



**Department of Chemical Engineering**  
Indian Institute of Technology Bombay

# **CL 452: Design Project**

## **Tertiary Butanol**

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# EXECUTIVE SUMMARY

This report explores the feasibility of establishing a Tert-Butyl Alcohol (TBA) production plant in India utilizing the isobutene hydration process.

## **Market Analysis:**

The global TBA market is projected for steady growth, driven by factors like demand for high-octane fuels and expansion in key end-use industries. Analyzing leading players and regional trends identifies potential market opportunities for Indian-produced TBA.

## **Production Process:**

The report evaluates various TBA production routes, ultimately justifying the selection of isobutene hydration for its advantages. DWSIM software is used to simulate the chosen process and perform a sensitivity analysis to optimize operating parameters. A finalized process flow diagram is presented.

## **Plant Design and Economics:**

Equipment sizing methodology is outlined for critical units like reactors, distillation columns, and heat exchangers. Total capital investment (TCI) estimation and a financial analysis including payback period and ROI are presented. Sensitivity analysis assesses the impact of economic fluctuations.

## **Detailed Engineering:**

The design of the first distillation column, crucial for TBA purification, is presented in detail. This includes specifications for the column skirt, nozzle placement, gasket and bolt selection, and tray design for efficient operation.

## **Environmental Considerations:**

Strategies for managing hazardous waste streams generated during production, adhering to Indian environmental regulations, are outlined. Material selection for plant construction is discussed, emphasizing factors like compatibility with process chemicals and corrosion resistance.

## **Conclusion:**

This report demonstrates the feasibility of establishing a TBA production plant in India using the isobutene hydration process. The analysis provides a strong foundation for further project development, paving the way for a successful venture in the growing TBA market.

# ACKNOWLEDGEMENTS

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# Ch. 1. INTRODUCTION

## 1.1 TERT BUTANOL

Tert-butyl alcohol or TBA ( $C_4H_{10}O$ ; IUPAC name: 2-methylpropan-2-ol) is the simplest tertiary alcohol in organic chemistry. It is a colourless oily liquid with a sharp alcohol odour. It floats and mixes with water in all proportions. Also miscible in ethanol and diethyl ether. It is found as a natural product in chickpeas and guava. Commercially it is obtained as a co-product of propylene oxide.

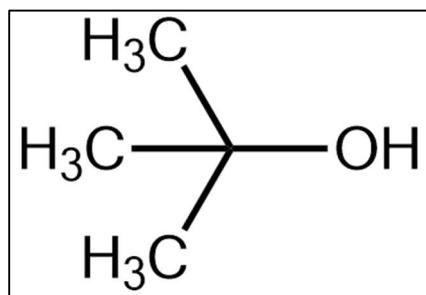


Figure 1: Structure of tert-butanol

PROPERTY <sup>1</sup>	VALUE
Molecular Weight	74.12 g/mol
Boiling Point	82.8 °C @ 760.00 mm Hg
Melting Point	25.4 °C
Flash Point	11 °C
Solubility in water	∞
Density	781 kg/m <sup>3</sup> @ 25°C
Vapor Pressure	4.1 kPa (at 20 °C)
Henry's Law Constant	9.05x10 <sup>-6</sup> atm-cu m/mole at 25 °C
Heat of Vaporization	39.07 kJ/mol

pKa	19.02
Heat Capacity	215.37 J / K . mol
Standard Enthalpy of Formation ( $\Delta_f H^\ominus_{298}$ )	-360.04 to -358.36 kJ/mol

Table 1.1: Properties of t-BuOH

### 1.1.1 Azeotropes of TBA<sup>2</sup>

Tert-butanol is often available in its homogeneous azeotropic form with water. This also causes difficulties in separation on an industrial level. Below is the tabulated data of all other azeotropes it forms.

Component	B.P. of component (°C)	B.P. of mixture (°C)	% Composition by weight
Water	100.0	79.9	11.8
Benzene	80.2	74.0	63.4
Cyclohexane	81.4	71.3	63.0

Table 1.2: Azeotropes of t-BuOH

### 1.1.2 USES

- Tert-butanol is used in the production of various flavors and fragrances for food and cosmetics. It is also used as a solvent for these products
- Tert-butanol is used as a fuel additive to increase the octane rating of gasoline, which improves engine performance and reduces emissions.
- Serves as an intermediate in the synthesis of various chemicals (MTBE and tert-butyl hydroperoxide), including pharmaceuticals and agrochemicals.
- It is an important solvent in the pharmaceuticals and paint industry.
- Tert-butanol is used as an adhesion/cohesion promoter, plasticizer, process regulator, and viscosity modifier.

### 1.1.3 Grades of tert-butanol

There are two major commercially available grades of tert-butanol:

1. Pure grade (99.65% minimum purity): This grade is commonly used in research and industry applications. It is used to manufacture organic peroxides, antioxidants, or pharmaceuticals. However, pure grade is liquid only above room temperature, hence causing transportation issues. It is flowable and pumpable only at elevated temperatures ( $> 30^{\circ}\text{C}$ ).
2. Azeotropic grade (87.25% minimum purity): Unlike pure grade, it is liquid and pumpable over a much wider temperature range, especially at room temperature and below. Majorly required by cosmetics and plastics producing industry

## 1.2 RAW MATERIALS

### 1.2.1 ISOBUTANE ( $\text{C}_4\text{H}_{10}$ )

Isobutane is a colorless gas with a faint petroleum-like odor. It is shipped as a liquefied gas under its vapor pressure. Contact with the liquid can cause frostbite. It is easily ignited. The vapors are heavier than air.

PROPERTY <sup>3</sup>	VALUE
Molecular Weight	58.12 g/mol
Boiling Point	-11.7 °C @ 760.00 mm Hg
Melting Point	-145 °C
Flash Point	-117 °C
Solubility in water	Insoluble
Density	563 kg/m <sup>3</sup> (at 15 °C, boiling liquid)
Vapor Pressure	310 kPa (at 21 °C)
Henry's Law Constant	8.6 nmol/ Pa . kg
Heat of Vaporization	4.570 kcal/mol at 25 °C
Heat Capacity	96.65 J/ K . mol

Standard Enthalpy of Formation ( $\Delta_f H^\ominus_{298}$ )	-134.8 – -133.6 kJ/mol
--	------------------------

Table 1.3: Properties of Isobutane

## USES

- Isobutane is used as a refrigerant in both domestic and commercial refrigeration systems. It is considered an environmentally friendly alternative to certain chlorofluorocarbons (CFCs) and hydrochlorofluorocarbons (HCFCs) due to its low ozone depletion potential.
- It is a common propellant in aerosol products such as deodorants, hairsprays, and spray paints.
- Isobutane is sometimes used as an additive in gasoline to improve its octane rating.
- Isobutane serves as a feedstock in the production of various chemicals, including isobutylene.

### 1.2.2 ISOBUTYLENE ( $C_4H_8$ )

Isobutylene is a colorless gas with a faint petroleum-like odor. For transportation it may be stenched. It is shipped as a liquefied gas under its own vapor pressure. Contact with the liquid can cause frostbite. It is easily ignited. Its vapors are heavier than air and a flame can flash back to the source of leak very easily.

PROPERTY <sup>4</sup>	VALUE
Molecular Weight	56.11 g/mol
Boiling Point	-7.0 °C @ 760.00 mm Hg
Melting Point	-140.3 °C
Flash Point	-76 °C
Solubility in water	Insoluble
Density	589 kg/m <sup>3</sup> (at 25 °C, P > 1 atm)
Vapor Pressure	257 kPa (at 20 °C)

Henry's Law Constant	0.218 atm-cu m/mole at 25 °C
Heat of Vaporization	395 kJ/kg

Table 1.4: Properties of Isobutene

## USES

- Primarily used to produce di-isobutylene, trimers, butyl rubber, and other polymers.
- Used to produce antioxidants for foods, packaging, food supplements, and for plastics.

# Ch. 2. MARKET ANALYSIS

## 2.1 Global Market Overview<sup>5, 6, 7</sup>

The global Tertiary Butyl Alcohol (TBA) market, totalling 1850 thousand tonnes in 2022, is poised to exhibit a growth rate of 5.4% annually until 2032. Driven by its versatile applications across industries, the market is anticipated to reach a notable capacity of nearly 3100 thousand tonnes by the conclusion of the forecast period in 2032.

### Applications:

TBA plays a pivotal role in various industries, including fuel additives, solvents, chemicals, rubber, pharmaceuticals, coatings, adhesives, and the food and beverage sector.

## 2.2 End-Use Industries

Flavors and fragrances constitute the largest consumer segment (42%) of the global TBA market in 2022. Paints and coatings follow, with TBA serving as a preferred solvent.

## 2.3 Key Players

Major players in the TBA market include LyondellBasell Industries N.V., Lotte Chemical Corporation, Kuraray Co. Ltd., Evonik Industries, Sinopec Corp., and others.

### 2.3.1 New Developments<sup>8</sup>

In March 2023, LyondellBasell commissioned the world's largest Tertiary Butyl Alcohol (TBA) and Propylene Oxide unit in Texas, with subsequent impacts on the market. TBA, a multifaceted chemical, experienced price fluctuations in the USA market in the first half of 2023.

The new facilities in Texas have an annual capacity of 470 thousand tonnes of Propylene Oxide and 1000 thousand tonnes of TBA. Isobutylene prices' slight decrease upstream affected TBA production expenses in the US market.

## Purity and Application Insights

TBA purity influences its applications, with >99% purity dominating the market. Solvents and intermediates constitute the largest application segment.

## 2.4 Regional Outlook<sup>9</sup>

1. Asia Pacific (44.3% Market Share): Driven by rising disposable income, population growth, industrialization, and increased polyurethane manufacturing in China and India.
2. Europe (26.3% Market Share): Significant presence due to increased construction activities and growing demand in chemical synthesis, freeze-drying agents, and flavors & fragrances applications.
3. North America (18.1% Market Share): U.S. demand rises with economic recovery, increased government spending on drug delivery and retrofitting, and consumer preference for luxury personal care products.

### Prices as of Dec 2023

- North America:US\$2.01/KG, 2.6% up
- Europe:US\$0.96/KG, 1.1% up
- Africa:US\$1.18/KG, 4.4% up
- Northeast Asia:US\$1.35/KG, 1.5% up
- South America:US\$1.21/KG, 4.3% up

### Prices as of Jan 2024

- North America:US\$1.92/KG, 3.8% up
- Europe:US\$0.97/KG, 2.1% up
- Africa:US\$1.15/KG, 3.6% up
- Northeast Asia:US\$1.29/KG, 2.4% up
- South America:US\$1.21/KG, 3.4% up

## 2.5 Market Drivers:

- Construction and Automotive Applications
  1. Paints, Coatings, and More: Tert-butanol role as a solvent/co-solvent in paints, coatings, inks, and adhesives, along with its use in varnishes, resins, gums, and other applications.
  2. Construction Boom: Growing demand in the building & construction sector, especially in expanding economies like China and India, fueled by rapid urbanization and industrialization.

- 3. Automotive Industry Growth: Increasing demand for tert-butanol in the automotive sector, driven by its application in rechargeable battery cells, aligning with the automotive industry's shift towards electric vehicles.
- Flavors and Fragrance Industry
  - 1. Complex Mixtures: Tert-butanol's utilization in fruit essence, perfume production, and its impact on the flavor of food products.
  - 2. Wide Industry Applications: Flavors and fragrances play a pivotal role in food, perfumes, toiletries, cosmetics, and chemical industries.
  - 3. Market Boost: Rising demand for traditional scents, branded perfumes, air fresheners, and deodorizers expected to elevate the global tert-butanol market share.
- Denaturants for Ethyl Alcohol Production
  - 1. Denaturant in Ethyl Alcohol:
    - Tert-butanol's role as a denaturant in the production of ethyl alcohol, contributing to the creation of denatured alcohol.
  - 2. Market Driving Factors:
    - Manufacturers' inclination towards effective denaturant alternatives.
    - Regulatory push for denatured alcohol in gasoline blending.
    - Increasing applications in medical disinfectant, cosmetics, specimen preservation, sanding, fuel, and pest control.

### 2.5.1 COMPANIES

COMPANY	CAPACITY	LOCATION
Alfa Aesar	-	USA
Evonik Industries Ag	0.21 Million TPA	GERMANY
Finar Limited	-	INDIA
Kuraray Co., Ltd.	0.1 Million TPA	JAPAN
Lotte Chemical Titan Corporation	0.11 Million TPA	MALAYSIA
Lyondellbasell Industries Holdings B.V.	1 Million TPA	USA

Merck Kgaa	-	GERMANY
Sisco Research Laboratories Pvt. Ltd.	-	INDIA
Tiande Chemical Holdings Limited	-	CHINA
Tokyo Chemical Industry Co., Ltd. (TCI)	-	JAPAN

# Ch. 3. PRODUCTION PROCESSES

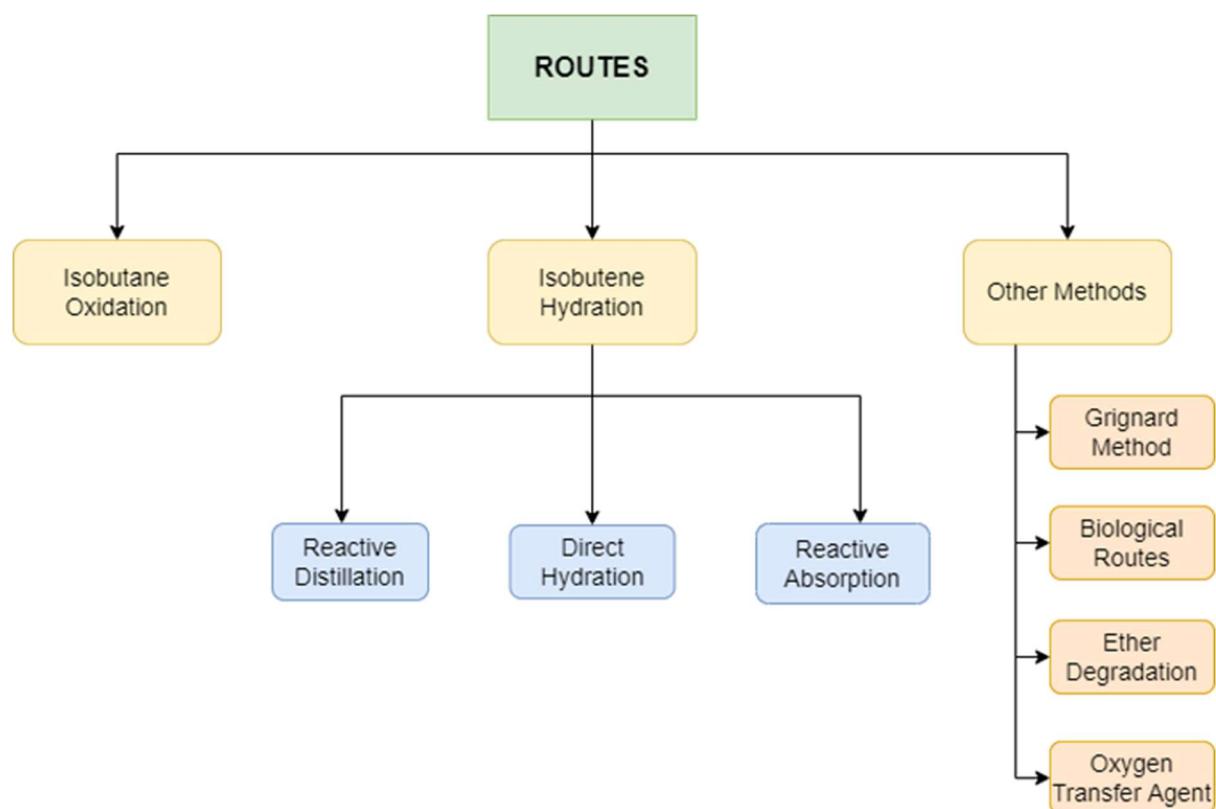
## 3.1 ROUTES

There are 4 major routes of synthesising Tertiary Butanol:

- 3.1.1 Oxidation of Isobutane
- 3.1.2 Hydration of Isobutene
- 3.1.3 Fermentation of Alkanes
- 3.1.4 Grignard Reagent

There are a few minor routes worth mentioning as well:

- 1. Cyclic Oxidation
- 2. Ester alkaline degradation



Let's discuss each of them in detail.

### 3.1.1 OXIDATION OF ISOBUTANE<sup>10, 11, 12</sup>



The manufacturing process of Tert-butanol involves several key steps:

a. Reaction of Isobutane with Oxygen

This step results in the formation of Tertiary Butyl Hydroperoxide and Tertiary Butanol (Reaction 1). The proportion of these products can be modulated by altering the catalyst<sup>1,2,3</sup> used.

b. Decomposition of peroxide

In this stage, Propene is employed as a reducing agent to decompose the peroxide while preserving the Tertiary Butanol. This process unfolds in two phases, with cooling occurring between the stages.

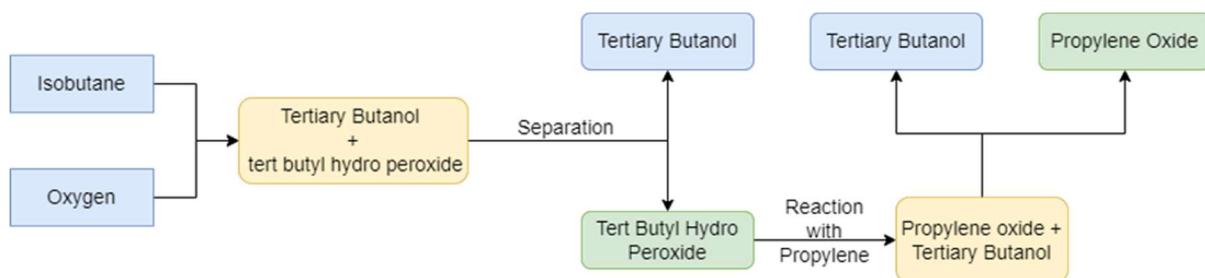
c. Cooling

The vapor stream is subjected to cooling, facilitating the extraction of a portion of the Tertiary Butanol.

d. Distillation and Separation

This constitutes the final step, wherein Tertiary Butanol is extracted.

It's important to note that the primary source of revenue in this process is Propylene Oxide, which holds a value 100 times greater than that of Tertiary Butanol. However, the process exhibits considerable inefficiency in terms of energy consumption due to the overoxidation and subsequent reduction involved.



**Because of this inefficiency in production, we are ignoring this route.**

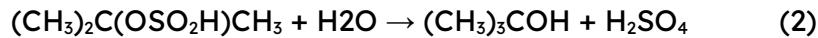
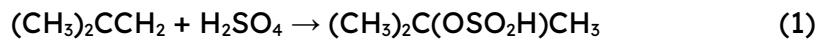
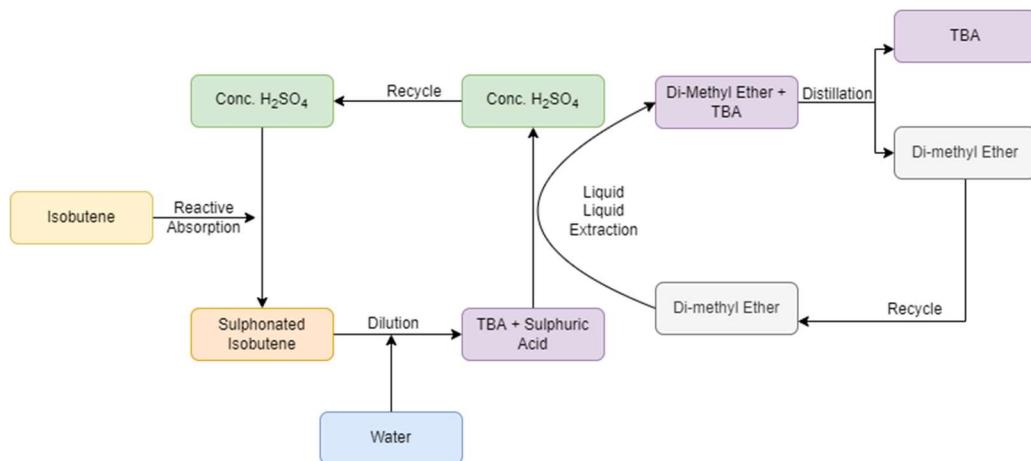
### 3.1.2 HYDRATION OF ISOBUTENE

#### 3.1.2.1 REACTIVE ABSORPTION<sup>13</sup>

The process commences with the absorption of isobutylene in concentrated sulphuric acid, a method that proves highly effective due to the reactive nature of the absorption. Subsequently, the solution undergoes dilution, facilitating the conversion of  $C_4H_9OSO_2H$  to  $C_4H_9OH$ . It's noteworthy that distillation at this stage would result in azeotropic distillation, a less desirable outcome. Thus, separation is done at a later stage.

The ensuing step involves the extraction of Tertiary Butanol using Diethyl Ether. This extraction is characterized by its selectivity and the ease with which it can be further processed via distillation. The details of this process are elaborated upon in the accompanying figure.

The only drawback of this method is that  $H_2SO_4$  also causes dimerization of isobutylene leading to formation of 2,4,4-trimethylpent-2-ene, but this happens at a lower concentration of acid (around 48% w/w). To ensure dimer formation does not take place, we shall use 67%  $H_2SO_4$  (w/w).



