PRODUCTION OF CRUDE TEREPHTHALIC ACID (CTA) FROM PARAXYLENE OXIDATION

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CERTIFICATE

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DEDICATION

This thesis is dedicated to our parents and our friends, who have held us back from losing it occasionally. And to our respected supervisor and faculty, without whose support and guidance we would not have been able to complete this thesis and degree.

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NOMENCLATURE

m	Mass flow rate
C_p	Specific heat capacity
ΔT	Temperature difference
H	Enthalpy of stream
H_r	Overall heat of reactions
X	Conversion
n	Moles of component
k	Rate constant
F_{ao}	Flow rate of component ‘a’ in feed of reactor
C_a	Consumed amount of component ‘a’ in reactor
C_{ao}	Concentration of component ‘a’ in feed of reactor
V	Volume of reactor
H	Height of reactor
D	Diameter of reactor
C_e	Purchase cost of equipment
S	Capacity of equipment
T_h	Required holding time
$-rA$	Rate of reaction
Ti	Inlet temp
To	Outlet temp
G	Mass Velocity
Re	Reynold’s number
K	Thermal Conductivity
μ	Viscosity

ΔPs	Shell side Pressure drop
ΔPt	Tube side Pressure drop
α	Flow area
h	Heat transfer coefficient
F_T	LMTD correction factor
Z	Height of Packing
A	Area
L_D	Ideal size of crystals
G_c	Crystal growth rate
Q	Heat energy
η	Isentropic pump efficiency
U_c	Clean coefficient of heat transfer
U_d	Dirt coefficient of heat transfer
	Dirt factor
R	

ABSTRACT

Terephthalic acid is a central component in polyester fibres , films, PET bottles, and other polyester products. It is a raw material for a variety of household products and clothing, and since much of the plastic and polyester needs of Pakistan are met through exports, there is an internal need to produce terephthalic acid. Most of the terephthalic acid now is commercially produced from the oxidation process of paraxylene.

The project will aim to design a process that produces crude terephthalic acid from paraxylene by an air oxidation reaction, focusing on obtaining a crude product that can be further purified. Crude Terephthalic Acid (CTA) produced is about 99.7% pure containing 4-Carboxybenzaldehyde impurities which weaken the strength of plastics and fibers and hence must be removed. For mass production, the AMOCO process is used, which uses a homogenous liquid phase catalyst at set conditions and results in the highest yield. Our project is centered around producing 100 tons of CTA per day and maximizing the potential of the plant by optimal design. Moreover, we have focused on reducing the plant load, increasing efficiency, and making our process more environmentally friendly and safer. Under assumed economic conditions, this plant is expected to produce an annual profit of $ 16.3 million and result in a payback period of 3 years and 6 months.

In our thesis, we will summarize the process design and simulation of a crude terephthalic acid production plant and describe how our final year project has been carried out. This will include all relevant stages such as determining the process and methodology, carrying out an efficient material and energy balance on every equipment, to designing those equipment and then carrying out an economic analysis to determine the total costs of the plant. Moreover, a hazard & operability study was carried out over the plant to account for all possible risks. Lastly, the plant was also simulated in Aspen Plus and relevant instrumentation for control loops on a reactor was identified.

CHAPTER 01

INTRODUCTION

Terephthalic acid is the main raw material of the polyester industry. It is used to make several daily use plastic products such as solid-state resins (bottle grade resins) for PET bottles, polyester films, and polyester fibers. The largest application of terephthalic acid is in the textile industry itself, because polyester can be commercially processed further into a variety of fabric goods and clothing. About 70% of the terephthalic acid produced comes from the oxidation of paraxylene, an aromatic hydrocarbon. Terephthalic acid is commercially produced largely in China, Europe, North America, and India. [1]

1.1 Terephthalic Acid and its Applications

Terephthalic acid is usually available as crystalline, white solid with the organic formula $C_6H_4(CO_2H)_2$. It has a density of 166.13 g/mol, a melting point of 300 ^{0}C and its particle size ranges from 50 µm to 150 µm.

