porous blocks), asphalt paving, and construction, spent catalysts can be entirely re-used. We are disposing it in enclosed bins at an approved waste disposal plant. After disposing empty containers should be brought to a licenced disposal facility and containers should heed the label warnings.

10.5.1 Catalyst recycling process

This process is used in Washington Mills', which is a company based in the US. Add the waste aluminium oxide with fresh bauxite first. Then this particular mixture is fed into specially built furnaces that heat and purify the liquid abrasive. The company has furnace resources, which helps it to recycle spent aluminium oxide into the raw materials required to

manufacture pure fused aluminium oxide.

10.6 Carbon Footprint and E-factor

A carbon footprint is the total amount of greenhouse gases (including carbon dioxide and methane) that are generated by our actions. Higher concentrations in the atmosphere result from increased greenhouse gas emissions. The amounts of greenhouse gases are estimated in parts per million, billions, and trillions. Any of these gases has a varying period of time in the atmosphere, ranging from a few years to thousands of years. Since all of these gases stay in the atmosphere long enough to become well blended, the volume measured in the atmosphere is approximately the same all over the world, regardless of the source of pollution.

Greenhouse gas emissions from our plant
CO_2 : 3942 MTPA
Water vapour: 3225 MTPA
Total carbon footprint from our plant: 7167 MTPA

(Note : water vapour is a greenhouse gas. This was taught in the core course ES200 and can also be found at [37],[38]. Also, note that global warming potential of water vapor is roughly thousand times lesser than carbon dioxide)

10.6.1 Environmental Factor (E factor) [39]

Environmental Factor is the ratio of the mass of waste per mass of product. More E factor means more waste or more negative environmental impact.

E factor = $\dfrac{\text{mass of waste}}{\text{mass of product}}$ = $\dfrac{4773}{12618}$ = 0.38

Table E-Factors across the chemical industry

Industry sector	Annual production (t)	E-factor	Waste produced (t)
Oil refining	$10^6 - 10^8$	Ca. 0.1	$10^5 - 10^7$
Bulk chemicals	$10^4 - 10^6$	$< 1 - 5$	$10^4 - 5 \times 10^6$
Fine chemicals	$10^2 - 10^4$	$5 - 50$	$5 \times 10^2 - 5 \times 10^5$
Pharmaceuticals	$10 - 10^3$	$25 - 100$	$2.5 \times 10^2 - 10^5$

We are operating in bulk chemicals. Comparing, our wastage is much less than typical values.

APPENDIX

A1. Reactor Code

```
clc
clear

P0=29*10^5;

ro_b=285.7;
vo=0.22;
phi=0.63;
Dp=0.001;
mu=2.31*10^(-5);
ro_o=21.9;
k_conv=36960320250;
k_cons = 1.034;

D= 0.302;
Ac=pi*D*D/4;
u=vo/Ac;
% u = 1.1210;
G=ro_o*u;

beta=G*(1-phi)/(ro_o*Dp*phi^3)*(150*(1-phi)*mu/Dp + 1.75*G);

latentMeoh = 400*32.04;
cp_meoh=64;
cp_hcl=29.5;
cp_mecl=81.2;
cp_steam=37.6;
cpData = [cp_meoh; cp_hcl; cp_mecl; cp_steam];

delH_298=-34.7*1000;
delCp=cp_steam+cp_mecl-cp_hcl-cp_meoh;
```

```matlab
thermSystem = [delH_298; delCp];


T0 = 273.15+280;
Tmeoh = 273.15+37;
Tout = T0;


global Tvalues
Tvalues= [];


Fa=70.13;
Fa0 = 0;
Fb0= 70.87; %hcl
Fc0= 0; %mecl
Fd0= 0; %steam
feedIn = [0.46 0.33 0.21];
x_out = [0.85 0.93 0.99];


feedIn = feedIn/sum(feedIn)


for i = 1:length(feedIn)

        FaN = Fa*feedIn(i);
        FaP = Fa0;
        Fa0 = Fa0 + Fa*feedIn(i); %meoh
        V = (Fa0+Fb0+Fc0+Fb0)*8.314*T0/P0;


        theta = [Fa0/Fa0; Fb0/Fa0; Fc0/Fa0; Fd0/Fa0; FaN/Fa0; FaP/Fa0];



        Tin = (theta(6)*cpData(1)*Tout + theta(2)*cpData(2)*Tout + theta(3)*cpData(3)*Tout +
theta(4)*cpData(4)*Tout ...
        + theta(5)*cpData(1)*Tmeoh  - latentMeoh*theta(5)) ...
        /(theta(1)*cpData(1)+theta(2)*cpData(2)+theta(3)*cpData(3)+theta(4)*cpData(4));



        zspan = [0 2];
        y0 = [P0; 0];

        if i == 1
        Tin = T0;
        end

        k = KCons(Tin)/k_conv;
        convConst = Ac*ro_b*k/Fa0;

        Tvalues = [Tin];
        [z, y]=ode45(@(z, y)ReactorODE(z,y,P0, Tin, beta, convConst, theta, cpData,
thermSystem),zspan,y0);

        P = y(:,1);
        x = y(:,2);
```

```matlab
        termin = find(x>x_out(i));

        if isempty(termin)

        x_t = x(end);
        P0 = P(end);
        l = z(end);
        Tout = Tvalues(end);

        else
        indi = termin(1);
        x_t = x(indi);
        P0 = P(indi);
        l = z(indi);
        Tout = Tvalues(indi);
        end

        Fb0 = Fb0 - x_t*Fa0;
        Fc0 = Fc0 + x_t*Fa0;
        Fd0 = Fc0 + x_t*Fa0;
        Fa0 = Fa0 - x_t*Fa0;

%        Ac = V/u;
%        D = sqrt(4*Ac/pi);

        fprintf('P = %16.6f \n',P0/ 101325);
        fprintf('x = %16.6f \n',x_t);
        fprintf('z = %16.6f \n',l);
        fprintf('D = %16.6f \n',D);
        fprintf('Tin = %16.6f \n',Tin-273.15);
        fprintf('Tout = %16.6f \n',Tout-273.15);

        Tvalues = [];

end

function k = KCons(T)

        T= T-273.15;

        if T<330
        k = 1.034;
        elseif T<360
        k = 2.202;
        elseif T<390
        k = 3.404;
        else
        k = 7.714;
        end
```

```matlab
end
```

```matlab
function Reactor_diff = ReactorODE(z,Yfuncvec, P0, T0, beta,convConst, theta, cpData, thermSystem)
  P = Yfuncvec(1);
  x = Yfuncvec(2);
%         T = Yfuncvec(3);
  global Tvalues

  Ti = (-x*thermSystem(1) ...
        + theta(1)*cpData(1)*T0 + theta(2)*cpData(2)*T0 + theta(3)*cpData(3)*T0 +
theta(4)*cpData(4)*T0 ...
        + x*thermSystem(2)*298) ...

        /(theta(1)*cpData(1)+theta(2)*cpData(2)+theta(3)*cpData(3)+theta(4)*cpData(4)+x*thermSystem(2
));
  dPdz = 0 - beta*(P0/P)*(Ti/T0);
  dxdz = convConst*(P/2.01)^(2)*((theta(2)-x))*((theta(1)-x));

  Tvalues = [Tvalues, Ti];

Reactor_diff = [dPdz; dxdz];
end
```

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