*Because of the simplicity of this process and absence of azeotropes, we initially selected this route but had to discard it later due to absence of kinetic data.*

Calculations done when this route was initially selected:

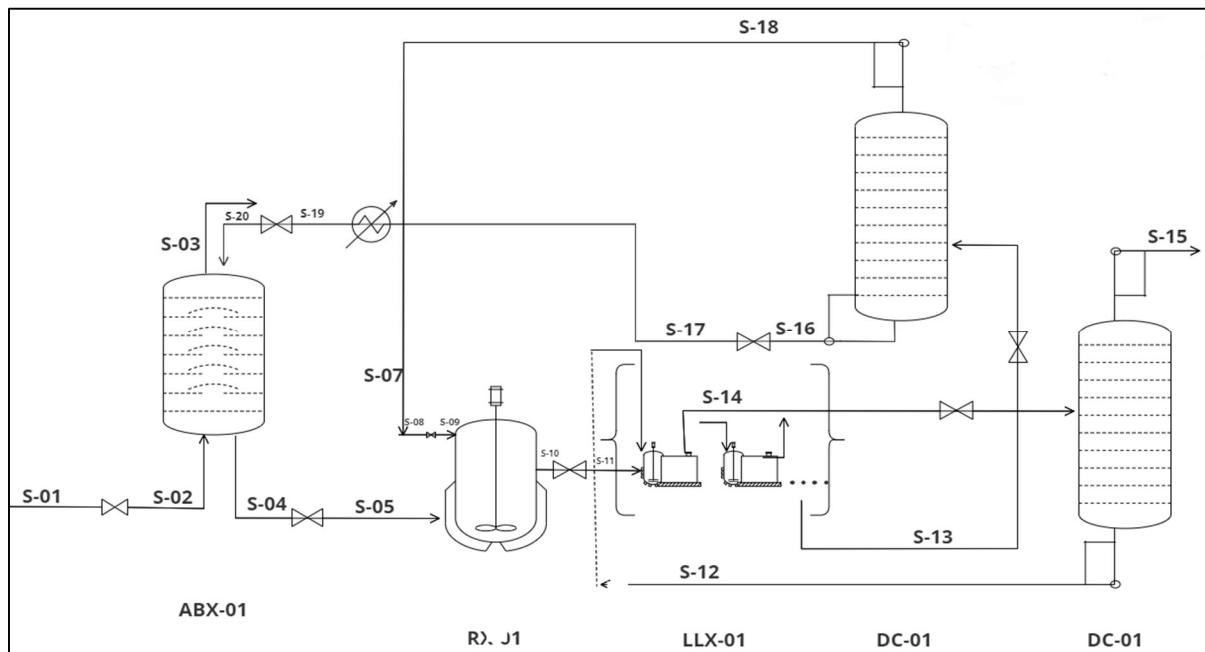


Figure 2: Overall PFD for Reactive Absorption process

	S-01	S-03	S-04	S-06	S-07	S-10	S-12	S-13	S-14	S-15	S-16	S-19
Temperature (celcius)	25	25	25	25	25	25	25	25	25	25	120	25
Pressure (atm)	1	1	1	1	1	1	1	1	1	1	1	1
Phase	G	G	L	L	L	L	L	L	L	L	L	L
Isobutane (TPH)	5.168	5.168	0	0	0	0	0	0	0	0	0	0
Isobutene (TPH)	98.192	0	0	0	0	0	0	0	0	0	0	0
Sulphuric acid (TPH)	0	0	17.164	0	0	188.8	0	188.8	0	0	188.8	188.8
Water (TPH)	0	0	92.933	31.51	347.51	92.933	0	440	0	0	92.933	92.933
Sulphonate ester (TPH)	0	0	269.83	0	0	0	0	0	0	0	0	0
Tert Butanol (TPH)	0	0	0	0	0	0	1.29	0	129.7	128.4	0	0
Diethyl Ether (TPH)	0	0	0	0	0	682.71	0	684	1.29	0	0	0
Total (TPH)	103.36	5.168	379.927	31.51	347.51	281.733	684	628.8	813.7	129.69	281.733	281.733

Table 3.1: Stream Data for Figure 2 PFD

### Selection of various unit operations:

#### 1] BUBBLE COLUMN REACTOR

For sulphonation of isobutylene, we use a bubble column reactor, owing to the reactant's gaseous phase nature.

- The sulphonated ester is somewhat hydrated in the column itself leading to a noticeable amount of tert-butanol.
- This is actually beneficial as this increases the solubility of isobutylene in the acid.

## 2] HYDRATION REACTOR

We don't need a dedicated and specialized reactor for the process, as we are just diluting the TBA and sulfonated ester mixture. The hydration process is exothermic. A CSTR with cooling jacket would be preferred.

*But why is dilution necessary?*

- a. The ester, despite being stable, is easily broken down into H<sub>2</sub>SO<sub>4</sub> and TBA upon gaining more water in its surroundings.
- b. Also, during the extraction process, as the solvent (diethyl ether) in this case is immiscible in water, so it only carries TBA with it hence preventing scope of any azeotrope formation and making it quite readily extractable.
- c. Diethyl ether is soluble with concentrated acid, but as it gets diluted, it splits into two separate phases.

## 3] LLE and Suitable SOLVENT SELECTION

It has been observed that TBA can be extracted almost completely from the acid phase, unlike secondary olefins. Upon reviewing various studies, certain solvents have demonstrated notable effectiveness in this extraction process. These promising solvents are highlighted based on the reported results in existing research

- Diluted product extraction with benzene (5 times), achieved a 74% tert-butanol extraction.
- 46% of tert-butanol was extracted with o-dichlorobenzene in the same condition (5 washes with the solvent).
- Ethyl ether identified as the most suitable solvent giving 100% extraction, although upon 10 times washing. When extraction was done 5 times, 91% of tert-butanol was recovered.

Furthermore, why diethyl ether should be the solvent was also emphasized above while discussing the necessity of dilution.

As 10 times extraction led to complete recovery of all the alcohol, we propose a 10-stage cross current setup for the LLE module.

A more simplified view of this process is:

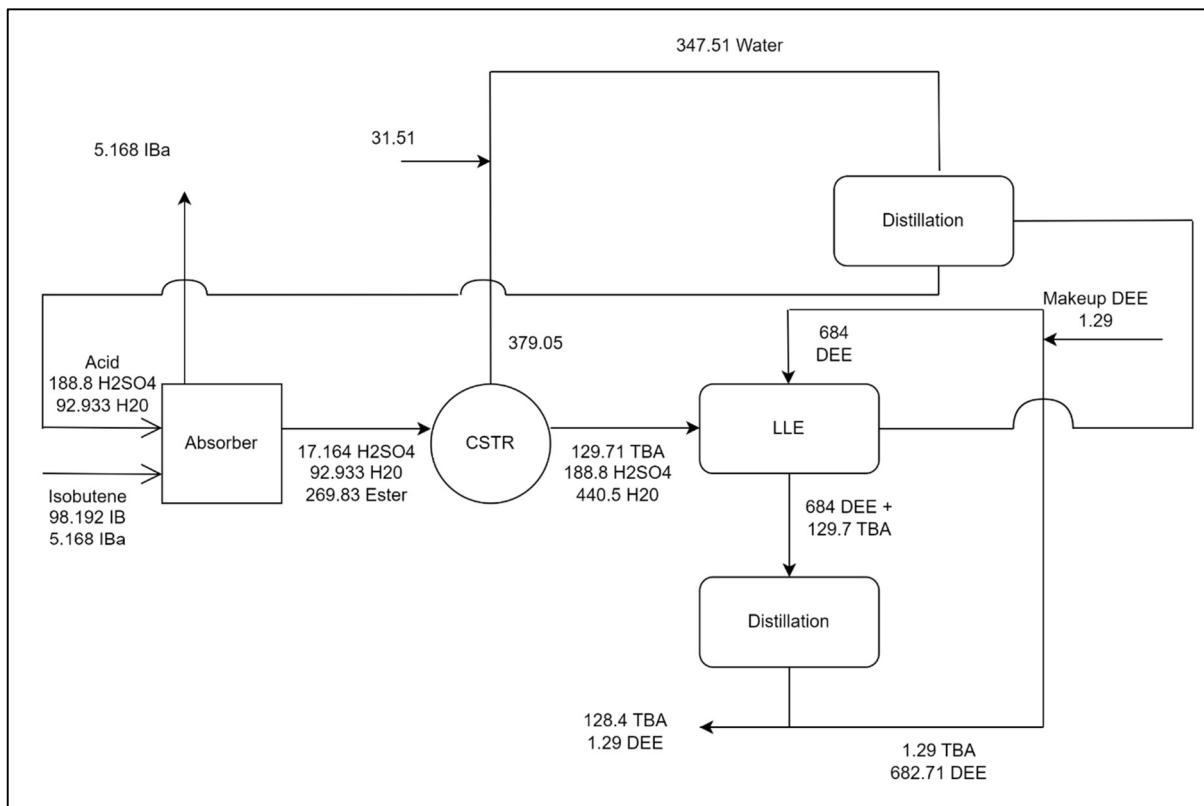
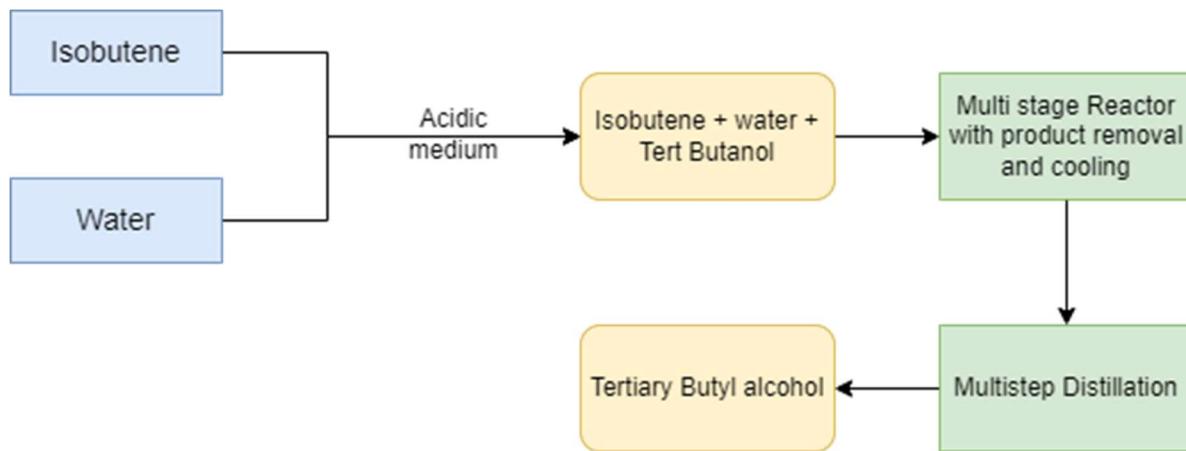


Figure 3: Overall Mass balance for Reactive Absorption process

### 3.1.2.2 DIRECT HYDRATION OF ISOBUTENE<sup>14, 15, 16, 17, 18, 19, 20</sup>



In this process, Isobutene is reacted directly with water. Given the reversible nature of the reaction, it necessitates the continuous removal of the product, thereby requiring the use of multiple reactors.

It's noteworthy that Isobutene, being a gas, is insoluble in water. Furthermore, the reaction proceeds too slowly in the vapour phase. Consequently, a solvent is required to maintain both reactants in the liquid phase. Intriguingly, for this reaction, the product t-butanol itself serves as the solvent.

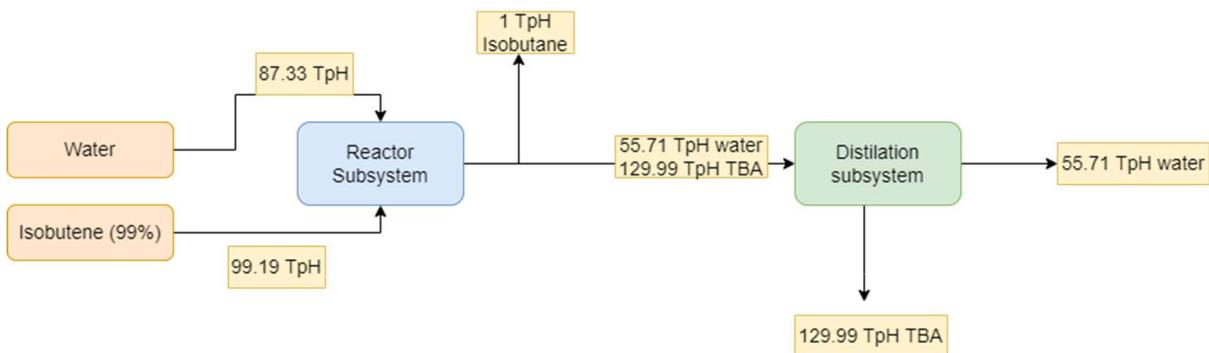
Given the reversibility of the reaction, the presence of the product in the reaction mixture can drive the reaction in the reverse direction. Therefore, a balance must be struck between the solubility of Isobutene and the forward progression of the reaction.

The catalyst employed in this process is unique. An acid is required as the catalyst, but in a liquid medium, an overly dilute acid would not exhibit any activity, while an excessively concentrated acid would induce corrosion and promote side reactions such as dimerization and ether formation. As a result, a solid acid catalyst, also known as a cation exchange resin, is utilized, which greatly simplifies the processes of recovery and regeneration.

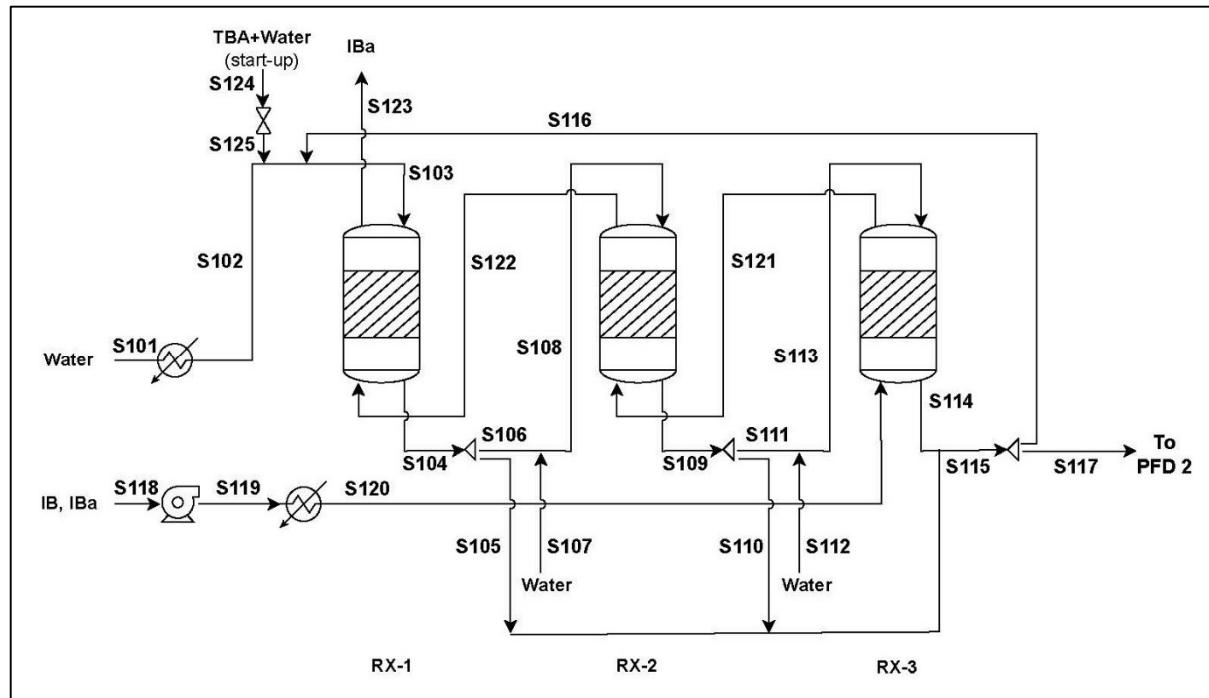
However, this route presents a challenge in the form of an azeotrope formed between water and butanol. The separation of this azeotrope would necessitate the use of specialized distillation columns, a requirement which is not present in the previous method.

**After rejecting the previous method, this was the next best possible method.  
Hence, we are using this.**

## Simplified Block Diagram with mass balances



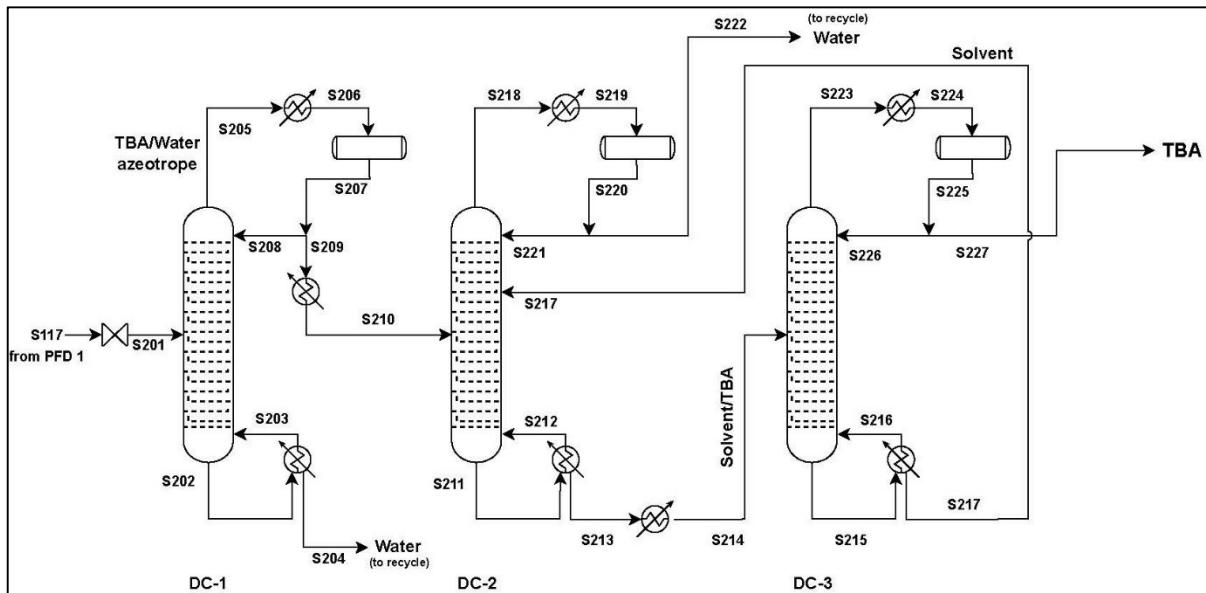
## PFD 1: Reactor Subsystem



	S102/S107/S112	S103/S108/S113	S104/S109/S114	S105/S110	S115	S117	S120	S121	S122	S123
Temperature(Celcius)	-	50	75	75	75	75	-	-	-	-
Pressure(atm)	1	1	1	1	1	1	1	1	1	1
Phase	L	L	L	L	L	L	G	G	G	G
Isobutene(TPH)	0	0	0	0	0	0	98.192	65.461	32.73	0
Isobutane(TPH)	0	0	0	0	0	0	0.9918	0.9918	0.9918	0.9918
Water(TPH)	29.11	35.665	25.122	18.57	62.262	55.71	0	0	0	0
TBA(TPH)	0	15.285	58.618	43.33	145.278	129.99	0	0	0	0
Total(TPH)	29.11	50.95	83.74	61.9	207.54	185.7	99.1838	66.4528	33.7218	0.9918

Table 3.2: Stream Data for PFD 1: Direct Hydration

## PFD 2: Distillation Subsystem



	S201	S204	S210	S214	S217	S222	S227
Temperature(Celcius)	75	100	79	-	247	100	80
Pressure(atm)	1	1	1	1	1	1	1
Phase	L	L	L	L	L	L	L
Solvent(TPH)	0	0	0	209.16	209.16	0	0
Water(TPH)	55.71	36.3	19.4	0	0	19.4	0
TBA(TPH)	129.99	0	129.99	129.99	0	0	129.99
Total(TPH)	<b>185.7</b>	<b>36.3</b>	<b>149.39</b>	<b>339.15</b>	<b>209.16</b>	<b>19.4</b>	<b>129.99</b>

Table 3.3: Stream Data for PFD 2: Direct Hydration

The conceptualization of this design primarily draws upon the innovative ideas presented in several patents advocating for a multi reactor setup, as well as the insights gleaned from a scholarly paper on trickle bed reactors. These sources collectively served as the inspiration and provided the foundational knowledge necessary for the development of this design.

The Process Flow Diagram (PFD) elucidates the process under discussion. The three units depicted on the left constitute the reactor network, while the three units on the right form the separation network. Several characteristics of this setup warrant attention.

Water and a stream labelled S116, which contains a mixture of alcohol and water, flow from left to right. Conversely, Isobutene flows from right to left. Notably, even within a reactor, the flow is counter current.

It's also important to observe that a portion of the liquid product from each reactor is separated and directed to a distillation column. Concurrently, water is added to the remaining part, which is then sent to the subsequent reactor.

Within the distillation subsystem, the initial step involves obtaining the Tert-butanol water azeotrope and recycling the remaining water. Subsequently, the azeotrope is broken down using extractive distillation, and the solvent is recycled.

The rationale behind each of these choices will be expounded upon in the following section.

## 1] Reasoning

### *Choice of Trickle Bed Reactor:*

The selection of a trickle bed reactor offers several advantages. It eliminates the need for an additional piece of equipment to dissolve Isobutene (IB) and allows for operation at slightly higher temperatures without concerns about solubility.

Compared to a slurry reactor, a trickle bed minimizes liquid side reactions such as ether formation.

### *Advantages of Trickle Bed over Bubble Column:*

The use of a solid catalyst in the process makes a bubble column unsuitable for this application. Furthermore, the formation of di-isobutene, a by-product expected from a competitive second-order reaction, is slowed due to lower dissolved concentrations of IB and lower operating temperatures, leading to higher selectivity towards the desired product, Tertiary Butanol (TBA).

### *Counter Current Flow:*

The counter current flow design is energy efficient as it reduces the energy required to cool the process fluid. The gas heats up from left to right, and the liquid heats up from right to left, maintaining high solubility at all points. This principle applies both within a single reactor and across multiple reactors.

### *Multiple Reactors:*

The reaction is reversible and exothermic, necessitating the removal and cooling of the product before each step, which is facilitated by using multiple reactors.

### *Alcohol in the Reaction Feed:*

The presence of alcohol in the reaction feed helps to keep IB soluble and the reaction in the liquid phase.

### *Reaction in the Liquid Phase:*

Conducting the reaction in the liquid phase ensures better contact with the solid catalyst.

*Use of Cold Water:*

Cold water is used because it is easier to cool the liquid by mixing than to cool the vapours. Moreover, direct mixing results in a better heat transfer coefficient. Each of these choices contributes to the efficiency and effectiveness of the process. However, it's important to note that these choices are interconnected, and changes to one aspect of the process may necessitate adjustments to others.

2] Solvent Selection <sup>21</sup>

The selection of an appropriate solvent for the separation of compounds necessitates careful consideration of several key factors. Foremost among these considerations is the establishment of a significant boiling point differential between the target compound and the chosen solvent. This characteristic facilitates an efficacious separation process by capitalizing on the disparity in vapor pressures between the components.

A second imperative criterion involves the miscibility of the extractive agent with the tert-butyl alcohol, as failure to achieve miscibility may result in the formation of a two-phase azeotrope in the recovery column. Such an occurrence would necessitate the implementation of alternative separation methods. In this context, it is particularly advantageous for the selected solvent to exhibit miscibility with tert-butyl alcohol to obviate complications in the separation process.

The third crucial consideration pertains to the economic viability of the chosen solvent, specifically the cost per kilogram. Cost considerations play a pivotal role in industrial processes, and selecting a solvent with a judicious balance of efficacy and economic feasibility is paramount for optimizing the overall efficiency of the separation procedure.