Figure 1.1 shows the major uses of terephthalic acid. Polyester fiber includes commercial grade yarns and filament for home textiles, sheets, apparel, and fiberfill. The end use applications include bottles and packaging. Some terephthalic acid is also used for polyester films and magnetic tape. [9]

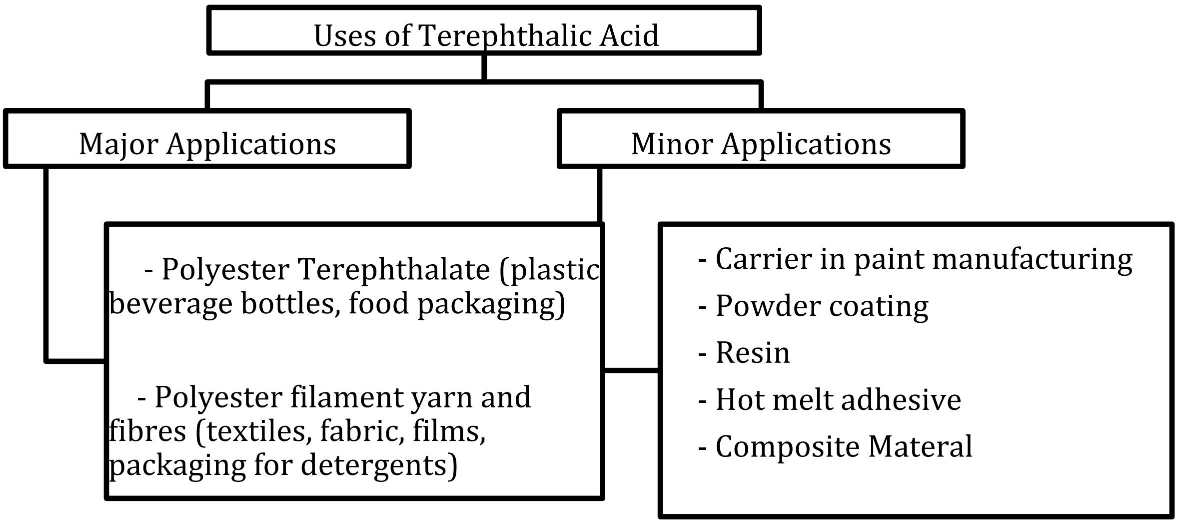


Figure 1.1: Commercial uses of Terephthalic Acid [9]

1.2 Paraxylene Oxidation History

The first oxidation reaction of paraxylene was carried out in 1912 by Ciamicin and Silber. [3] Paraxylene, a derivative of benzene was studied when exposed to sunlight. Molecular hydrogen was used as oxidant and terephthalic acid was produced along with p-toluic acid. This was later modified by use of dimmed light and the reaction time was around 24–60 days with xylenes and monoaldehydes as major product. [4] This revealed that step wise oxidation took place because many ketones and aldehydes were formed as intermediates. But these could not be replicated on an industrial scale because of long reaction times. Therefore, the oxidation process of paraxylene to terephthalic acid has gained popularity for the use of catalysts, either heterogeneous or homogeneous for reducing reaction times.

1.3 Oxidation of Paraxylene using different conditions

There are different methods used to commercially produce terephthalic acid. These are mentioned below:

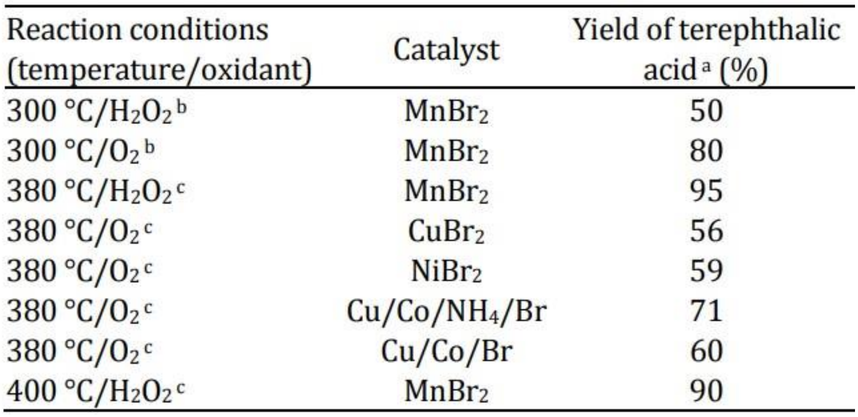
1.4 Heterogeneous Catalysis using Water as Solvent

Oxidation in sub and super critical water can be carried out to give safe working conditions for the reaction and make it environmentally friendly. Water is used a solvent that replaces the non-environmentally friendly acetic acid and acetonitrile solvents. However, the drawbacks of this process are that high temperatures are required. A poor solvent will lead to low paraxylene solubility, and thus, a low yield of terephthalic acid. Thus, a temperature higher than 300°C must be used to ensure high solubility of paraxylene. At the critical temperature, physical properties of water will be like an organic solvent, which show increased solubility for terephthalic acid as well. [8] Furthermore, as temperature of the supercritical fluid is increased, its behavior will be modified. The dielectric constant will decrease because of disruption of hydrogen bonds and thus increase solubility. Hence yield can be adjusted by changing the reaction temperature.