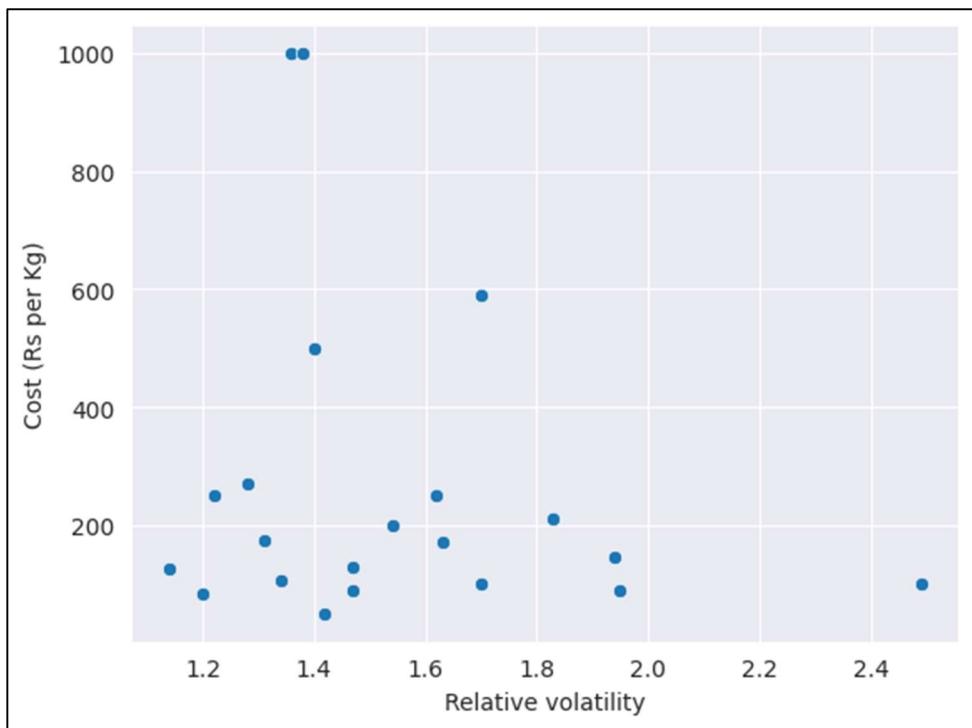


Figure 4: Cost vs  $\alpha$  for various solvents  
*(The data of different solvents is given in Appendix)*

In alignment with these criteria, ethylene glycol phenyl ether has emerged as the solvent of choice. Possessing a boiling point of 247 °C, it satisfies the prerequisite of a substantial boiling point difference from the compound being separated, facilitating efficient vapor-phase separation. Moreover, its miscibility with water ensures compatibility with tert-butyl alcohol, mitigating the risk of azeotropic complications in the recovery column. Finally, with a cost of 100 Rs/Kg, ethylene glycol phenyl ether not only meets economic considerations but also exhibits the highest relative volatility, further enhancing its suitability for the designated separation process. This meticulous solvent selection aligns with the imperative of balancing technical efficacy, compatibility, and economic prudence in industrial chemical processes.

Upon further processing, it was found that this solvent wasn't available on DWSIM. Thus, we use the next best solvent, which is **Triethylene Glycol**.

### 3] Heat Exchanger Selection

The utilization of a shell-and-tube heat exchanger in the context of direct hydration is underpinned by a series of strategic considerations, driven by the specific requirements of the isobutene hydration process. Notably, the choice of this heat exchanger configuration is attributed to the need to compress isobutene (IB) before its introduction into the reactor, resulting in elevated pressures that render plate heat exchangers less suitable.

Other advantages are listed below:

- Exothermic Reaction
- Efficient Heat Transfer
- Temperature Control
- Scalability
- High Heat Transfer Surface Area
- Ease of Maintenance

#### 4] Catalyst Selection <sup>a</sup>

In the quest for an ion exchange catalyst that boasts high porosity and is economically viable, two primary contenders emerge:  
Amberlyst 15 and DuPont™ Duolite™ A568.

Both of them share similar characteristics in terms of pore volume and diameter. The specifications are as follows:

##### **Amberlyst 15:**

- Total Pore Volume: 0.40 cc/g
- Average Pore Diameter: 300 Å

##### **DuPont™ Duolite™ A568:**

- Total Pore Volume: 0.78 – 1 mL/g
- Average Pore Diameter: 300 – 500 Å

While both options present comparable pore volumes and diameters, other factors come into play when choosing between them. Duolite™ A568, often employed for enzyme holding, is presumed to be more expensive due to its specialized use. Additionally, it is a weak ionic resin, which could result in lower activity. In contrast, Amberlyst 15 is a cost-effective and strong ion exchange resin, making it a more appealing choice given the requirements. Therefore, Amberlyst 15 emerges as the preferred option in this context.

### 3.1.2.3 REACTIVE DISTILLATION <sup>22</sup>

This process mirrors the one previously discussed, with the notable exception that the product, Tertiary Butanol, is continuously removed. The accompanying figure from a referenced paper provides a more detailed illustration of this process:

The continuous removal of TBA serves to drive the reaction forward. Additionally, the integration of the reactor and separator results in capital cost savings. However, it's important to note that this method necessitates the breaking of the azeotrope between TBA and water, which in turn requires the use of complex distillation columns. This is a key consideration when evaluating the feasibility and efficiency of this process.

**Thus, this is the least preferred alternative and not considered further.**

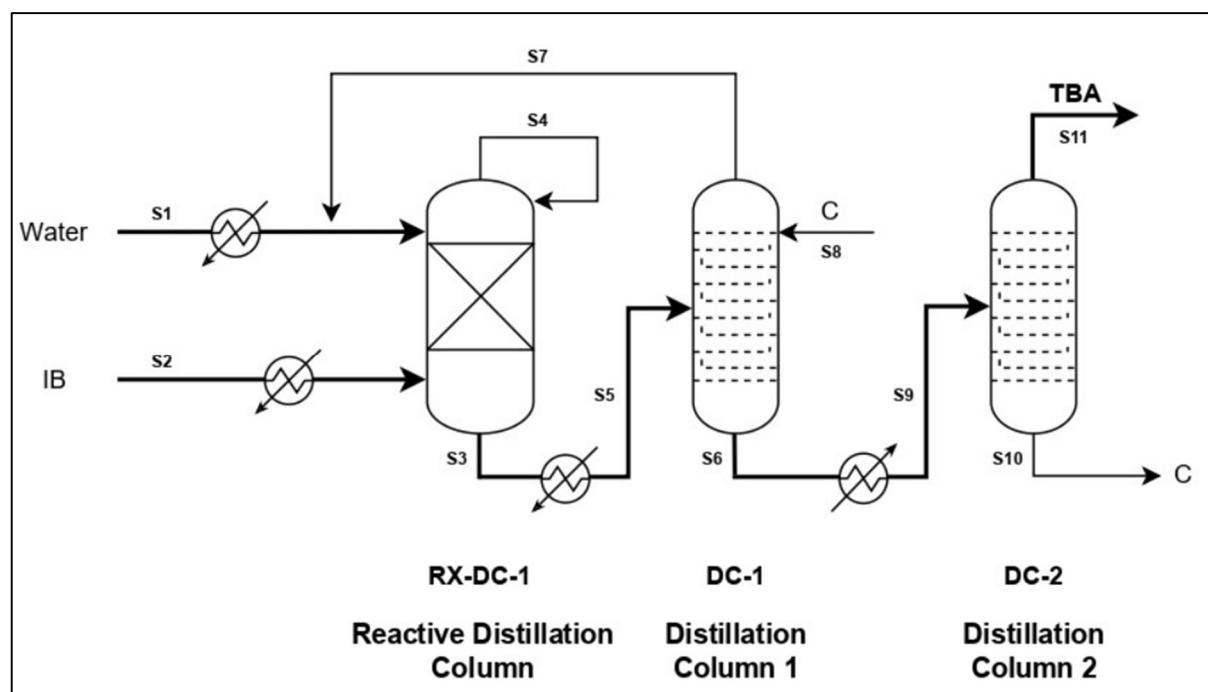


Figure 5: PFD for Reactive Distillation

### Heat Exchanger Selection

The designated heat exchanger for this process is a Plate Heat Exchanger, selected for its distinct advantages in facilitating the heat transfer requirements integral to the operational dynamics.

- Enhanced Heat Transfer Efficiency: The plate heat exchanger excels in augmenting heat transfer efficiency due to its intricate plate structure, fostering increased surface area for effective thermal exchange between fluids.
- Compact Design: Characterized by a compact configuration, the plate heat exchanger optimizes spatial utilization, making it particularly suitable for applications where space constraints are a consideration.

- **Flexibility in Temperature Control:** The design of the plate heat exchanger affords a high degree of flexibility in regulating temperature, providing nuanced control over the thermal conditions of the process.
- **Rapid Heat Transfer Response:** The inherent characteristics of the plate heat exchanger contribute to swift heat transfer responses, facilitating dynamic adjustments to temperature variations within the system.
- **Ease of Maintenance and Cleaning:** The accessibility of the plate heat exchanger's components facilitates facile maintenance and cleaning procedures, ensuring sustained operational efficiency over extended durations.
- **Versatility with Corrosive Fluids:** The materials employed in the construction of plate heat exchangers confer resistance to corrosive fluids, broadening the applicability of this exchanger in scenarios involving chemically aggressive media.
- **Energy Efficiency:** The plate heat exchanger, through its optimized design and efficient heat transfer capabilities, manifests as an energy-efficient component, contributing to overall process sustainability by minimizing energy consumption.

## Other Routes

### 3.1.3 FERMENTATION OF ALKANES<sup>23</sup>

Since Butanol is an alcohol, we can also explore fermentation as a method of production.

The fermentation reaction that produces t-Butanol is referred to as ABE fermentation, since the products are Acetone, Butanol, and Ethanol. This has never been done at industrial scale and has the following steps:

**1] Selection of feedstock** - there are 4 potential feedstocks to be used for the reaction:

Starch and sucrose feedstocks made from crops like corn, sugarcane, or beets. They consist of easily fermentable sugars, which are formed of complex polysaccharides. Lignocellulosic biomass: This includes forestry waste, crop residues, and crops grown specifically for energy. Because lignocellulosic biomass is abundant and inexpensive, it is preferred over the other substrates

Algal Biomass

Syngas: Syngas can also act as a substitute carbon source for the fermentation of ABE.

**2] Preparing the feedstock** - The feedstock is prepared for the reaction via 3 steps:

- Breakdown and Size Reduction: To break down complicated structures, increase surface area, and improve porosity, the feedstock is treated to physical, chemical and biological processes.
- Hydrolysis of Cellulose: Enzymatic hydrolysis is used to break down the cellulose molecules into smaller sugars like glucose, making sugars available for fermentation. This process also produces some inhibitors which need to be removed.
- Detoxification: Detoxification involves the removal of inhibitors produced in the hydrolysis of cellulose and uses methods like centrifugation, activated charcoal treatment, and electrodialysis. This increases the effectiveness of fermentation.

**3] Fermentation** - Typically, strains of clostridium bacteria are used for the fermentation process. They break down the feedstock's carbohydrates into metabolic byproducts like ethanol, butanol, and acetone. This fermentation happens through 2 steps. 1st, which involves the production of organic acids, which are then converted to alcohols (butanol, ethanol) and acetone.

**4] Separation** - The alcohol, butanol, and ethanol need to be removed from the fermentation broth. Theoretically, distillation seems like the appropriate choice (although energy-intensive). *This is a small-scale method and not used in large scale*

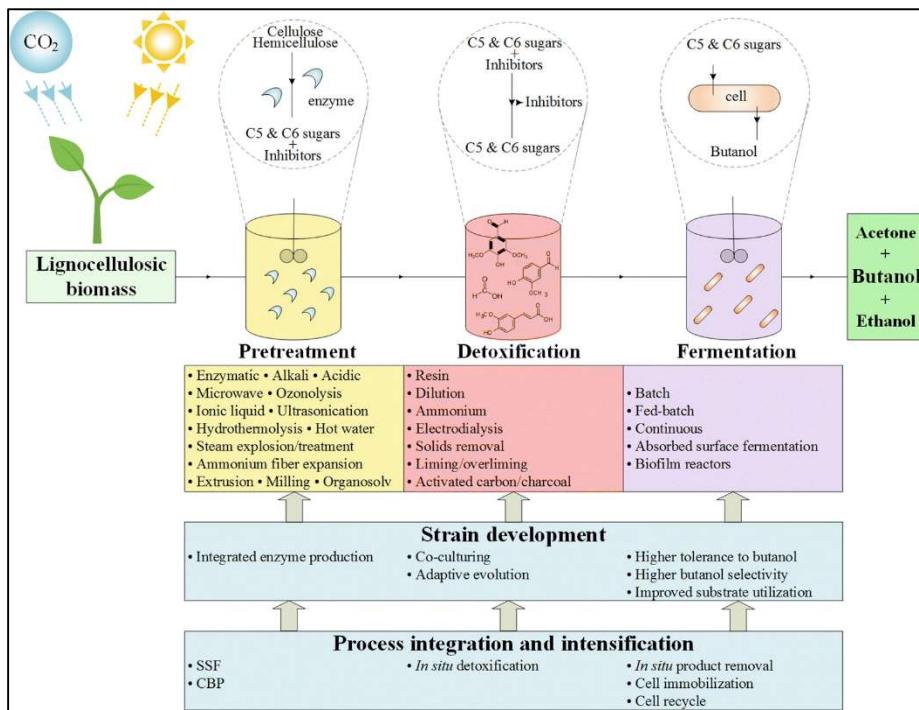
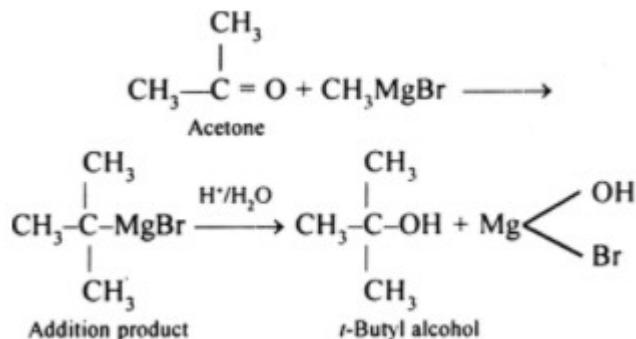


Figure 6: Fermentation Route

### 3.1.4 VIA GRIGNARD REAGENT



The synthesis of tert-butanol via the Grignard reaction, specifically the reaction between methyl magnesium bromide and acetone, presents certain drawbacks that impede its favorability for industrial applications. These limitations primarily stem from low atom efficiency and high effluent generation.

The Grignard reaction necessitates the use of stoichiometric quantities of magnesium metal and halogenated organic compounds, both of which are costly and contribute to a substantial degree of wastefulness. The resulting magnesium salt of the alcohol byproduct lacks intrinsic value and requires appropriate disposal.

measures. The atom efficiency, a crucial metric in evaluating the resource utilization of a synthetic process, is notably low in this context. The atom efficiency is computed as the ratio of the molecular weight of the desired product to the sum of the molecular weights of all reactants. In the synthesis of tert-butanol from methylmagnesium bromide and acetone, the atom efficiency is merely 40%, signifying that a significant 60% of the atoms are squandered.

Moreover, the Grignard reaction engenders a considerable volume of effluent, posing environmental concerns and economic challenges associated with its treatment. The effluent, characterized by the presence of the magnesium salt of the alcohol, excess Grignard reagent, solvent, and impurities, necessitates intricate and resource-intensive disposal procedures. Typically, acidic and corrosive, the effluent may contain trace amounts of heavy metals, halides, and organic compounds, further complicating its management. Disposing of the effluent mandates procedures such as neutralization, filtration, extraction, and incineration, all of which entail substantial energy consumption and resource utilization.

In light of these considerations, the Grignard reaction's limited atom efficiency and substantial effluent generation underscore the need for more sustainable and economically viable alternatives in the industrial synthesis of tert-butanol. Efforts to optimize synthetic methodologies and develop greener alternatives are imperative for ensuring the ecological and economic sustainability of chemical manufacturing processes.

### 3.2 PROS and CONS OF THE METHODS CONSIDERED

Isobutane Oxidation	Isobutene Hydration		
	Reactive Distillation	Direct Hydration	Reactive Absorption
Inefficient (overoxidation then reduction)	Need to break azeotrope	Need to break azeotrope	Lot of steps needed
Low atom efficiency	Very efficient compared to others due to constant product removal	Equilibrium driven, hence needs multiple reactors	No azeotrope formed
Safety concerns are high due to inflammable material	High Atom efficiency		
Propylene oxide is produced	Ion exchange catalyst is easy to recover and doesn't cause corrosion		All reagents can be recovered and recycled

*After considering many factors (and lack of kinetic data etc.) we decided to choose Direct Hydration as our primary route since kinetic data for Reactive Absorption was missing.*

## 3.3 DWSIM SIMULATION

### 3.3.1 MODEL SELECTION

The distillation system consists of 3 main components: Tert-butanol, water and Triethylene Glycol. All of these have -OH groups and hence are polar. Thus, we need to use an activity coefficient model. Generally, these 3 models are used:

- UNIQUAC
- NRTL
- Wilson

While NRTL and UNIQUAC are more robust and reliable, Wilson can be used for homogeneous systems and is a simpler model. All these models use a set of binary interaction parameters, which are either built into the system or available as datasets in DECHEMA. Unfortunately, in this case, the parameters are neither present beforehand nor are found in the databases. The only pair for which the parameters are available is the TBA-Water pair. Consequently, the Wilson model is a safe choice until the process reaches the stage of extractive distillation. At this point, the model of choice becomes UNIFAC, a more generalised model that generates parameters based on molecular structure. Although this approach may introduce some errors, it currently provides the best estimate available.

The simulation was done using a mixture of models. The reactor and the first distillation are modelled using Wilson. The extractive distillation was simulated using UNIQUAC, and the results matched the UNIFAC results (The only explanation is that the other parameters were estimated internally). The Flash was done using UNIFAC.

The reason for doing Distillation using a UNIQUAC instead of UNIFAC is due to the slightly higher computational cost of UNIFAC and DWSIM not being able to handle UNIFAC for distillation.

### 3.3.2 REACTOR SUBSYSTEM

Three options were tested for designing the trickle bed reactor system.

#### A] Reaction Kinetics <sup>24</sup>

The intrinsic isobutene hydration kinetic rate constant using pure water can be expressed as

$$k = 2.34 \times 10^8 \times e^{8323/T}$$

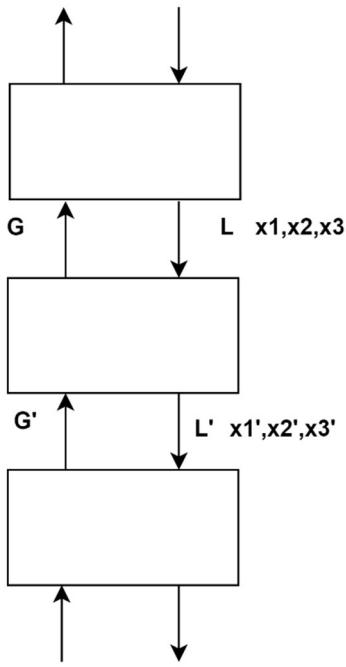
$T$ (K)	$\eta_m$	$\eta_0$	$r$ (kmol m $^{-3}$ s $^{-1}$ ) $\times 10^7$	$C_{iB}$ (kmol m $^{-3}$ ) $\times 10^3$	$k$ (s $^{-1}$ ) $\times 10^3$
325	0.882	0.100	3.85	2.69	1.43
333	0.844	0.0963	5.12	1.93	2.62
343	0.788	0.0900	6.02	1.12	5.38

Table 3.1: The intrinsic kinetic reaction constants in the CFFBR using the model of the micropore and the macropore structure

The reaction rates are proportional to the isobutene partial pressures:  $r = k \times P_{iB}$

$$k_{\text{overall}} = \eta m_c k / H = 3.78 \times 10^{-12}$$

## B] PFR simulation using CSTR cascade



In the investigation of reactor design, a CSTR cascade resembling a counter-current flow fixed bed reactor is under consideration. We have used 8-10 CSTRs. Prior to conducting simulations using DWSIM, it is imperative to establish key quantities such as flow rates for the streams. To facilitate this calculation, a series of assumptions will be made, and subsequent adjustments will be implemented gradually.

$$x_1 = \text{IB} \quad x_2 = \text{Water} \quad x_3 = \text{TBA}$$

### Assumptions:

1. No isobutane
2. K is known
3. Conversion is constant across all reactors
4. The liquid stream leaving( $L'$ ) and the gas stream leaving( $G'$ ) are in equilibrium. So we can use henry's law.

These are the following equations that we get:

$$Lx_1 + G' - (L'x_1' + G) - R = 0$$

$$Lx_2 - R - L'x_2' = 0$$

$$Lx_3 + R - L'x_3' = 0$$

$$x_3' = kP \text{ (Henry's Law)} \Rightarrow P \text{ is the total pressure}$$

$$R = (Lx_3)X \quad (X = \text{conversion})$$

The challenge lies in solving these nonlinear equations. Unfortunately, we were not able to solve these equations.

## C] PFR with co-current flow of streams

The main idea behind using a trickle bed reactor was to provide a counter current flow for the gaseous stream (Isobutene-Isobutane inlet) and liquid stream (Water-TBA inlet). Since a trickle bed reactor is not available as a preset in DWSIM, we opted for a PFR which resembles the trickle bed reactor the most (considering catalyst loading too).

- Initially, the reactor type was 'Define Outlet Temperature' and sensitivity analysis was also performed on it.

- However, we changed the reactor type to ‘Adiabatic’ mode. This had 2 major benefits: higher conversion and decreased operating expenditure in terms of energy savings.

For detailed & final values and an in-depth study of the simulation, please refer to the section 3.4 SENSITIVITY ANALYSIS.

### 3.3.3 SEPARATION SUBSYSTEM

#### Modelling for EXTRACTIVE DISTILLATION

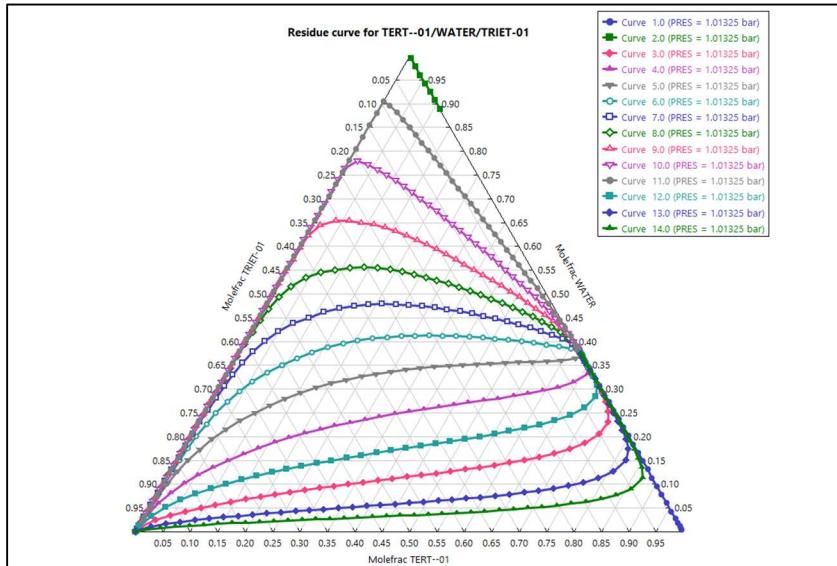


Figure 7: RCM for TBA-Water-TEG

Table: RCM - [https://docs.google.com/spreadsheets/d/10XNIAruKx2VF2-hRaBQwsHr32GkI6TowEv-u9JZB\\_xI/edit?usp=sharing](https://docs.google.com/spreadsheets/d/10XNIAruKx2VF2-hRaBQwsHr32GkI6TowEv-u9JZB_xI/edit?usp=sharing)

There are no clear Pinch points. Hence, it lies in our hands to select the end composition we want for water and TBA. Moreover, we have the freedom to choose the starting point of the middle section.

Let's work with the following assumptions:

We get 99% pure TBA at the top, with 1% impurity of TEG. (We can add an additional distillation column/flash vessel to reach that purity later. We can even reach higher if needed)

Assume that RS is a binary between TBA and TEG.

For SS, we will consider three different curves and three different Middle section beginnings. This way, we will get the trend so that we can optimise later.

Basic Theory:

<https://www.mathcha.io/editor/OMPxrSpXSQqTkxEM3XFr1E0vEHPQ1VL1sO17E8D>

Actual Equations: Calculations -

<https://www.mathcha.io/editor/NEOVESIOfE6f6BswBNZeFVK3nzLsB7Jvd2iV09pPK>

## 3.4 SENSITIVITY ANALYSIS

### 3.4.1 REACTOR SUBSYSTEM

CASE I: When reactor type is ‘**Define Outlet Temperature**’

Parameter 1: Temperature of reactor inlet stream

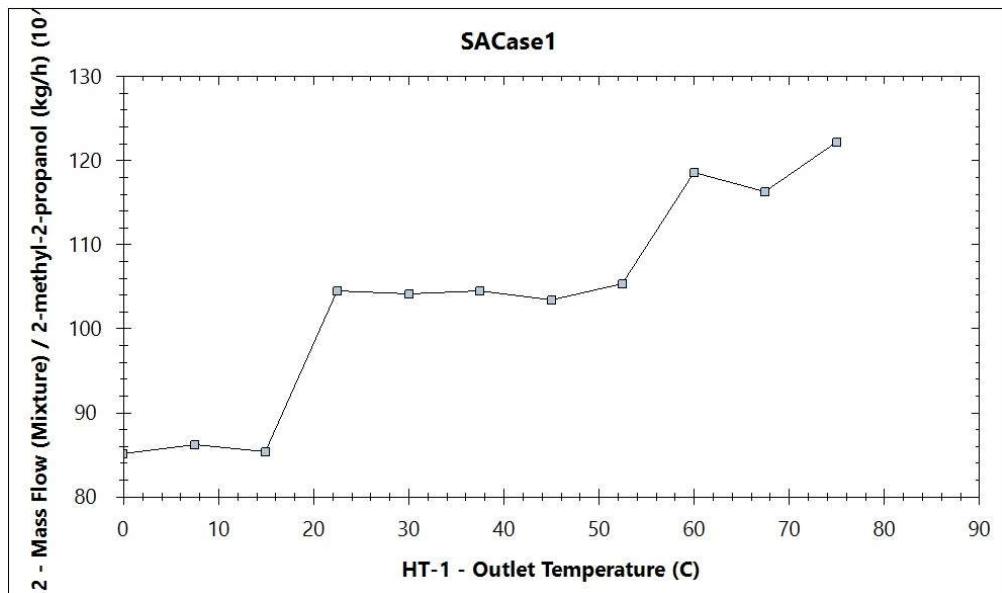


Figure 8: Mass flowrate of TBA in outlet stream vs temperature of inlet stream

As temperature increases, mass flowrate of TBA in reactor outlet increases (basically conversion increases), but we cannot keep temperatures high, i.e., close to 78 °C as it is the boiling point of TBA-water azeotrope.

We cannot even keep it low as we need to heat the stream to provide enough energy to overcome the threshold energy barrier to ignite the reaction.

By reviewing the patents, we fix the temperature around 50 °C.

Parameter 2: Pressure of the reactor inlet stream

Had to do manually as we were facing problem while performing on DWSIM.  
Optimized pressure: 0.62 bar

However, with the current reactor type we observed bit counterintuitive results upon increasing pressure

1. Conversion was decreasing, which should not be the case, as the rate law is directly proportional to partial pressure of isobutene.
2. Higher pressure would lead to higher solubility of isobutene in TBA-water mixture, but that was not observed.

Parameter 3: Volume of the reactor

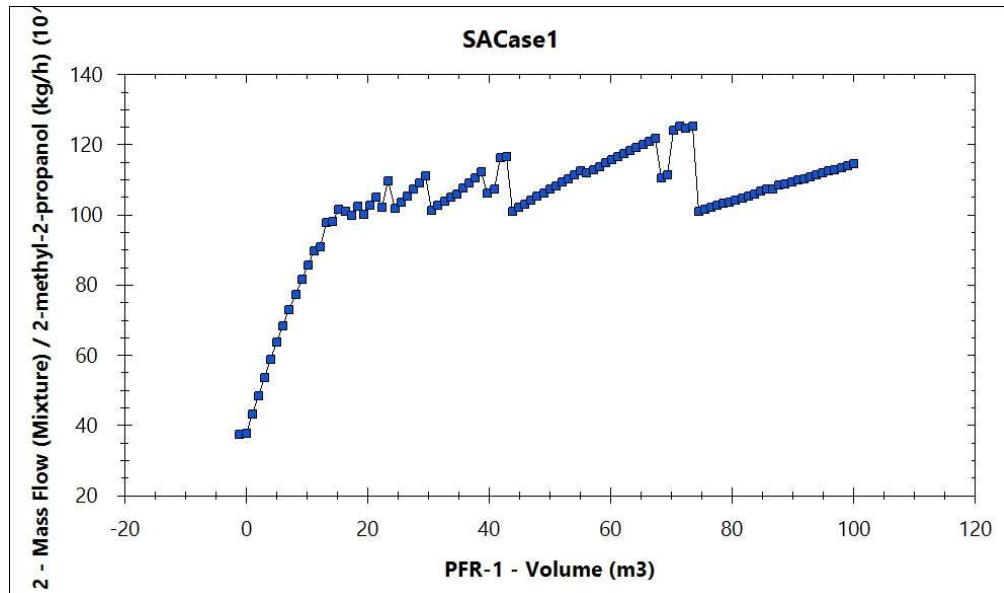


Figure 9: Mass flowrate of TBA in outlet stream vs volume of the reactor

Conversion peaked around  $73 \text{ m}^3$ , but we choose  $67 \text{ m}^3$  as at the former value other parameters were causing conversion to decrease.

CASE II: When reactor type is ‘Adiabatic’

Parameter 1: Pressure of the reactor inlet stream

In this case higher pressure (as close to 1 bar) gave good conversion which is not contradictory unlike previous case.

Further increase in pressure, i.e., from 1 bar – 1.5 bar; the increase in mass flowrate of TBA in outlet stream was negligible (only 0.4 TPH), hence it is meaningless to increase the pressure as it only increases our operating expenditure and not our product yield.

Parameter 2: Volume of the reactor

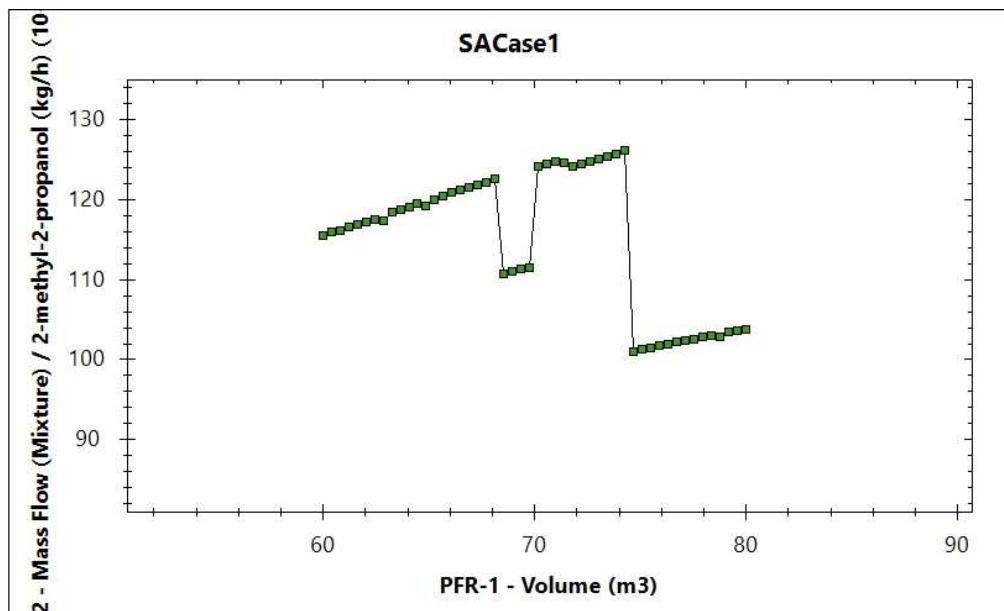


Figure 10: Mass flowrate of TBA in outlet stream vs volume of the reactor

When the reactor type was ‘Define Outlet Temperature’, the volume chosen was 67 m<sup>3</sup> but when the reactor was operated in ‘Adiabatic’ mode, the conversion peaked around 74 m<sup>3</sup>, hence we are choosing volume of the reactor to be 74 m<sup>3</sup>.

Final values of reactor:

1. Length = 10 m
2. Volume = 74 m<sup>3</sup>
3. Number of tubes = 10
4. Catalyst loading = 419.713 kg/m<sup>3</sup>
5. Catalyst Particle Diameter = 0.68 mm
6. Catalyst void fraction = 0.65

### 3.4.2 EXTRACTIVE DISTILLATION SUBSYSTEM

The prescriptions are given below:

$$S = 1.51, S/F = 4, R = 12.63, N = 40, N_f = 20, N_s = 25, D = 160000 \text{ Kg/hr}$$

After substitution and slight modification, this is what Aspen gives us:

$$R = 12, D = 16E4 \text{ Kg/Hr}, N = 45, N_f = 30, N_s = 10,$$

Purity = 99.5% by mole, Reboiler duty = 1.12E12 KJ/Hr

(This is different from conceptual design because Aspen takes care of non-idealities, too)

After this, we start optimisation:

N: 35-45

Nf: 20-30

R: 2-12

Check the effect on Duty and Purity

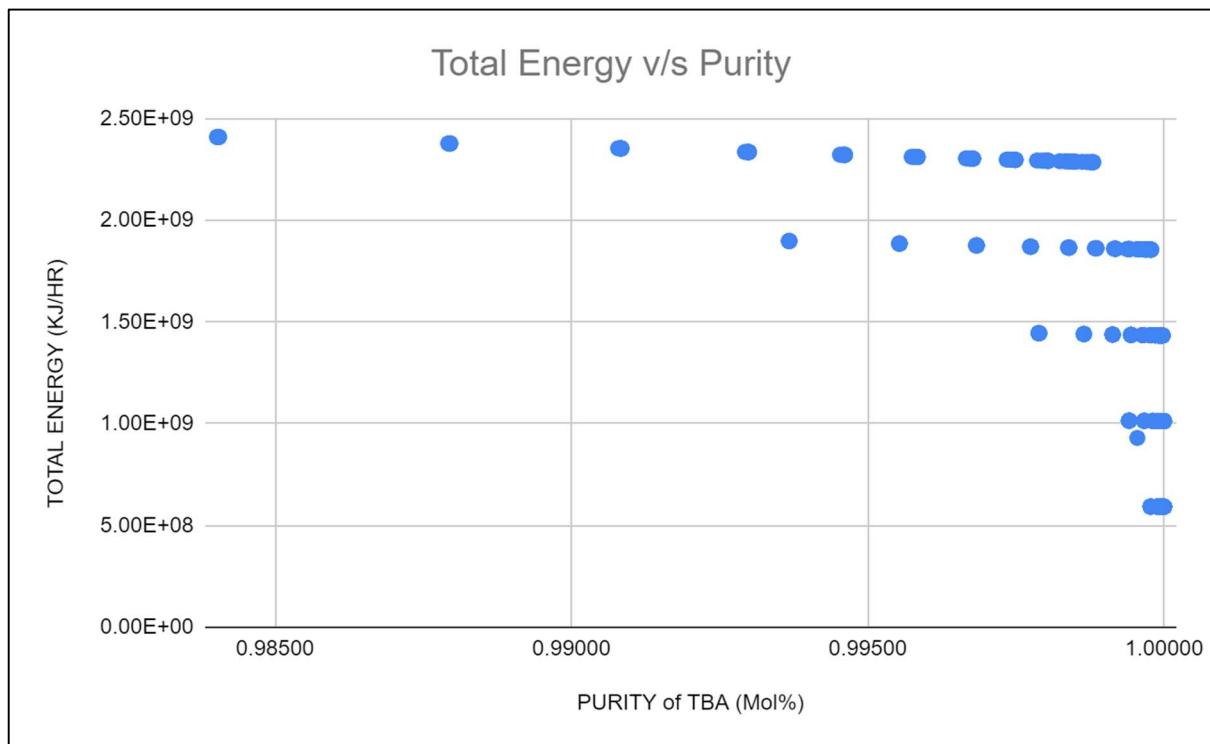


Figure 11: Total Energy vs Purity of TBA

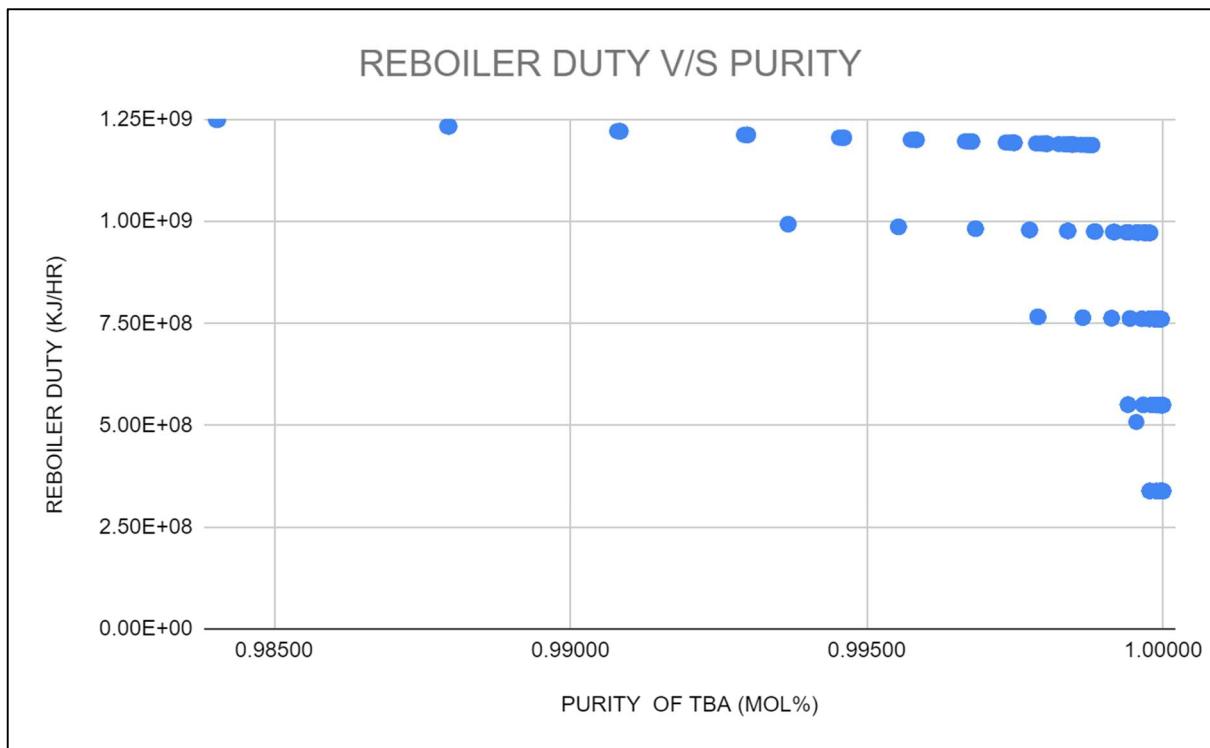


Figure 12: Reboiler duty vs Purity of TBA

#### Observations:

1. High purity and lowest energy consumption happen simultaneously.
2. High purity and lowest reboiler duty also happen simultaneously.

Thus, if we minimise Energy consumption while maximising purity, we will be able to reach an optimum. Thus, we use the sorting feature of excel to achieve these 3 targets (in the same order):

1. Highest purity
2. Least Energy consumption
3. Min number of stages

This gives us the optima to be:

$$N = 35$$

$$N_f = 30$$

$$N_s = 10$$

$$R = 2$$

$$\text{Impurity} = 1 \text{ ppm}$$

$$\text{Reboiler Duty} = 3.4E8 \text{ KJ/hr}$$

$$\text{Condenser Duty} = -2.5E8 \text{ KJ/hr}$$

Now, to decrease the energy consumption even further, let's play with the Pressure:

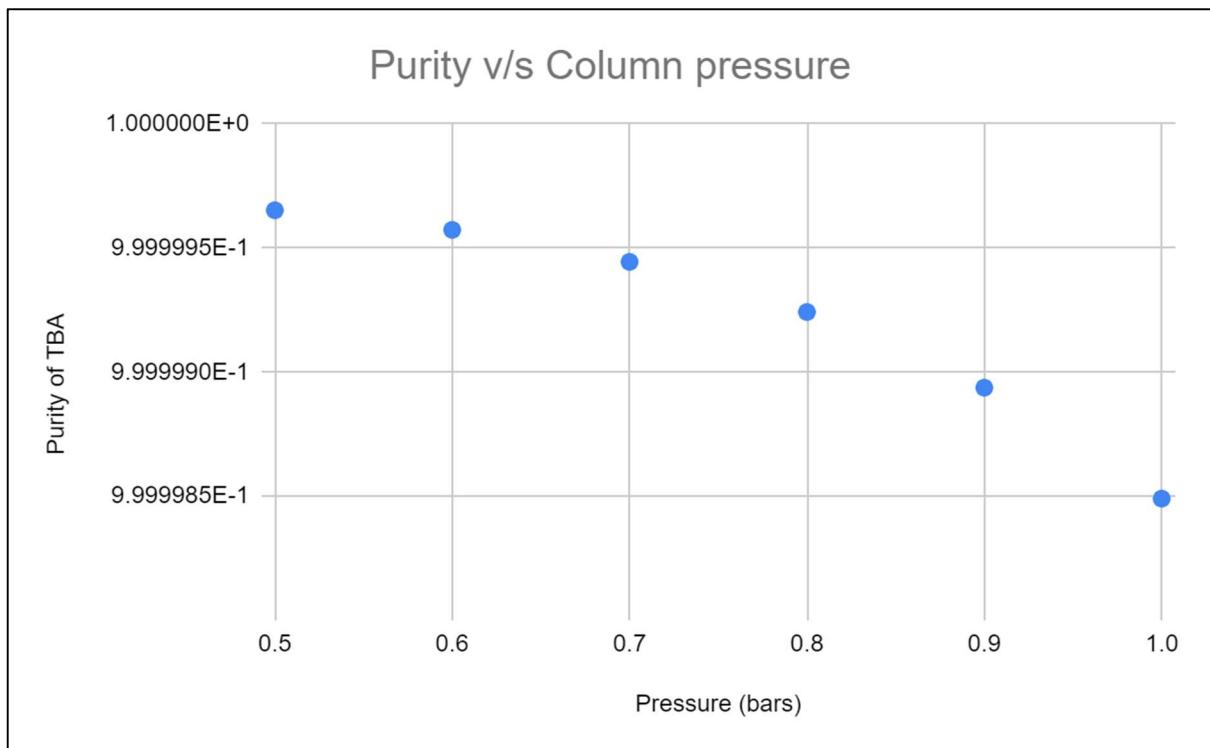


Figure 13: Purity of TBA vs Pressure

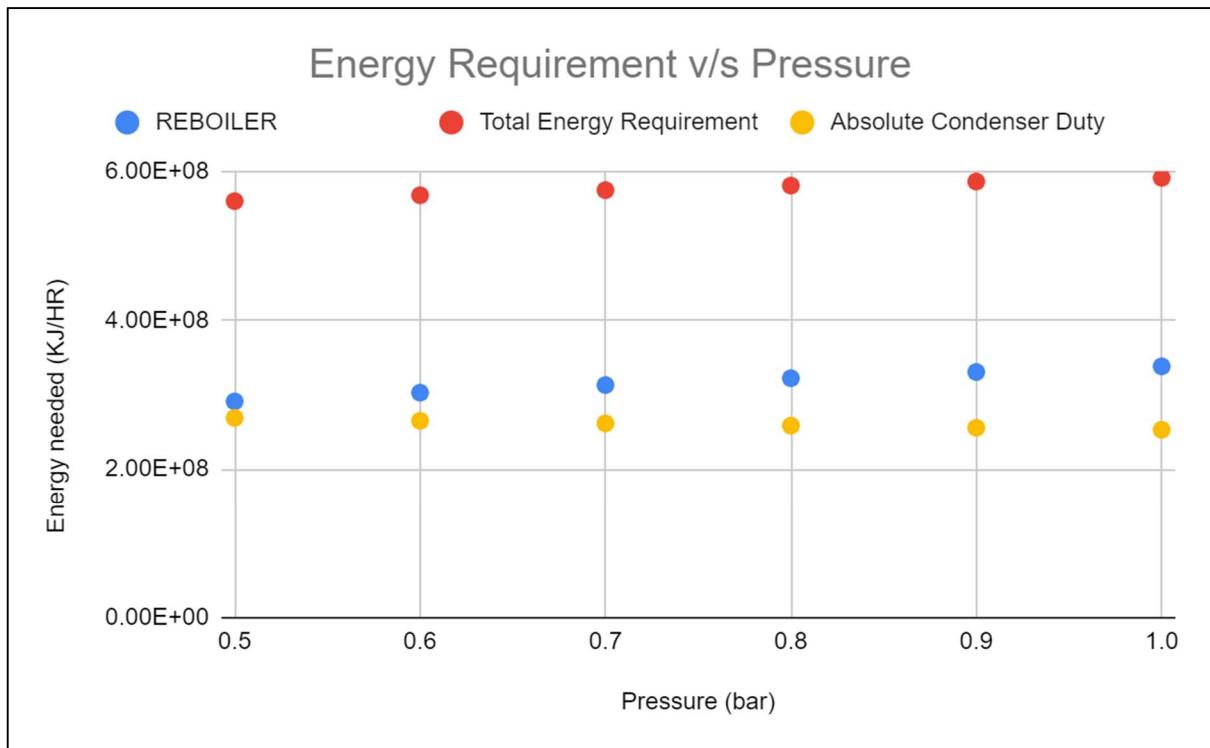
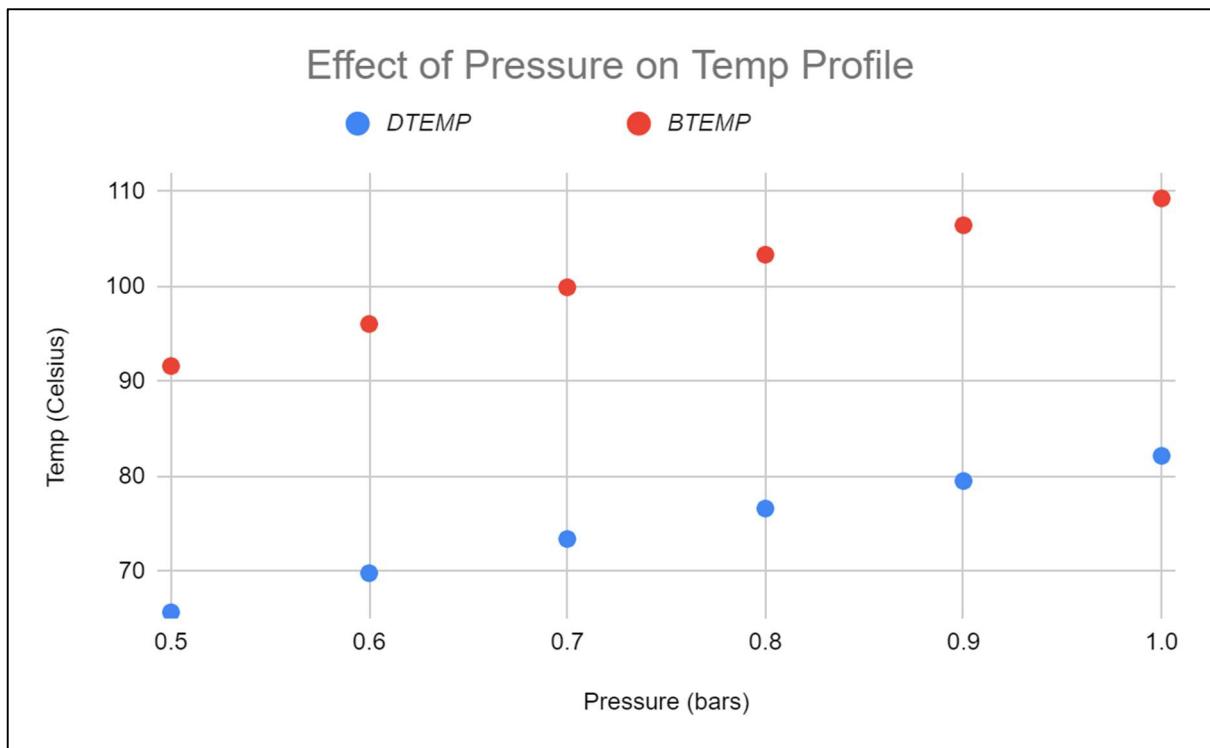


Figure 14: Energy needed vs Pressure



**Figure 15: Temperature vs Pressure**

#### Observations:

1. With increasing Vacuum, the purity increases
2. With increasing vacuum, the reboiler duty decreases, and condenser duty increases, but the net duty decreases
3. With increasing Vacuum, the Temperatures come down, but the condenser will still have a delta T of 35 degrees

With the given delta T, we can handle a huge amount of cooling needs. Thus, it is ok to go to 0.5 bar to reduce the reboiler duty.

Next, we use a flash separation to purify the solvent before reuse. This choice is made due to the huge boiling point difference between the effluent stream components (namely water and TEG). We optimise this to in the following range: T: 115 - 130 degrees, P: 0.1 - 0.5 bar check purity.

As expected, we get the highest purity for 130 degrees at 0.1 bar.

For all the sensitivity data, kindly refer: Sensitivity Study Aspen:

[https://docs.google.com/spreadsheets/d/1NoDnimxXo71OvTXrl\\_JltZkq7bn1u7IPJB\\_R3gxmBWIo/edit#gid=0](https://docs.google.com/spreadsheets/d/1NoDnimxXo71OvTXrl_JltZkq7bn1u7IPJB_R3gxmBWIo/edit#gid=0)

### 3.5 PROCESS FLOW DIAGRAMS

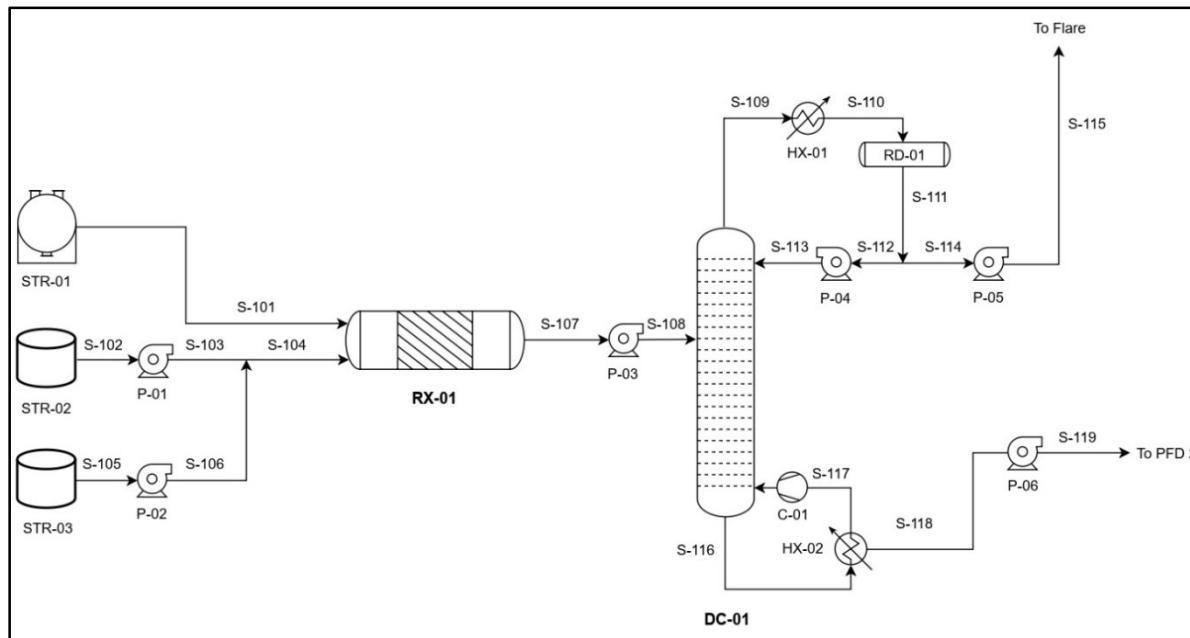


Figure 16: Final simulated PFD Part 1 for Reactor and Gaseous Stream Separation

Table 3.4: Stream Data for Figure 16 PFD

	S101	S103	S104	S106	S107	S109	S110	S113	S114	S116	S117	S118
Temperature(Celcius)	25	45	45	45	80	8.94	8.94	8.94	8.94	80	80	80
Pressure(bar)	1	1	1	1	1	1	1	1	1	1	1	1
Phase	V	L	L	L	V+L	V	L	L	L	L	V	L
Isobutene(TPH)	98.19	0	0	0	1.34	12.73	12.73	11.39	1.34	0	0	0
Isobutane(TPH)	0.99	0	0	0	0.99	9.405	9.405	8.415	0.99	0	0	0
Water(TPH)	0	87.33	0	0	56.23	0	0	0	0	84.91	28.68	56.23
TBA(TPH)	0	0	37.43	37.43	165.38	0.285	0.285	0.255	0.03	249.68	84.33	165.35
Total(TPH)	99.18	87.33	124.76	37.43	223.94	22.42	22.42	20.06	2.36	334.59	113.01	221.58

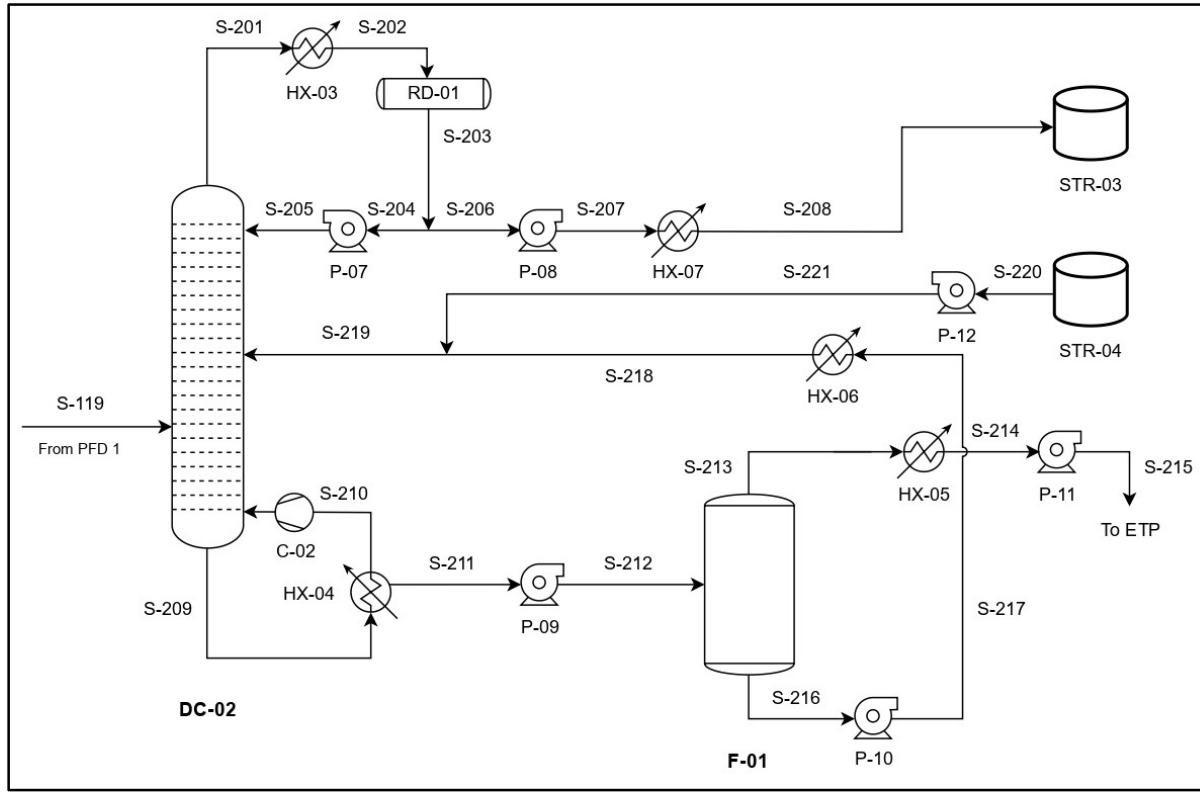


Figure 17: Final simulated PFD Part 1 for Reactor and Gaseous Stream Separation

Table 3.4: Stream Table for Figure 17 PFD

	S201	S202	S205	S206	S208	S209	S210	S211	S213	S215	S216	S218	S219	S221
Temperature(Celcius)	65	65	65	65	45	108	108	108	120	45	120	70	70	35
Pressure(bar)	0.5	0.5	0.5	0.5	1	0.5	0.5	0.5	0.1	1	0.1	1	1	1
Phase	V	L	L	L	L	V	L	V	L	L	L	L	L	L
Isobutene(TPH)	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Isobutane(TPH)	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Water(TPH)	0.18	0.18	0.12	0.06	0.06	197.12	140.96	56.16	56.34	56.34	17.03	17.03	17.03	0
TBA(TPH)	479.19	479.19	319.46	159.73	159.73	19.73	14.11	5.62	5.45	5.45	0.17	0.17	0.17	0
TEG(TPH)	0	0	0	0	0	3088.8	2208.8	880	5.04	5.04	874.96	874.96	880	5.04
Total(TPH)	479.37	479.37	319.58	159.79	159.79	3305.65	2363.87	941.78	66.83	66.83	892.16	892.16	897.2	5.04

### 3.5.1 PFDs SUMMARY

The Process depicted here is to generate Tert Butanol by reacting Isobutene with Water. The Process Flow diagram is divided into two parts. The first part consists of the Reactor and the first Distillation column.

The process is as follows:

1. Isobutene with impurity of Isobutane (S-101) is taken from the spherical tank (STR-01), where it is stored as a liquified gas. This forms the gas phase reactant for the Trickle bed reactor, modelled as a PFR (RX-01)
2. We take water from a cylindrical storage tank (STR-02) and pump it using P-01
3. Next, we take a small part of the product from the Product Storage tank (STR-03) and mix it with the water stream (S-106 and S-103, respectively). This gives us the Liquid phase reactant (S-104) for the reactor.
4. After reacting, the exit stream (S-107) contains isobutane, isobutene, water and TBA. This stream is sent to the first Distillation column (DC-01), where it gets separated into the non-condensable gases (S-115) and the Liquid components (S-118). Note that this was impossible with a simple flash, as Isobutane and Isobutene have high solubility in TBA.
5. The Distillate(S-115) is flared before releasing into the atmosphere, and the Bottoms stream(S-119) is taken to the next Distillation column (in PFD 2)

PFD 2 contains the second Distillation column (DC-02) and a Flash vessel (F-01).

6. The Stream S-119 has water and TBA in a near azeotropic state. Hence, DC-02 is an extractive distillation column, whereas S-219 is the solvent stream that contains Triethylene Glycol, which can take water with it.
7. The Distillate (S-206) is cooled and stored in STR-03 as this is our final product. Part of this is used to start the process, as TBA also acts as a solvent for Isobutene.
8. STR-04 contains fresh solvent used for make up and process startup.
9. The Bottoms stream (S-211) contains water and TEG, which can be separated by a flash separation (F-01).
10. The vapour from flash contains mainly water, which is liquified and sent to ETP.
11. The liquid from flash contains mainly TEG which is recycled back to the column.

# Ch. 4. EQUIPMENT SIZING AND COSTING

## 4.1 REACTOR

### 4.1.1 REACTOR SIZING

MoC  $\Rightarrow$  SS304

Reactor Volume = 74.28 m<sup>3</sup>

Length = 10 m

Tube Diameter (inner) = 50 mm

No. of tubes = 3900

c = 0 mm

m = 12.5%

E = 0.8 (spot welding)  $\Rightarrow$  worst case

P<sub>operating</sub> = 1 bar  $\Rightarrow$  P<sub>w</sub>

$$P_D = \max \{1.1 P_w, P_w + 2 \text{ atm}\}$$

$$= \max \{1.08562 \text{ atm}, 2.986923 \text{ atm}\}$$

$$= 2.986923 \text{ atm}$$

$$= 3.0265 \text{ bar} \Rightarrow \text{Internal Pressure}$$

T<sub>operating</sub> = 35 °C

T<sub>D</sub> = 55 °C

S<sub>Y</sub> = 205 MPa @ T<sub>D</sub>

S<sub>a</sub> = S<sub>Y</sub>/1.5 = 136.67 MPa

Thickness (Hoope's) obtained from ASME code

$$t = \frac{P_D D_i}{2 (S_a E - 0.6 P_D)}$$

$$t = 0.07014 \text{ mm}$$

$$t = \frac{t_{reg} + c}{1 - \frac{m}{100}} = 1.223 \text{ mm}$$

Recommended thickness = 4.7625 mm

$$D_o = D_i + 2t$$

$$D_o = 59.525 \text{ mm}$$

#### 4.1.2 REACTOR COSTING

Number of tubes = 3900

Inner diameter of tubes = 50 mm

Outer diameter of tubes = 59.525 mm

Length of each tube = 10 m

Volume of each tube =  $(\pi/4) \times (D_o^2 - D_i^2) \times L$

Volume of each tube =  $8.1934 \times 10^{-3} \text{ m}^3$

Total volume of tubes =  $31.954 \text{ m}^3$

Density of material (SS 304) = 7930 kg/m<sup>3</sup>

Mass = Volume × Density

Total weight =  $2.53395 \times 105 \text{ kg}$

Cost of SS304 = INR 195/kg (2024)<sup>25</sup>

**Total cost of material for reactor = 4.9412 INR Crores as of 2024**

Catalyst cost: 9.2\$/kg = 761.944 INR/kg<sup>26</sup>

Catalyst void fraction = 0.65

Catalyst volume = Reactor volume × (1 - Catalyst void fraction)

Catalyst volume:  $0.35 \times 74.28 = 25.998 \text{ m}^3$

Catalyst loading = 419.713 kg/m<sup>3</sup>

Catalyst weight = 10911.698 kg

**Catalyst cost = 0.8314 INR Crores as of 2024**

Total cost of reactor = Catalyst cost + Material cost

**Total cost of reactor = 5.7726 INR Crores = 0.696 million USD**

## 4.2 PUMPS

The plant incorporates a total of nine primary pumps, complemented by an equal number of standby units, bringing the aggregate to eighteen single-stage centrifugal pumps. Each pump operates at a rotational speed of 3500 revolutions per minute. The selection of pump type has been diligently determined by an evaluation of both the flow rate and the head, utilizing pump characteristic curves as delineated by Towler et al. for the design process

Calculation for P-02 is shown below:

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

$$P = \frac{W_p m}{\rho}$$

where,

$W$  = work done by pump (J/kg)

$\Delta P$  = Difference in pressure =  $P_2 - P_1$  (N/m<sup>2</sup>)

$\Delta z$  = Difference in elevation =  $z_2 - z_1$  (m)

$\Delta P_f$  = Pressure drop due friction in pipe fittings (N/m<sup>2</sup>)

$\rho$  = Density of liquid (kg/m<sup>3</sup>)

$g$  = Acceleration due to gravity (m/s<sup>2</sup>)

$m$  = Mass flow rate (kg/s)

$\eta_p$  = Pump efficiency

$P$ =power required

$\Delta P = 10000$

$\Delta z = 0$

$\rho = 998 \text{ kg/m}^3$

$\eta_p = 0.8$  (Pump efficiency is based on the pump capacity and head, Towler et. al.) <sup>27</sup>

$W = 10.02 \text{ J/kg}$

$P = 434.05 \text{ W}$

Total power required = 434.05 W

Similar calculations have been performed for all the pumps. The results are tabulated in Table 4.1

Table 4.1: Pumps' Specifications

Pump no.	Stre -am	Type	$\Delta P$ (Pa)	Head (m)	Mass Flow (kg/s)	Flow Rate (gpm)	W (J/Kg)	Power (W)
P-01	102	Centrifugal	10000	3.3545	24.2	385.273	10.02	303.8
P-02	105	Centrifugal	10000	4.0664	10.39	200.17	114.06	8268
P-03	107	Centrifugal	10000	4.0664	62.2	1197.64	114.07	8869
P-04	112	Centrifugal	10000	3.0434	5.57	152.834	159.40	8276.7
P-05	114	Centrifugal	10000	0.3062	0.65	17.98	159.40	9617
P-06	118	Centrifugal	10000	4.0664	61.55	1185.01	114.07	87761
P-07	204	Centrifugal	50000	21.432	88.7	1801.62	64.02	64.020
P-08	206	Centrifugal	50000	21.432	44.3	900.81	64.02	44.4
P-09	211	Centrifugal	10000	0.3354	15.91	252.79	1.002	19.94
P-10	216	Centrifugal	91192	27.75	61.55	886.89	82.90	6378.3
P-11	214	Centrifugal	50000	21.43	0.27	5.59	64.02	22.04
P-12	220	Centrifugal	10000	0.304	61.55	886.89	206.7	15903.6

The cost estimation for centrifugal pumps within the project scope employs a set of relations sourced from Walas et al.

$$C = F_M F_T C_b$$

$$C_b = 1.55 \exp(8.833 - 0.6019(\ln Q\sqrt{H}) + 0.0519(\ln Q\sqrt{H})^2), \quad Q \text{ in gpm, } H \text{ in ft}$$

$$F_T = \exp(b_1 + b_2(\ln Q\sqrt{H}) + b_3(\ln Q\sqrt{H})^2)$$

For single stage 3500 rpm centrifugal compressor:

$$b_1=0.0632, b_2= 0.2744, b_3 = -0.0253$$

MoC factor is as follows: Carbon steel FM = 1.35

Based on the cost relations, the results obtained for centrifugal pump costs in dollars as of 2002 and 2024 are tabulated below in Table 4.2.

Table 4.2: Cost Summary for Pumps

Equipment	Quantity	Total Cost (2002)	Cost (2024, USD)	Cost (2024, INR)
PUMPS	12	99968.43	199835.91	16564398.49
BACKUP PUMPS	12	99968.43	199835.91	16564398.49

## 4.3 DISTILLATION COLUMN

### 4.3.1 THEORY

We use the Sinnott Procedure to calculate Diameter :

$$\hat{u}_v = \left( -0.17 l_t^2 + 0.27 l_t - 0.047 \right) * \left[ \frac{\rho_L - \rho_V}{\rho_V} \right]^{0.5} \quad (1)$$

Here,  $\hat{u}_v$  is the max allowable vapour velocity ( $m/s$ )  
 $l_t$  is the plate spacing( $m$ ) and  $\rho$  is density ( $kg/m^3$ )

$$D_c = \sqrt{\frac{4\hat{V}_w}{\pi\rho_v\hat{u}_v}} \quad (2)$$

To calculate thickness of the column, we use the standard code :

$$t = \frac{P D_i}{2 [S_a E - 0.6 P]} \quad (3)$$

We will ignore effect of winds here. That will be considered in detailed design

Here,  $D_c$  is column diameter ( $m$ ) and  $\hat{V}_w$  is max vapour rate ( $kg/s$ )

### 4.3.2 DISTILLATION COLUMN # 1

Borrowing the values from the simulation, we have :

$$\begin{aligned} N &= 29 \\ l_t &= 0.5 \\ P &= 1 \text{ bar} \end{aligned}$$

This gives the  $\hat{u}$  value as  
 $0.977 m/s$

Thus, the Diameter becomes  
 $4.02 m$

*recommended thickness becomes : 0.00245 m*

$$L = 29*0.5 = 14.5 \text{ m}$$

### 4.3.3 DISTILLATION COLUMN #2

$$\begin{aligned}N &= 35 \\l_t &= 0.5 \text{ m} \\N_f &= 30 \\N_{solvent} &= 10 \\P &= 0.5 \text{ bar} \\R &= 2\end{aligned}$$

*This is an external pressure vessel and hence the caluclations need to be done accordingly*

*let's start with a thickness estimate of 4.7625 mm*

$$D_C = 3.48 \text{ m}$$

$$\text{Now, } D_o/t = 793.7$$

$$\begin{aligned}L &= 17.5 \text{ m} \\L/D_o &= 4.62\end{aligned}$$

*This gives A = 0.00001*

*Thus, we get B = 140 (From CS chart becuase that's the best we have)*

$$T = 90^\circ\text{C} = 194^\circ\text{F}$$

*This gives us Factor B = 160*

$$P_{all} = \frac{4B}{3(D_o/t)} = \frac{160*4}{3*793.7} = 0.26878 \text{ psi}$$

*But we need, P<sub>ext</sub> = 0.9 bar  $\implies 0.9 * 1.25 * 14.696 = 16.533 \text{ psi}$*

$$B = P * \frac{3}{4} * \frac{D_o}{t} = 16.533 * 0.75 * 793.7 = 9841.68$$

*Now, we can conter calculate to get A = 0.0006*

*Let's assume we take no stiffening rings then :*

*This gives that our thickness is pretty huge. Now, we can have fixed value of  $t$  and  $L$*   
 $t_{\text{recommended}} = 50.8 \text{ mm}$

*After removing milling and corrosion correction, we get  $t_{\min} = 57.06 \text{ mm}$*

*Also, we have a fixed value of  $L = 17.5 \text{ m}$*

*Now, let's see the different intersection values for  $A = 0.0006$*

*If we still get the same  $D$ , we get  $D_o/t = 79$*

*But if we take this, we get  $A = 0.0003$*

*Clearly, this is not enough even with the thickest available sheet.*

*Lets say the column is broken into 2 parallel columns.  $D$  goes down by 1.414*

*Thus,  $D_o/t = 55.86$*

*using this, we get Factor  $A = 0.0006$*

*Thus, we need 2 columns each with thickness of 50.8 mm*

*But observe that we can simply circumvent this problem by simply including stiffening rings*

*If we have  $t = 11.1125 \text{ mm}$*

$D_o = 3.78 \text{ m}$

*This gives  $D_o/t = 340.15$*

*Let's first take  $L = 17.5 \text{ m}$  and find  $A$*

*Factor  $A$  is just 0.000003*

*Clearly, we need stiffening rings*

*We get  $L/D = 0.25$ . This means we would need 18 stiffening rings*

*Let's try one more  $t$  value = 25.4 mm*

$D_o = 3.78 \text{ m}$

#### 4.3.4 DISTILLATION COLUMN PRICING

##### Theory

$$C_b = 1.218 \exp(7.123 + 0.1478 (\ln W) + 0.02488 (\ln W)^2 + 0.0158 (L/D) \ln(T_B / T_D))$$

*W is in pounds and T in K*

$$C_t = 456.6 \exp(0.1739 D) \quad (2)$$

*D in ft*

$$C_{p1} = 249.6 D^{0.6332} L^{0.8016}$$

*D and L in ft*

$\rho$  of SS 304 is 7930 Kg/m<sup>3</sup>

*installation factor = 1.7*

$$C_{purchase} = 1.218 * [f_1 C_b + N f_2 f_3 f_4 C_t + C_{pt}]$$

$$C_{install} = f_1 * C_{purchase}$$

*Now, lets get the value from our design*

	<i>Volume</i>	<i>Weight in Kg</i>	<i>Weight in Lb</i>	<i>D</i>	<i>L</i>	<i>T<sub>B</sub></i>	<i>T<sub>D</sub></i>
<i>Column 1</i>	1.744 m <sup>3</sup>	13829.92	30494.97	13.19	47.57	352.83	281.75
<i>Column 2</i>	10.557 m <sup>3</sup>	83875.61	184945.72	12.40	57.41	363.15	338.15

*Subsittute to get*

	<i>C<sub>b</sub></i>	<i>C<sub>t</sub></i>	<i>C<sub>p1</sub></i>	<i>C<sub>purchase</sub></i>	<i>C<sub>install</sub></i>
<i>Column 1</i>	99869.75	4525.79	28257.51	241207.95	410053.51
<i>Column 2</i>	354111.88	3944.856	31593.93	771705.47	1311899.3

*Thus, the final installed costs are :*

*Column 1: 410053.51 USD (2002)*

*Column 2: 1311899.3 USD (2002)*

## 4.4 FLASH SEPARATOR

### 4.4.1 THICKNESS

*Operating pressure = 0.1 bar*

*Operating temperature = 120 °C = 393 K*

$$D = 7.87 \text{ ft}$$

$$L = 31.9 \text{ ft}$$

*Material of construction = SS 304 (Yield stress =  $205 \times 10^6 \text{ Pa}$ )*

$$\text{Allowable stress} = \frac{\text{Yield stress}}{1.5} = 136 \text{ MPa}$$

*Flash vessel is treated as an external pressure vessel*

*However, pressure difference during operation = 0.9 bar*

$$\therefore P_D = 0.9 \text{ bar} \times 1.25 = 1.125 \text{ bar}$$

*Assume  $t = 0.1875 \text{ inches}$*

$$L/D = 4.05$$

$$D/t = 503$$

*Looking at factor A and factor B chart – factor:*

$$\text{factor } B = 250$$

$$\text{factor } B = \frac{P_{all} \times D}{t}$$

$$P_{all} = 0.5 \text{ psi} = 0.03 \text{ Bar}$$

*Since  $P_{all} < P_D$ , we try for a higher thickness*

*Repeating with commercially available metal plate thicknesses (inches)*

$$0.25 : P_{all} < P_D$$

$$0.3125 : P_{all} < P_D$$

$$0.375 : P_{all} < P_D$$

$$0.4375 : P_{all} < P_D$$

$$0.5 : P_{all} < P_D$$

$$0.5625 : P_{all} < P_D$$

$$0.625 : P_{all} < P_D$$

$$\mathbf{0.75 : P_{all} > P_D}$$

$$\therefore t_{reg} = 0.75 \text{ inch} = 19.05 \text{ mm}$$

$$t_{rec} = \frac{t_{reg} + c}{1 - \frac{m}{100}} = \frac{19.05 + 1}{1 - \frac{12.65}{100}} = 22.91 \text{ mm}$$

*∴ Taking next commercially available plate thickness,  
We get  $t_{rec} = 25.4 \text{ mm} = 1 \text{ inch}$*

#### 4.4.2 COSTING

Calculating the material cost formulae from Walas et. al. have been used

$$\begin{aligned} \text{Vertical Vessels : } C &= F_m C_b + C_a \\ C_a &= 240 \times D^{0.7396} \times H^{0.7068} \quad (D, H \text{ in m}) \\ C_b &= 1.218 \times \exp(9.1 - 0.2889 \times \ln(W) + 0.04576 * \ln(W)^2) \quad (W \text{ in lb}) \\ F_m &= 3.1 \text{ for Stainless Steel} \\ \text{Total purchased cost (\$)} &= C_a + 3.1 \times C_b \end{aligned}$$

$$\begin{aligned} \text{Material of construction} &= SS 304 \\ \text{Mass of material used} &= \text{Volume of material} \times \text{Density} \\ \text{Volume of material} &= \frac{\pi}{4} (D_o^2 - D_i^2) l + \frac{4}{3} \pi \frac{(D_o^3 - D_i^3)}{8} \\ D &= 7.87 \text{ ft} = 2.40 \text{ m} \\ l &= 31.9 \text{ ft} = 9.72 \text{ m} \\ t &= 1 \text{ inch} = 0.833 \text{ ft} \\ \text{Volume of material} &= 26 \text{ ft}^3 = 0.736 \text{ m}^3 \\ \text{Mass of material (W)} &= 0.736 \times 7930 = 5,836 \text{ kg} = 12,866 \text{ lbs} \end{aligned}$$

$$\begin{aligned} C_a &= 2,288\$ = INR 1,89,625 \\ C_b &= 42,646\$ = INR 35,34,419 \\ C &= INR 1,07,92,882 \\ (\$ \text{ to INR conversions are as of } 15^{th} \text{ March 2024}) \end{aligned}$$

## 4.5 HEAT EXCHANGERS

### 4.5.1 HEAT EXCHANGER DESIGN

*There are three major heat exchangers needed :*

1. To cool down the solvent stream before it goes to Distillation column
2. To cool down the distillate of the 2nd Distillation Column
3. To cool the Liquid Effluent

#### Heat Exchanger 1

*Target : To cool down 880 TPH from 120 °C to 70 °C*

*Let's say we use Cooling water that goes from 35 degrees to 45 degrees*

$$\Delta T_{LMTD} = 52.48 \text{ } ^\circ\text{C}$$

*Taking a U value of 500 W / m<sup>2</sup>K*

$$Q = C_p \text{ of solvent} * \dot{m} * \text{Temp change}$$
$$Q = 330 \text{ J/mol. K} * \frac{880*1000*1000}{3600*150} \text{ mol/s} * 50 \text{ K}$$

$$Q = 26.89 \text{ MW}$$

$$Q = UA\Delta T_{LMTD}$$

*This gives us an Area of 1024.73 m<sup>2</sup>*

#### Heat Exchanger 2

*Target : To cool down the product of flow 160 TPH from 65.65 to 45°C*

*Let's say we use Cooling water that goes from 35 degrees to 40 degrees*

$$\Delta T_{LMTD} = 16.37 \text{ } ^\circ\text{C}$$

*Taking a U value of 500 W / m<sup>2</sup>K*

$$Q = C_p \text{ of product} * \dot{m} * \text{Temp change}$$
$$Q = 2949 \text{ J/Kg. K} * \frac{160*1000}{3600} \text{ Kg/s} * 20 \text{ K}$$

$$Q = 3.93 \text{ MW}$$

This gives us an Area of  $320.26 \text{ m}^2$

### Heat Exchanger 3

Target : To cool 66.83 TPH from  $120 \text{ }^\circ\text{C}$  to  $45 \text{ }^\circ\text{C}$

Let's say we use Cooling water that goes from 35 degrees to 40 degrees

$$\Delta T_{LMTD} = 32.26 \text{ }^\circ\text{C}$$

Taking a U value of  $413.99 \text{ W/m}^2\text{K}$

$$Q = C_p \text{ of feed} * \dot{m} * \text{Temp change}$$

$$Q = \frac{(56.34*4186 + 5.51*2949 + 5.9*350)}{66.83} \text{ J/Kg. K} * \frac{66.83*1000}{3600} \text{ Kg/s} * 75 \text{ K}$$

$$Q = 5.29 \text{ MW}$$

This gives us an Area of  $271.28 \text{ m}^2$

Summary :

Heat Exchanger	$T_h \text{ (}^\circ\text{C)}$	$T_c \text{ (}^\circ\text{C)}$	Area ( $\text{m}^2$ )
HX - 1	$120 - 70$	$35 - 45$	1024.73
HX - 2	$65.65 - 45$	$35 - 40$	320.26
HX - 3	$120 - 45$	$35 - 40$	271.28

## 4.5.2 HX COSTING

The cost estimation for heat exchangers within the project scope employs a set of relations sourced from Walas et al.

We have assumed that all our coolers are shell and tube heat exchangers and fixed head.

$$C = 1.218 f_d f_m f_p C_b$$

$$C_b = \exp [8.821 - 0.30863(\ln A) + 0.0681(\ln A)^2]$$

$$f_d = \exp [-1.156 + 0.0906(\ln A)]$$

$$f_p = 0.7771 + 0.04981(\ln A)$$

$$f_m = g_1 + g_2(\ln A)$$

For Stainless Steel 304,  $g_1 = 0.8193$  and  $g_2 = 0.15984$

Table 4.3: Cost Summary for Coolers

Equipment	Area (m <sup>2</sup> )	Total Cost (2002)	Cost (2024, USD)	Cost (2024, INR)
Cooler 1	1024.73	371544.98	742713.9565	61563559.85
Cooler 2	320.26	105322.32	210538.0538	17451499.28
Cooler 3	271.28	89241.96	178393.6071	14787046.1

## 4.6 VALVES

### 4.6.1 SAMPLE CALCULATIONS for VALVE 1 for S-113

S-113 is bottoms product for DC-01 and feed for DC-02. It needs to expand to a pressure of 0.5 bar from 1 bar.

$$Q = 261.625 \text{ m}^3/\text{hr}$$

$$Q_{\max} = 1.1Q = 287.79 \text{ m}^3/\text{hr} = 1266.276 \text{ gpm}$$

$$\Delta P = 0.5 \text{ bar} = 7.252 \text{ psi}$$

'Fail Close'

Valve type  $\Rightarrow$  Gate (good for strictly maintaining pressure drop)

MoC  $\Rightarrow$  Stainless Steel

$$T = 80.2 \text{ }^{\circ}\text{C}$$

$$\rho = 848 \text{ kg/m}^3$$

#### Design Calculations

1) Maximum allowable pressure:

$$\begin{aligned} \Delta P_w &= \max \{68947.6 \text{ Pa}, 1.5 P_{\text{operating}}\} \\ &= 75000 \text{ Pa} = 10.877 \text{ psi} \end{aligned}$$

2)  $C_v$  calculation:

$$C_v = Q \sqrt{\frac{S}{\Delta P_w}}$$

$$C_v = 1266.276 \sqrt{\frac{0.848}{10.877}} = 353.567$$

Chosen Valve: 6" Equal Percentage, Gate Valve

(Selected by looking at  $C_v$  Tables for standard industrial valves)<sup>28</sup>

### 4.6.1 VALVE 2 for S - 121

S-113 is bottoms product for DC-02 and feed for F-01. It needs to expand to a pressure of 0.1 bar from 0.5 bar.

The calculations done for this valve are also same as above. It is neatly summarized in the following table.

Table 4.x: Valve Specs

Valve	Stream	$Q_{\max}$ (gpm)	$\Delta P_w$ (psi)	S	$C_v$	Valve Size (inches)	Type
1	S-113	1266.28	10.88	0.848	353.567	6	Equal Percentage, Gate
2	S-112	4032.81	10.00	1.028	1293.017	8	Equal Percentage, Gate

## 4.7 STORAGE VESSELS

In this process we have 4 components which are stored namely: water, isobutene, tertiary butyl alcohol and makeup TEG (solvent). We have considered 30-day storage for all the components.

1. <sup>29</sup> Isobutene storage: The isobutene is transported and stored at 1.65 bar and 70 F (21.1 °C) as a liquefied gas. We have used 12 spherical storage tanks to store isobutene.

The thickness of the vessel is obtained from the following relation:

$$T_{spher} = \frac{PD}{4(S_aE + 0.4P)}$$

Here,

P = Design pressure = 3.628 atm = 0.367 MPa

S<sub>a</sub> = Allowable stress = 120 MPa (S<sub>a</sub> = 180/1.5 = 120 MPa)

E = Weld joint efficiency = 0.85

Total weight of Isobutene that need to be stored = 71412336 kg

Density of liquid Isobutene = 587.9 kg/m<sup>3</sup>

Total Volume of Isobutene = 1201470.2 m<sup>3</sup>

Volume of each tank = 10122.02 m<sup>3</sup>

Diameter of each tank = 28.52 m

Thickness (t<sub>regulation</sub>) = 25.61 mm

We have considered corrosion thickness of 2 mm and a milling tolerance of 12.5%

t<sub>rec</sub> = 31.75 mm

2. Water storage: The water is taken from Rangmati river near Jamnagar and stored at 1 bar and 35 °C. We have used 6 cylindrical storage tanks to store water.
3. TBA storage: The TBA produced is stored at 1 bar and 35 °C. We have used 20 cylindrical storage tanks to store TBA.
4. TEG storage: The solvent required for makeup and startup has been stored in a single cylindrical storage tank at 1 bar and 35 °C.

$$T_{cylinder} = \frac{PD}{2(S_aE + 0.4P)}$$

The cost of Field Erected Storage Tanks is as follows:

$$C = 1.218F_M \exp [11.662 - 0.6104 \ln(V) + 0.04536(\ln V)^2]$$

Where, V - Volume in Gallons

Here, we have used  $F_M = 1$  for carbon steel

Corrosion allowance of 2 mm has been considered for carbon steel with 12.5% milling tolerance.

<sup>30</sup> These relations give cost in \$ and are valid for a base year of 2002. These have to be scaled up 2024 using the following index:

$$\text{CEPCI}_{2002} = 395.6$$

$$\text{CEPCI}_{2024} = 790.8$$

$$F_c = 1.99898$$

$$C = F_c \times C_{2002}$$

Using the above correlations, the following costs of storage tanks have been tabulated below.

Table 4.x: Storage Tanks' Specifications

Tank	Type	Dimensions of each tank			Operating conditions		Number of tanks	Total Capacity (m <sup>3</sup> )	Process fluid	MoC	Cost (\$ in 2024)
		L (m)	D (m)	t (mm)	T (°C)	P (bar)					
STR -01	Sphere	-	28.52	31.75	21.11	1.65	12	121470.20	Isobutene	CS	5679742.09
STR -02	Cylinder	12	23	50.8	35	1	6	29901.53	Water	CS	1622066.69
STR -03	Cylinder	12	25.22	50.8	35	1	20	119812.22	TBA	CS	5605530.69
STR -04	Cylinder	12	20.31	38.1	35	1	1	3885.52	TEG (Solvent)	CS	359857.727

For detailed calculation of each storage tank and cost, please refer to following spreadsheet:

[https://docs.google.com/spreadsheets/d/1KZaZDmCrgTYSuOQWD3pQl2GhmFIIs3diHfv\\_McH-evNk/edit?usp=sharing](https://docs.google.com/spreadsheets/d/1KZaZDmCrgTYSuOQWD3pQl2GhmFIIs3diHfv_McH-evNk/edit?usp=sharing)

## 4.8 EQUIPMENT LIST

Equipment	Number	Type
Compressor	2	Centrifugal compressor
Heat Exchangers (Coolers & Heaters)	7	1. Shell and Tube Heat Exchangers 2. Kettle type HX
Distillation Column	1	Distillation Unit
Extractive Distillation Column	1	Distillation Unit
Reactor	1	Trickle Bed Reactor
Storage Tanks	3	Cylinder
Storage Tanks	1	Sphere
Pumps	24	Centrifugal Pump
Flash Tank	1	Vertical Flash Tank
Valves	2	Gate

# Ch. 5. PLANT ECONOMICS

## 5.1 INTRODUCTION

Till now whatever we did was the costing of different equipment that are being used in this plant. We haven't looked upon whether our plant is generating enough revenues to overcome the cost incurred in building and installing equipment. In this part, we focus on the plant economics, by estimating the plant investments, production costs and the payback period for the tertiary butyl alcohol.

## 5.2 MAJOR EQUIPMENT COSTING

The tertiary butyl alcohol plant has many major equipment including reactor, distillation columns, heat exchangers, pumps, flash tank and storage tanks. We used costing relations provided by Peter-Timmerhaus and Stanley-Walas<sup>31</sup> to determine the total purchased cost of each of these equipment.

The following data are used for the cost estimation:

- India location factor w.r.t US = 0.7
- Dollar to INR = 82.89
- Cost Index - Chemical Engineering Plant Cost Index  
 $CEPCI_{2002} = 395.6$   
 $CEPCI_{2024} = 790.8$

<sup>30</sup> We have used Dec 2023 data as a proxy for 2024 data due to unavailability.

## 5.3 TOTAL PURCHASED EQUIPMENT COST

Table 5.1

Equipment	Total equipment cost (Million \$ in 2024)
Reactor	0.696
Flash Tank	0.1302
Storage Tanks	13.267
Distillation Columns	1.7219
Coolers	1.131
Pumps	0.356

Valves	0.00011
<b>Total</b>	<b>17.34521</b>

## 5.4 CAPITAL INVESTMENT ESTIMATION

Total purchased equipment costs calculated in the earlier sections are used to calculate the total capital investment in the plant. The plant is considered to be a Vapor-Fluid Processing plant. Working capital is taken to be as 15% of the total capital investment. The total capital investment is determined using the method of percentage of delivered equipment cost. India factor is considered to be 0.7.

The results of this analysis are as follows:

Table 5.2

Direct costs	Percentage	Normalized	Cost (million \$ as in 2024)
Purchase Equipment Cost	100	0.17	17.35
Equipment Delivery Cost	10	0.02	1.73
Purchased Equipment Installation	37	0.06	6.42
Instrumentation and controls	36	0.06	6.24
Piping	68	0.11	11.79
Electrical Systems	11	0.02	1.91
Buildings	18	0.03	3.12
Yard Improvements	10	0.02	1.73
Service Facilities	70	0.12	12.14
Land	5	0.01	0.87
<b>Total direct plant cost</b>	<b>365</b>	<b>0.62</b>	<b>63.31</b>
Indirect cost	Percentage	Normalized	Cost (million \$ as in 2024)
Engineering and Supervision	33	0.06	5.72
Construction Expenses	41	0.07	7.11
Legal Expenses	4	0.01	0.69

Contractor's Fee	22	0.04	3.82
Contingency	44	0.07	7.63
Total indirect plant cost	<b>144</b>	<b>0.24</b>	<b>24.98</b>
Fixed Capital Investment	509	0.86	88.29
Working capital (15 % of TCI)	89	0.15	15.44
TCI (according to USA)	593	1.00	102.86
India factor			0.70
TCI (according to India)			<b>72.00</b>

Since our plant has a flare system, effluent treatment plant and cooling tower requirement, the percentage for service facilities has been considered to be on the higher side of the ranges given in Peters et. Al

**Total Capital Investment = 72.00 million USD**

Using an exchange rate of 1\$ = 82.89 INR,

We estimate the final value of **Total Capital investment = 596.808 Crore INR**

## 5.5 RAW MATERIAL COST

The estimation of the total product cost comes from raw material cost. We require isobutene as a raw material, which is acquired from Reliance Jamnagar Refinery and we also require TEG which is our solvent for makeup in this process which we are buying. Raw material cost calculation is provided below:

Table 5.3

	Amount (tons/year)	Cost (\$/ton)	Cost (Million \$/year)
<b>Isobutene</b>	785535.69	1235	970.13
<b>TEG</b>	47100.24	1214	57.18
<b>Total cost</b>			<b>1027.31</b>

Hence, our total raw material cost = **1027.31 million USD/year**

= **8515.42 Crores INR/year**

## 5.6 REVENUE GENERATION

The plant revenue is calculated from the price of tertiary butyl alcohol which is priced at 1.83 USD/kg.

The results are:

Table 5.4

	Amount (tons/year)	Cost (\$/ton)	Price (Million \$/year)
TBA	970777.37	1830	1776.52
<b>Total revenue</b>			<b>1776.52</b>

Hence, our total revenue (at 100% capacity) = **1776.52 million USD/year**

= **14725.574 Crores INR/year**

## 5.7 TOTAL PRODUCT COST

Total Product cost is calculated using normalized percentage method from Peters et. al. Since the plant is setup in India, India factor of 0.7 is applied to Operating Labour, Supervising Labour and Admin costs.

Table 5.5

Category	Factor	Normalized	Cost Mn \$/yr
Raw material	60	0.59	1027.316276
Operating Labour	5.5	0.05	94.17065863
Supervising Labour	2	0.02	34.24387586
Utilities	15	0.15	256.829069
Repairs and Maintenance	1	0.01	17.12193793
Operating supplies	0.5	0.00	8.560968966
Laboratory charges	1	0.01	17.12193793
Patents	1	0.01	17.12193793

Fixed charges	6	0.06	102.7316276
Plant overhead	5	0.05	85.60968966
Admin costs	1	0.01	17.12193793
Distribution and marketing	1	0.01	17.12193793
R&D cost	2	0.02	34.24387586
<b>Total product cost</b>	<b>101</b>	<b>1</b>	<b>1729.315731</b>

Hence, our total product cost = **1729.316 million USD/year**  
**= 14334.298 Crores INR/year**

## 5.8 PAYBACK PERIOD

The following assumptions were made while making the payback period calculations:

- 90% of Fixed Capital Investment (FCI) excluding the land costs is considered to be depreciable over a period of 10 years.
- Average depreciation is calculated using a linear depreciation model.
- Bank interest rate of 6% over the total capital is also used.
- Final Product and Raw Material costs are assumed to be constant for-profit calculations.

Total FCI = 60.697 million USD/ year

Total Depreciable FCI = 54.627 million USD/ year

Total Depreciation per year = 5.462 million USD/ year

Taxation Rate, including surcharge and education cess = 28.3% = 0.283

Total Product Cost = 1729.316 million USD/ year

Revenue = 1776.52 million USD/ year

Bank Interest Rate = 6%

We are taking a loan of entire TCI for 10 years; with yearly instalments of:

$$\text{Using } \frac{R}{iP} = \frac{(1+i)^n}{(1+n)^n - 1}$$

We get  $R = 9.7037$  million USD

**Gross Profit = Revenue - Total Product Cost**

**Gross Profit = 47.21 million USD/ year**

**Net Profit = (Gross Profit – Depreciation – Interest) \* (1 - Taxation Rate)**

**Net Profit = 22.97 million USD/ year**

Using 70% production capacity for year 1, 80% for year 2, 90% for year 3, 100% for year 4 and thereafter, the following cash flow diagram was generated from the plant production. All values in the following table are in million USD.

Table 5.6

Year	Capacity (%)	Investment	Cost	Revenue	Gross profit	Interest	Depreciation	Net Profit	Cash flow	Cumulative position
0		-72.00							-72.00	-72.00
1	70		-1,210.52	1,243.57	33.04	9.70	5.46	12.82	8.58	-63.42
2	80		-1,383.45	1,421.22	37.77	9.70	5.46	16.20	11.96	-51.46
3	90		-1,556.38	1,598.87	42.49	9.70	5.46	19.59	15.35	-36.11
4	100		-1,729.32	1,776.52	47.21	9.70	5.46	22.97	18.73	-17.38
5	100		-1,729.32	1,776.52	47.21	9.70	5.46	22.97	18.73	1.35
6	100		-1,729.32	1,776.52	47.21	9.70	5.46	22.97	18.73	20.08
7	100		-1,729.32	1,776.52	47.21	9.70	5.46	22.97	18.73	38.81
8	100		-1,729.32	1,776.52	47.21	9.70	5.46	22.97	18.73	57.55
9	100		-1,729.32	1,776.52	47.21	9.70	5.46	22.97	18.73	76.28
10	100		-1,729.32	1,776.52	47.21	9.70	5.46	22.97	18.73	95.01

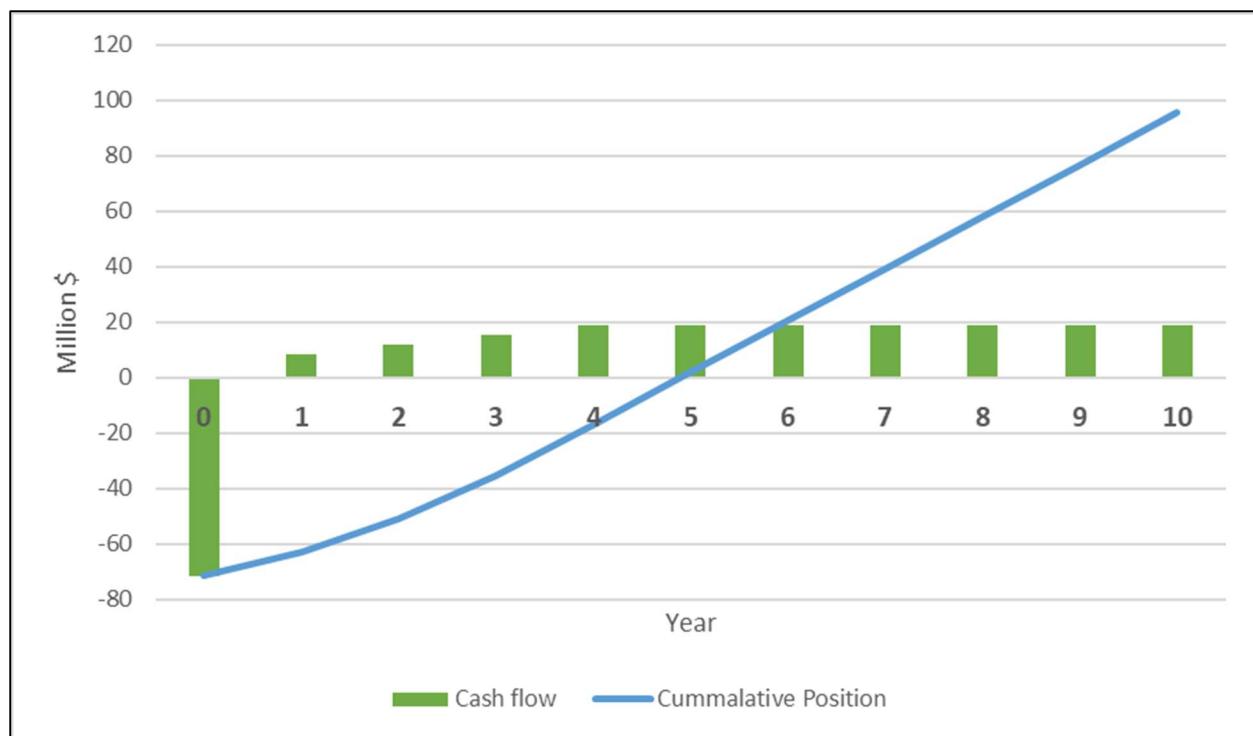


Figure 18: Cash Flow Projections

Detailed calculation: [https://docs.google.com/spreadsheets/d/1j8LKYNB9-n8m8ETJDmh1JOjB8wu7kuGHOwB\\_Pcfk/edit?usp=sharing](https://docs.google.com/spreadsheets/d/1j8LKYNB9-n8m8ETJDmh1JOjB8wu7kuGHOwB_Pcfk/edit?usp=sharing)

**Payback period = 5 years**

## 5.9 EFFECT OF VARIOUS PARAMETERS ON PAYBACK PERIOD

In this section, we estimate the sensitivity of the payback period on the raw material costs and the product selling price. We have considered last 3-year prices of both the parameters and the effect on payback period is studied.

Table 5.7

TBA Price (\$/ton)	2010	1950	1920	1830	1660	1570	1470	1350
Isobutene Price (\$/ton)	Payback Period (years)							
1331	2	8	-	-	-	-	-	-
1235	1	1.1	1.33	5	-	-	-	-
1115	0.41	0.5	0.58	1	6.3	-	-	-

<b>1050</b>	0.33	0.39	0.41	0.5	1.5	6.6	-	-
<b>970</b>	0.31	0.33	0.36	0.42	0.75	1.25	4.75	-
<b>880</b>	0.21	0.24	0.25	0.3	0.5	0.7	1.1	4.4

Here:

1. All the bold prices are actual prices of TBA and Isobutene in the last 3 years
2. All the payback period cells which have no value means the economic potential is negative and no realistic payback period is there

From the above analysis, it can be concluded that the payback period is very sensitive to the raw material cost and the product selling price.

# Ch. 6. DETAILED DESIGN

## Distillation Column 1

### 6.1 SKIRT DESIGN

#### 6.1.1 COLUMN 1

The design velocity for both columns is taken as 123.031 MPH, this data was taken from “Wind zones in India”. Based on this velocity, the wind pressure ( $P_w$ ) exerted on the columns is calculated using the formula:

$$\text{Wind Pressure} = 0.0025V_w^2 = 1449.48 \text{ Pa}$$

where  $V_w$  is the design velocity in MPH, design velocity = 123.031 MPH

Height = 14.5 m

$$\text{Area} = 14.5 \times 4.02 \text{ } m^2 = 58.29 \text{ } m^2$$

The force (F) acting on each column due to wind pressure is calculated using the formula:

$$F = GAP = 1.4 \times 1449.48 \times 58.29 = 118286.84 \text{ N}$$

where the A is area which is the product of the column height and its diameter. The moment (M) due to this force is determined by:

$$M = F \cdot \frac{H}{2} = 857579.621 \text{ N.m}$$

$$S_a = 110316000$$

The regulated thickness ( $t_{reg}$ ) is then calculated from the moment and the allowable stress ( $S_a$ ) as follows:

Regulated thickness,

$$t_{reg} = \frac{M}{\pi R^2 S_a}$$

$$= 0.0006125 \text{ m} = 0.6125 \text{ mm}$$

$$\text{Recommended thickness (t_r)} = 4.7625 \text{ mm}$$

The recommended thickness ( $t_r$ ) is determined using the Commercially available metal plate thicknesses table.

### 6.1.2 COLUMN 2

The design velocity = 123.031 MPH

$$\text{Wind Pressure} = 0.0025V_w^2 = 1449.48 \text{ Pa}$$

Height = 17.5 m

$$\text{Area} = 17.5 \times 4.02 \text{ } m^2 = 70.35 \text{ } m^2$$

$$F = GAP = 1.4 \times 1449.48 \times 70.35 = 142759.99 \text{ N}$$

$$M = F \cdot \frac{H}{2} = 1249149.864 \text{ N.m}$$

$$S_a = 110316000$$

Regulated thickness ( $t_{reg}$ )

$$t_{reg} = \frac{M}{\pi R^2 S_a}$$

$$= 0.000892 \text{ m} = 0.892 \text{ mm}$$

Recommended thickness ( $t_r$ ) = 4.7625 mm

The initial thickness calculation for the column skirt was predicated on the premise of it withstanding internal pressure. However, the actual scenario presents a condition wherein the column is subjected to external pressure, not internal. We are considering this because there is a big difference between the regulated thickness and recommended thickness. Therefore, we proceed with the assumption that the thickness determined under the assumption of internal pressure will also be adequate for resisting an equivalent external pressure. This approach ensures that the skirt's design is robust enough to meet the structural demands imposed by external forces.

## 6.2 NOZZLES

Nozzles are the entry exit of fluids inside the column. These are then connected to the piping system. There would be nozzles around the inlets and outlets of fluids.

For the distillation column, a total of 4 nozzles will be used:

1. Feed inlet of mixture of isobutene, TBA and water mixture
2. Reflux stream from condenser
3. Vapor inlet to condenser at top
4. Bottoms stream from column

### 6.2.1 DIAMETER

To attain the required flow rate and pressure drop, you must choose the right diameter for your nozzle design. In general, the flow rate and pressure drop of a nozzle can be related using the following equation:

$$Q = 28.9 D_i^2 \sqrt{P}$$

Where  $Q$  = Flowrate from the nozzle (gpm)

$D_i$  = Inner diameter (in)

$P$  = Nozzle pressure (psi)

Refer table 6.1 for calculated diameters of all nozzles.

### 6.2.2 THICKNESS

Using '**Area Compensation Method**'

$T_R = 0.00136$  mm (regulation thickness of vessel)

$T = 4.7625$  mm (recommended thickness of vessel)

$S_a = 136.67$  MPa

$E = 1$

$m = 0.125$

$P_D = 1$  bar =  $10^5$  Pa

Regulation thickness formula as per ASME codes based on inner diameter

$$t_R = \frac{P_D D_i}{2 (S_a E - 0.6 P_D)}$$

$t_R$  would be different for every nozzle

$t = 4.7625$  mm (recommended thickness of nozzle; this is same for all nozzles)

$$M_T = mT$$

$$M_t = mt$$

$$H_1 = \min(2T_R, 2t_R)$$

- Area Lost =  $A_L = T_R \times (di + 2c)$
- $A_A^1 = (T - T_R - c - M_t) \times (di + 2c)$
- $A_A^2 = 2H_1 \times (t - t_R - c - m_t)$
- $A_A^3 = 0$ , as we assume the nozzles are non-protruding
- $A_A^4 = 0$  (assumption)
- $A_D = \text{Area Deficit} = A_L - (A_A^1 + A_A^2 + A_A^3 + A_A^4)$

Table 6.1: Nozzle Design Overall Summary

Nozzle	Flowrate (gpm)	Diameter (mm)	$t_R$ (mm)	Area Deficit (mm <sup>2</sup> )
1	230261.93	1161.78	0.4252	-4838.23
2	28386.75	407.92	0.1493	-1698.78
3	3371.64	140.58	0.0515	-585.48
4	1151.94	82.17	0.0300	-342.23

We can see that the area deficit < 0 for all nozzles, therefore none of them requires a reinforcement plate.

Refer Appendix B] to view MATLAB code used for calculations.

## 6.3 GASKET and BOLTS

### 6.3.1 GASKET

The steps for designing a gasket are as follows:

1. Identification of the gasket material and determination of the requisite thickness.
  2. Acquisition of the yield stress ( $y$ ) associated with the chosen gasket material, as well as the pertinent gasket factor ( $m$ ).
  3. Calculation of the ratio of the gasket's outer diameter ( $G_o$ ) to its inner diameter ( $G_i$ ).
  4. Selection of an optimal inner diameter ( $G_i$ ) for the gasket, ensuring there is a sufficient clearance from the inner perimeter of the vessel.
  4. Derivation of the gasket's outer diameter ( $G_o$ ), the mean gasket diameter ( $G$ ), and the gasket width ( $N$ ).

We have selected “Iron Solid Flat metal” as the gasket material

$$m = 3.75$$

y = 52.4 MPa

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

Putting the values of y and m, we get,

$$\frac{G_o}{G_i} = 1.0029 \quad \dots \dots \dots \quad (1)$$

$$G_i = D_i + 50 \text{ mm}$$

$$D_i = 4.02 \text{ m}$$

$$G_i = 4.07 \text{ m}$$

So, using the result in (1), we get

$$G_0 = 4.082 \text{ m}$$

Now, the mean gasket diameter

$$G = \frac{G_o + G_i}{2}$$

$$G = 4.076 m$$

### The Gasket width.

$$N = \frac{G_o - G_i}{2} = 0.006 \text{ m} = 6 \text{ mm}$$

### 6.3.2 BOLTS DESIGN

The gasket area of contact during bolt-up conditions can thus be estimated as ' $\pi Gb$ ' with b suitably related to N depending on flange surface roughness characteristics. Gasket seating force during bolt up conditions which will also be the tensile force acting on the bolts,  $W_2$  will thus be as follows.

$$W_2 = \pi G b y$$

where, b is the effective gasket width ( $N/2$ ,  $3N/8$ ,  $N/4$  etc.)

Here, we will consider both the flange surfaces are corrugated, b is taken as  $N/4$ .

From using the value of G and y calculated in the previous section, we get

$$W_2 = 1.017 \text{ MN.m}$$

After the gasket has deformed to conform to the surface irregularities of the mating flanges, it achieves complete contact across its width, designated as N. Consequently, during normal operational conditions, the actual effective gasket width is equivalent to its physical width. To maintain a seal and prevent leakage, the gasket must sustain a minimum compressive stress of  $mP$ , where m is the gasket factor and P is the internal pressure. The resulting compressive force required on the gasket is therefore expressed by  $\pi G N m P$ , where G is the mean gasket diameter.

Simultaneously, the gasket exerts an equivalent and opposing tensile force on the bolts. Additionally, the bolts are subjected to a tensile force equivalent to the end thrust borne by the vessel closure due to the internal pressure. This end thrust force can be calculated using the formula  $\pi G^2 P / 4$ , which represents the product of the projected area of the closure and the internal fluid pressure.

The operating load on the bolts,  $W_1$ , is thus

$$W_1 = \pi G N m P + \pi G^2 \frac{P}{4} = 4.055 \text{ MN.m}$$

The governing load W on the bolts is taken as the maximum of these two loads (gasket seating force and operating load).

$$W = \max \{W_1, W_2\}$$

$$W = 4.055 \text{ MN.m}$$

Minimum total bolt cross-sectional area (A) can thus be calculated as:

$$A = \frac{W}{(S_a)_{bolt}}$$

The bolt here is ASTM A193 B7. The  $(S_a)_{\text{bolt}}$  is 228 MPa.

$$A = 0.017785 \text{ m}^2$$

The Bolt Circle Diameter (BCD) is the diameter of the circle on which the bolt holes are arranged. With a wrench clearance ( $c$ ) of 0.02 m added to the vessel's outer diameter of 4.02 m, the BCD is calculated to be 4.04 m.

For a bolt size of 25 mm with a root area of 355.5 mm<sup>2</sup>, the minimum number of bolts required is found by dividing the total cross-sectional area by the root area of a single bolt. We get that we need a total of 50.98 bolts. Rounding this number off to multiple of 4 gives us 52 bolts.

## 6.4 TRAY DESIGN<sup>32</sup>

We are using Sieve Trays due to their high  $\eta$

$$\begin{aligned} D_{tray} &= D_{column} - 2 t_c \\ &= 4.02 - 0.004 \text{ m} \\ &= 4.016 \text{ m} \end{aligned}$$

$$A_{tray} = \pi D_t^2 / 4 = 12.66 \text{ m}^2$$

$$V_{flooding} = C_F * \left( \frac{\rho_L - \rho_V}{\rho_V} \right)^{0.5}$$

$$C_F = (a * \log(1 / f_{design}) + B) * (\gamma / 0.02)^{0.02}$$

$$f_{design} = (q / Q) * (\rho_L / \rho_V)^{0.5}$$

Substituting values, we get :

$$V_{flooding} = 0.57 \text{ m/s}$$

$$V_E = 0.8 * V_{flooding} = 0.46 \text{ m/s}$$

$$A_n = Q / V_E = 15.98 \text{ m}^2$$

$$A_d = 0.088 * A_n / 0.912 = 1.54 \text{ m}^2$$

$$Active area = A_a = A_T - 2A_d = 14.44 \text{ m}^2$$

$$\begin{aligned} A_h &= 0.1 * A_a = 1.44 \text{ m}^2 \\ \text{Area of 1 hole} &= 19.63 \text{ mm}^2 \\ \Rightarrow \text{Total number of holes} &= 735 \end{aligned}$$

$$A_d / A_c = 0.11$$

$$\begin{aligned} This gives l_w / D_c &= 0.72 \\ l_{weir} &= 0.72 * 4.016 = 2.89 \text{ m} \\ h_W &= 45 \text{ mm} \end{aligned}$$

$$Hole pitch = 3 * hole Diameter = 15 \text{ mm}$$

*Tray design :*

<i>Type of Tray</i>	<i>Sieve Trays</i>
<i>Diameter</i>	$4.016\ m$
<i>Tray cross section area</i>	$12.66\ m^2$
<i>Down comer area</i>	$1.54\ m^2$
<i>Net area</i>	$15.98\ m^2$
<i>Active area</i>	$14.44\ m^2$
<i>Hole area</i>	$1.44\ m^2$
<i>Hole diameter</i>	$5\ mm$
<i>Active holes</i>	734
<i>Weir height</i>	$45\ mm$
<i>Weir Length</i>	$3.04\ m$
<i>Plate thickness</i>	$3\ mm$
<i>Hole pitch</i>	$15\ mm$

## 6.5 HOLD UP and VAPOUR GAP

$$L_V = \text{Liquid volumetric flow rate} = 261.65 \text{ m}^3/\text{hr}$$

$$D_V = \text{Vessel Diameter} = 4.02 \text{ m}$$

Assuming a liquid holdup time of 10 minutes

$$V_L = \text{Volume of liquid holdup} = L_V \times 10 / 60 = 43.6 \text{ m}^3$$

$$\text{Depth of liquid holdup} = \frac{\text{Volume of holdup}}{\text{Vessel cross sectional area}} = \frac{V_L \times 4}{\pi \times D^2}$$

$$\text{Depth} = 3.44 \text{ m}$$

Vapour gap can be taken approximately to be the same as liquid holdup = 3.44 m

# Ch. 7. Hazardous Waste Management

## 7.1 POLLUTANTS AND THEIR ADVERSE EFFECTS 33, 34, 35

Next, we will assess the environmental impact of our TBA manufacturing plant. To do this, we will look at the effluent streams coming out from our plant - we will identify the components, evaluate the potential environmental hazards of each, and other related handling risks. We will also discuss the treatment methods for these effluent streams.

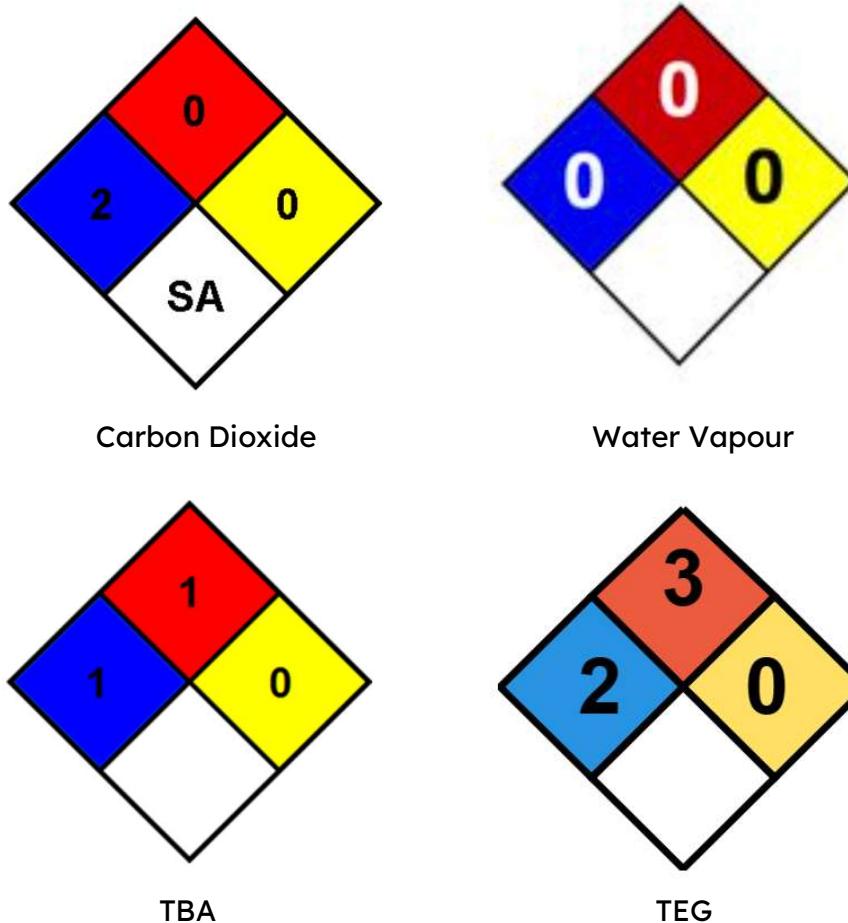
### 7.1.1 WASTE STREAMS

Our process has 2 effluent streams, out of which 1 is gas and 1 is liquid. We'll look at their treatment individually. The constituents of the streams are as follows

Stream number	Components	State
	Isobutane, Isobutene	Gas
	TBA, TEG	Liquid

### 7.1.2 SAFETY

To assess the safety risks, we look at the safety diamonds of all effluents from our plant. The safety diamond is a diagram that summarizes the potential health hazards, fire hazards, and chemical hazards of a compound. We look at the diagram for CO<sub>2</sub>, H<sub>2</sub>O, TBA, and TEG since they are the final compounds leaving.



## 7.2 LIQUID EFFLUENT TREATMENT

### 7.2.1 CHARACTERIZATION OF THE TERT-BUTANOL PRODUCTION PLANT EFFLUENT

Industrial wastewater treatment plays a crucial role in protecting our water resources. This section outlines the treatment process designed for the effluent stream generated by a tert-butanol production plant. The effluent stream from the tert-butanol production process is a complex mixture with a flow rate of 146 kmol/hr. The primary component is water (56.34 TPH), but it also contains concerning organic compounds, including tert-butanol (TBA) (5.51 TPH) and triethylene glycol (TEG) (5.9 TPH).

The presence of these organics is a significant environmental concern. TBA and TEG can contribute to eutrophication, a process where excess nutrients stimulate

excessive plant growth in bodies of water. This rapid plant growth can deplete oxygen levels, harming aquatic life.

Disposing of hot effluent streams into waterways is another environmental concern. Hot water can disrupt natural temperature cycles, impacting fish spawning and other aquatic life processes. Therefore, it's important to cool the effluent stream before treatment.

## 7.2.2 INDUSTRY STANDARDS FOR WASTEWATER DISCHARGE

Discharges of industrial wastewater are subject to regulations to protect water resources. Two key metrics that regulate wastewater quality are chemical oxygen demand (COD) and biological oxygen demand (BOD).

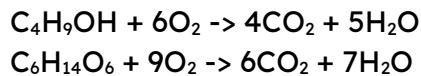
- **Chemical Oxygen Demand (COD):** COD measures the oxygen required to chemically oxidize all organic and inorganic matter in a water sample. A high COD indicates a high concentration of pollutants that can deplete oxygen levels in waterways.
- **Biochemical Oxygen Demand (BOD):** BOD measures the amount of oxygen required by microorganisms to decompose organic matter in water over a specific time period (typically 5 days at 20°C). A high BOD indicates a high concentration of biodegradable organic matter that can deplete oxygen levels as microorganisms decompose it.

BOD is generally considered a more specific indicator of the potential impact of wastewater on aquatic life compared to COD, as it only considers biodegradable organic matter. However, BOD analysis is a laboratory test, whereas COD can be determined more rapidly.

Industrial wastewater regulations utilize COD and BOD to assess water quality. BOD, typically limited to 30 ppm, reflects the impact on aquatic life. Additionally, regulations limit effluent temperature to prevent thermal shock. A common standard restricts discharge temperature to 7°C above the receiving water body's ambient temperature. This safeguards aquatic ecosystems.

## 7.2.3 BOD ESTIMATION

We can't calculate BOD directly as experiments determine it. However, we can calculate COD, which is a good estimate of the BOD value. The following are the reactions to be considered:



Converting mass flow rates to molar flow rates, we get TBA = 73.5 Kmol/hr and TEG = 33.5 kmol/hr.

Oxygen needed = 742.5 kmol/hr = 23.76 TPH

This gives a COD of 518777.3 ppm

Clearly, this indicates that BOD is also a very high value (of the order  $10^6$  PPM), and the stream needs to be treated before discharging.

#### 7.2.4 ACTIVATED SLUDGE PROCESS: A BIOLOGICAL SOLUTION <sup>36</sup>

The high COD in the effluent stream from the tert-butanol production plant necessitates treatment to reduce its organic content before discharge. A biological treatment method, the activated sludge process, is well-suited for this purpose.

The activated sludge process is a widely used and effective biological wastewater treatment technology that utilizes microorganisms to remove organic pollutants from wastewater. Here's a breakdown of the key stages involved:

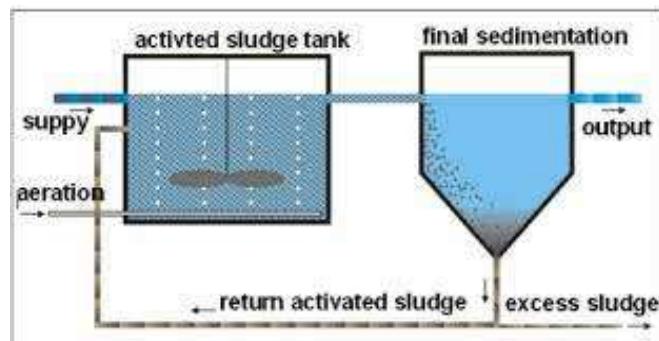


Figure 19: Activated Sludge Process

**1. Equalization:** The raw effluent stream first enters an equalization tank. This tank serves to homogenize the flow rate and composition of the influent stream over time. Fluctuations in flow rate and organic content are common in industrial wastewater. The equalization tank helps to ensure a more consistent stream entering the biological treatment stage, optimizing treatment efficiency.

**2. Biological Treatment in an Aeration Tank:** After equalization, the effluent stream flows into the aeration tank, the heart of the activated sludge process. The aeration tank is a large tank that houses a mixture of wastewater and activated sludge, a suspension of microorganisms (bacteria and protozoa) that have been clumped together into flocs. The aeration tank is continuously aerated to provide a constant supply of dissolved oxygen for the microorganisms.

The microorganisms in the activated sludge consume the organic pollutants (TBA and TEG) in the wastewater stream as food for their growth and reproduction. This biological process is called biodegradation. As the microorganisms feed on the organic pollutants, the COD of the wastewater is significantly reduced.

**3. Solids Separation in a Secondary Clarifier:** Following biological treatment in the aeration tank, the effluent stream containing the treated wastewater and the activated sludge mixture flows into a secondary clarifier. The secondary clarifier is a large settling tank that allows the heavier activated sludge to settle out of the wastewater due to gravity. The settled sludge, with a high concentration of microorganisms, is then recycled back to the aeration tank through a recycle stream. This recycled sludge maintains a high concentration of microorganisms in the aeration tank, ensuring efficient biodegradation of incoming pollutants. The treated wastewater exiting the secondary clarifier, with a significantly reduced organic content, can then be discharged to a publicly owned treatment works (POTW) or reused in the tert-butanol production process, depending on regulatory requirements and water quality standards.

The activated sludge process offers several advantages, including its effectiveness in removing a wide range of organic pollutants, its relatively simple operation, and its ability to handle fluctuating organic loads. However, maintaining optimal conditions in the aeration tank, such as dissolved oxygen concentration and solids concentration, is crucial for efficient treatment.

## 7.2.5 SIZING THE AERATION TANK: CONSIDERATIONS AND CHALLENGES

The activated sludge process relies on maintaining a sufficient population of microorganisms within the aeration tank to effectively biodegrade pollutants. A key factor in achieving this is the aeration tank volume.

One common formula used to estimate the required aeration tank volume (V) is:

$$V = (SRT \times Q \times \text{Influent SS}) / (\text{MLSS})$$

Where:

V = Aeration tank volume ( $\text{m}^3$ )

SRT = Solids Retention Time (h) - This represents the average amount of time solids (microorganisms) spend in the aeration tank system.

Q = Influent wastewater flow rate ( $\text{m}^3/\text{hr}$ ) [Conversion needed!\*]

Influent SS = Influent suspended solids concentration ( $\text{kg}/\text{m}^3$ )

MLSS = Mixed liquor suspended solids concentration ( $\text{kg}/\text{m}^3$ )

Values used in our case:

SRT: 10 hours

Q: 57.21 Tonnes/hr (Calculated below)

Influent SS: 3  $\text{kg}/\text{m}^3$

MLSS: 0.3  $\text{kg}/\text{m}^3$

We know that the density of water is 1 Tonne /  $\text{m}^3$ , and the stream is mostly water. Hence, the flow rate becomes  $57.21 \text{ m}^3/\text{hr}$ .

Substituting the values, we get  $V = 57.21 \text{ m}^3$ .

## 7.2.6 COMPLETE FLOW OF TREATMENT

STEPS:

- Liquify the stream by cooling it to  $40^\circ\text{C}$
- Pump up to bring the pressure back to 1 atm
- Use the activated sludge method to bring down the organic content
- Check temperature and cool to  $37^\circ\text{C}$  before releasing

## 7.3 GASEOUS WASTE MANAGEMENT

### 7.3.1 ADVERSE IMPACTS

Next, we will look at how we will manage the gaseous waste. We have already seen earlier that the gaseous effluents are isobutene and isobutane, and they are used as fuel. We also look at the potentially hazardous effects of these compounds on the environment and health in case of leakage.

Isobutene

Health effects	Result
Acute Toxicity	Low acute inhalation toxicity

Oral / inhalation / dermal	High vapor concentrations may produce narcosis or cause asphyxia by reducing the available concentration of oxygen
Genotoxicity / Mutagenicity Carcinogenicity	Not mutagenic/genotoxic. Low concern for repeated exposure toxicity.
<b>Environmental effects</b>	<b>Result</b>
Aquatic Toxicity	Not expected to be toxic to aquatic life
Biodegradation, Bioaccumulation	Rapidly biodegradable and not expected to accumulate

### Isobutane

<b>Health effects</b>	<b>Result</b>
Acute Toxicity	Inhaling Isobutane can irritate the nose and throat
Oral / inhalation / dermal	Exposure to high concentrations can cause dizziness, lightheadedness, irregular heartbeat and passing out. Very high levels can cause suffocation from lack of Oxygen with loss of consciousness, convulsions, coma and death
Genotoxicity / Mutagenicity Carcinogenicity	Genetic defects and cancer has been observed but no strong conclusive evidence
<b>Environmental effects</b>	<b>Result</b>
Aquatic Toxicity	Toxic for aquatic life
Biodegradation, Bioaccumulation	Low potential for bioconcentration in aquatic organisms

### 7.3.2 GASEOUS STREAM AND ITS TREATMENT

Major effluent gaseous stream is S-115 leaving from top of first distillation column. The components of the gaseous stream are isobutane and isobutene. We have 2 options to process this stream.

1. Separate them and sell them
2. Use as fuel

Our production rate for them is 0.991 TPH isobutane and 0.978 TPH isobutene. This is almost a 50 - 50 mixture of the 2 byproducts and is not a commercial product to be sold. For us to sell them, we will first have to separate them. The separation costs for such a small quantity of products is going to be very high, looking at the relatively smaller revenue from selling them, so it would not make economic sense to do this.

Hence, we use the isobutane and isobutene as fuel in the reactor wherever heating is needed as utilities. The combustion will produce water and carbon dioxide, both of which are safe for the environment and do not need to be processed.

### 7.3.3 REGULATORY STANDARDS

The current regulatory standards for isobutane and isobutene emissions are as follows:

- NIOSH: The recommended airborne exposure limit (REL) for isobutane is 800 ppm averaged over a 10-hour work shift
- ACGIH: The threshold limit value (TLV) for isobutane and isobutene is 1,000 ppm (as Aliphatic hydrocarbon gasses) averaged over an 8-hour work shift

Since our emissions are way higher than the norms, we flare the stream. The calorific value of isobutane is also comparable to methane, implying that it is a very good fuel.

### 7.3.4 FLUE GAS COMPOSITIONS

We used simple mole balance for combustion reactions for components present in S115, to calculate oxygen required to completely oxidize them. Upon calculating oxygen requirement, we accounted for the air needed. Furthermore, we took around 20% excess, to avoid unnecessary coke formation. These are the final compositions of flue gas.

<b>Flue gas composition</b>	<b>Source (kg/hr)</b>	<b>Permissible limit</b>
CO <sub>2</sub> (18.67 %)	7251.2	1.08 kg/m <sup>3</sup>
H <sub>2</sub> O (8.45 %)	3283.2	
N <sub>2</sub> (68.66 %)	26664.42	
O <sub>2</sub> (4.22 %)	1636.48	

### 7.3.5 GAUSSIAN PLUME DISPERSION MODEL

Concentration of the pollutants on the ground is calculated using Gaussian plume dispersion model since the emissions from the plant are steady state continuous emissions. The formula for steady state continuous plume dispersion is:

The formula for *steady state continuous* plume dispersion is:

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

Figure 21: Formula for calculating the concentration through the Gaussian Plume Dispersion Model

Here,

x,y,z = distance from source (x = downward, y = crosswind, z = vertical)

C = concentration (kg/m<sup>3</sup>) at location x,y,z;

G<sub>v</sub> = vapor emission rate (kg/s)

H = height of source above ground level + Plume rise (m);

U = wind velocity (m/s);

$\sigma_y$ ,  $\sigma_z$  = dispersion coefficients (m), the function of downward dispersion

The following considerations have been taken while considering the stack height:

- Pollutant concentration on the ground should be less than emission limits

- The heat effects due to radiation on the ground should be up to a safe level

Hence, a stack height of 100m is considered (Standard value)

Wind speed (m/s) @ Jamnagar ~ 6m/s

$$\sigma_y = 6.91 \text{ m} \mid \sigma_z = 8.94 \text{ m} \mid y = z = 0$$

After calculating,  $C (\text{kg/m}^3) = 12.20 \text{ kg/m}^3$  for  $\text{CO}_2$  and  $1.2 \text{ kg/m}^3$  for  $\text{NO}_2$

### 7.3.6 TREATMENT OF $\text{CO}_2$

Our flue gas has  $12.20 \text{ kg/m}^3$  of  $\text{CO}_2$  and the permissible limit is just  $1.08 \text{ kg/m}^3$ .  $\text{CO}_2$  produced in our plant is more than 10 times the permissible limit. Therefore, treating it before release is necessary.

We will use the **Amine-based Carbon Capture** (scrubbing).

It is a regenerative process that uses amine as a solvent, which removes  $\text{CO}_2$  from the flue gas. Also, reversing this reaction gives us pure  $\text{CO}_2$  for capture. Thus, freeing up the solvent for re-use. This is a well-proven method and a commercially available technology.

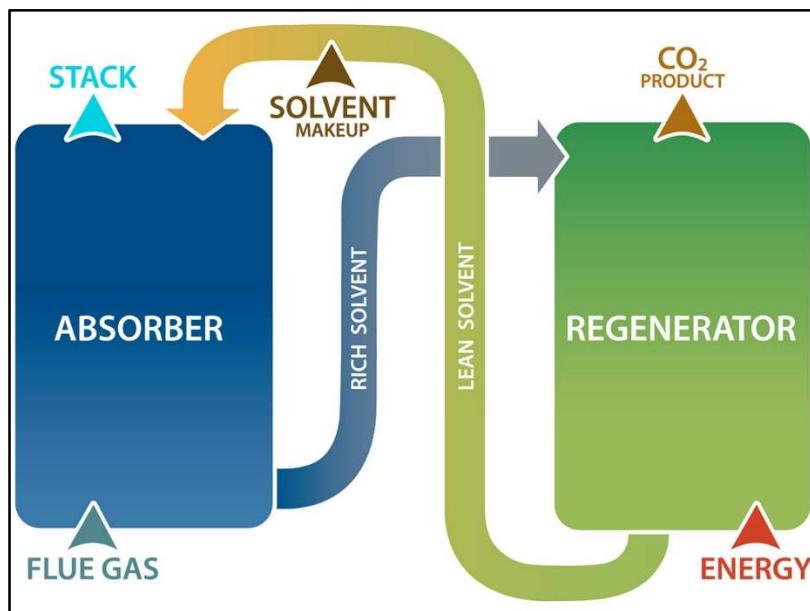


Figure 20: A simple flow diagram of how amine-based carbon recovery system works

# Ch. 8. Other Topics

## 8.1 MATERIAL of CONSTRUCTION

Material of Construction chosen is SS 304 since we are dealing with mildly acidic solutions.

When comparing 304 stainless steel vs 316, they both have pros and cons to consider when deciding which one to use for different applications. We used the following parameters:

1. Corrosion Resistance: 316 stainless steel offers superior resistance to salt and other corrosives compared to 304, making it ideal for products exposed to harsh chemicals or marine environments.
2. Economical Choice for Less Harsh Conditions: For applications where strong corrosion resistance is not critical, 304 stainless steel is a more cost-effective option.
3. Interchangeability: In many cases, 304 and 316 stainless steels can be used interchangeably, depending on the specific environmental conditions and requirements.
4. Chromium Content: Both 304 and 316 stainless steels have high chromium content, providing a protective layer against corrosion and rust.
5. Carbon Steel Vulnerability: Unlike stainless steel, carbon steel, which is high in carbon, is prone to quick corrosion and rust when exposed to moisture.
6. Selection for LLE Method: Given the use of 67% concentrated H<sub>2</sub>SO<sub>4</sub> in the liquid-liquid extraction (LLE) method, SS 316 is chosen for the bubble column, LLE, and reactor due to its corrosion resistance, with costs ranging around 240 - 280 Rs/Kg.
7. Distillation Tower Material: For the distillation tower, where corrosion resistance is less of a concern, either carbon steel or SS 304 can be used, considering cost and application requirements.

Cost of materials:

<sup>37</sup> SS 316: 255 Rs/kg

<sup>25</sup> SS 304: 195 Rs/kg

## 8.2 SAFETY

A hazard is something which has the potential to cause an accident and every manufacturing process comes with their own sets of hazards. Some common hazards in most of the industries are Slips, trips and falls, Electrical Hazard or Environmental Hazard.

Hazards happen because of actions that aren't safe, the characteristics of materials, things that are left out, and situations that are not safe. A hazard is something that can cause harm or danger to health. The best way to avoid accidents and health problems is to get rid of the hazard or make sure it is well controlled.

The HE is divided into two categories:

1. Qualitative HE Technique
2. Quantitative HE Technique

Among the HE techniques, industries commonly utilise What-If Analysis, What-If/Checklist Analysis, and HAZOP. Conducting a hazard evaluation study involves gathering essential information, including the type of chemicals, catalyst properties, data on reacting chemicals, kinetic data like reaction order and rate constants, equilibrium considerations, area electrical classification drawings, equipment electrical classifications, mechanical equipment data sheets, and a diverse range of material property information and most of the info are provided the material safety data sheet

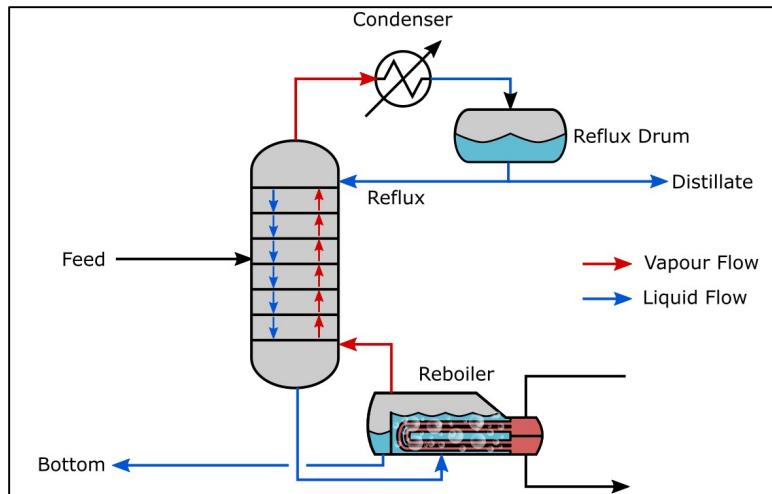
Of the various HE techniques we selected HAZOP since it is more comprehensive than other techniques such as what-if analysis, and suitable for a qualitative study. HAZOP is commonly used in analysing processes during the design stage or after the design stage. Different versions of HAZOP Analysis technique is applied in the chemical industry

The primary objective of HAZOP Analysis is to methodically examine processes or Plant operations to assess whether deviations in the process could result in undesirable consequences. This analytical method is suitable for continuous and batch processes and can be adapted to evaluate documented procedures. The outcomes of a HAZOP Analysis encompass the identification of hazards and operational issues. It involves suggesting modifications to the design, making changes in procedures, etc., to enhance the overall system. Additionally, the analysis recommends conducting further studies in areas where conclusions are challenging due to a lack of knowledge about the design.

The HAZOP procedure uses the following steps to complete an analysis:

- a. Defining individual process units
- b. Selecting nodes
- c. Definition of parameters
- d. Application of guide words
- e. Identify source
- f. Evaluate consequences
- g. Recommendations for safety and hazard mitigation

### HAZOP STUDY OF DISTILLATION COLUMN



<b>Process unit</b>	<b>Nodes:</b>	<b>Parameters</b>	<b>Deviations</b>	<b>Possible causes</b>	<b>Consequences</b>	<b>Recommendations</b>
Distillation column	Reboiler	Flow	No flow Less flow	Pipe blockage, Control valve shut, Valve fail,	Column dry out, Possible dangerous concentration, no operation, Changes in product quality	Installation of alarms Installation of controllers
	Condenser		More flow	Control valve is fully opened in case of more flow	Product loss, Changes in product quality, Ineffective separating process,	Placement of valves Emergency shutdown options Instruct operator on procedure
	Reactive section	Temperature	Low temperature	Instrumentation failure, Less steam flow, Loss of heating		
			High temperature	More steam flow, Exchanger tube failure, High steam pressure, Cooling water in condenser failure.	Separation cannot be done, Film boiling in column and reboiler Phase effect	

		Pressure	Low pressure	Vapour line leakage	Low efficiency of separation, Loss of products	
			High pressure	High Vapour pressure, Pressure indicator controller fail	Low efficiency of separation, Rupture of column or other related equipment	



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## Appendix A]

Data for Figure 4: Cost vs  $\alpha$  for various solvents

Solvent	Relative volatility	Cost (Rs/kg)	Molecular Weight	Vapour pressure (in Pa at 25 °C)	Boiling Point
Polyethylene glycol 200	1.95	90	200		NA
Polyethylene glycol 300	1.34	105	300		NA
1,4-Butanediol	1.38	60	90.12	1.9	235
Dipropylene glycol	1.32	180	134.18	2.1331	232
O Triethylene glycol	2.33	70	150.17	n/a	288
2-Methyl-1,3-propanediol	1.32	250	90.12	5.3328	214
Diethylene glycol	1.26	90	106.12	1.3332	245
Polyethylene glycol 400	1.92	115	400	1.3332	NA
Methylbenzoate	1.21	245	136.15	53	198
Anisole	1.31	174	108.14	468	154
Diisobutyl ketone	1.42	50	142.26	319.9728	216
n-Butyl acetate	1.14	125	116.16	1999.83	126
Hexyl alcohol	1.7	589	102.18	133.322	155
isodecanol	1.63	170	170.29	2.7597	257
alpha-Methyl benzyl alcohol	1.36	1000	122.16	n/a	205
Cyclododecanol	1.47	130	182.31	0.050529	272
Diisobutyl carbinol	1.94	145	130.22	40.3965	194
2-Octanol	1.47	90	130.22	31.9972	180
3-Heptanone	1.7	100	114.19	533.288	157
Dinethyl sulfoxide	1.51	480	78.13	55.9952	189
2-Hydroxyacetophenone	1.32	3000	136.15	26.6644	180

Dimethyl formamide	1.35	70	73.09	493.2914	153
Isophorone	1.54	199	138.19	40	215
2-Undecanone	1.33	75000	170.29	5.33288	245
Mesityl oxide	1.83	210	136.15	1199.898	140
Benzyl benzoate	1.28	270	212.25	0.0298	323
Ethylene glycol diacetate	1.23	1800	134.13	10.31912	230
Ethyl salicylate	1.32	7500	166.21	6.6661	243
3-Hexanone	1.97	5000	98.15	1853.176	144
Ethylene glycol phenyl ether	2.49	100	162.22	0.9332	247
Isobutylbutyrate	1.22	250	130.22	n/a	144
Ethylene glycol butyl ether	1.2	85	162.22	n/a	171
Ethylbutyrate	1.62	250	116.16	2066.491	121
Methyl caproate	2	23500	130.22	495.9578	186
Amyl propionate	1.4	500	144.22	n/a	208
Ethyl n-valerate	1.38	1000	130.22	626.6134	195
Dimethyl phthalate	1.4	325	194.19	0.4132	282
Dimethyl adipate	1.28	124	174.2	n/a	205

## Appendix B]

### MATLAB Code for Nozzle Calculations

```
%% DIAMETER CALCULATIONS
```

```
% [Feed Reflux VtoC Boilup]  
  
P = [14.5038 14.5038 14.5038 14.5038]; % in psi  
sP = sqrt(P);  
Q = 4.403*[52296.6 6447.138 765.76 261.625]; % in gpm  
  
sD = (Q./sP)/28.9;  
  
D = sqrt(sD); % in inches  
di = 25.4*D; % in mm  
  
disp(di)
```

```
%% THICKNESS CALCULATIONS
```

```
Tr = 0.00136; % in mm  
T = 4.7625; % in mm  
Sa = 136.66667*1000000; % Allowable Stress in Pascal  
E = 1;  
m = 0.125;  
PD = [100000 100000 100000 100000]; % Design Pressure in Pascal  
  
for i = 1:4  
    tr_m(i) = ((PD(i)*di(i)*0.001)/(2*(Sa*E-0.6*PD(i)))); % in m  
end  
  
tr = tr_m*1000; % regulation thickness of nozzles in mm  
disp(tr)  
  
t = 4.7625; % in mm  
  
MT = T*m;  
Mt = t*m;  
ET = T - (Tr + MT); % Extra thickness available in vessel in mm  
  
H1 = 2*Tr;  
  
for i = 1:4  
    AL(i) = (di(i))*Tr; % Area lost in mm2  
    A1(i) = ET*(di(i)); % Aa1 in mm2  
  
    et(i) = t - (tr(i) + Mt); % Extra thickness available in nozzle in mm  
    A2(i) = 2*H1*et(i); % Aa2 in mm2  
  
    AD(i) = AL(i) - (A1(i) + A2(i)); % Area Deficit in mm  
end  
  
disp(AD)
```