Subcritical water temperature range (100 °C - 374 °C)

Supercritical water temperature > 374 °C

Table 1: Homogeneous catalytic oxidation of paraxylene [8]



Reaction conditions (temperature/oxidant)	Catalyst	Yield of terephthalic acid[a] (%)
300 °C/H_2O_2[b]	$MnBr_2$	50
300 °C/O_2[b]	$MnBr_2$	80
380 °C/H_2O_2[c]	$MnBr_2$	95
380 °C/O_2[c]	$CuBr_2$	56
380 °C/O_2[c]	$NiBr_2$	59
380 °C/O_2[c]	Cu/Co/NH_4/Br	71
380 °C/O_2[c]	Cu/Co/Br	60
400 °C/H_2O_2[c]	$MnBr_2$	90

Analysis of data from this table shows that for industrial application, that high yields can be achieved, however because of high temperature and energy requirements applied in this method and the operation cost are high. Commercially, these are also not safe.

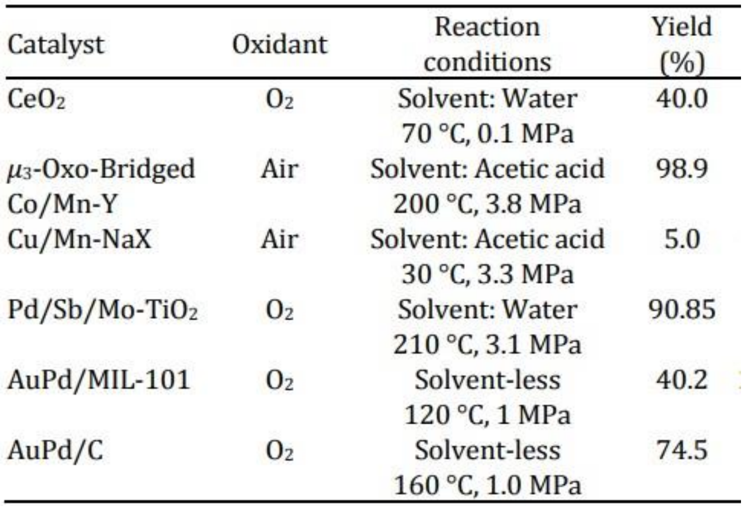
1.4.1 Heterogeneous catalytic oxidation

Several heterogeneous catalysts can be used with the main goal of reducing its limitations. Bentonite was utilized as a medium to heterogenize the cobalt and manganese homogeneous catalyst. The catalyst can be reused after this stage. By encasing active metal complexes and Co/Mn in zeolites, other researchers have also reported attempts to heterogenize the homogeneous catalyst, which have increased the popularity of heterogeneous catalysts.

The problems with heterogenous catalysts are:

(1) metal precipitation, which inhibits the catalyst from working effectively.
(2) the need for a separation procedure once the reaction is finished.
(3) limited reuse of the catalyst.

Table 2: Comparison of heterogeneous catalysts for paraxylene oxidation [8]



Catalyst	Oxidant	Reaction conditions	Yield (%)
CeO_2	O_2	Solvent: Water 70 °C, 0.1 MPa	40.0
μ_3-Oxo-Bridged Co/Mn-Y	Air	Solvent: Acetic acid 200 °C, 3.8 MPa	98.9
Cu/Mn-NaX	Air	Solvent: Acetic acid 30 °C, 3.3 MPa	5.0
Pd/Sb/Mo-TiO_2	O_2	Solvent: Water 210 °C, 3.1 MPa	90.85
AuPd/MIL-101	O_2	Solvent-less 120 °C, 1 MPa	40.2
AuPd/C	O_2	Solvent-less 160 °C, 1.0 MPa	74.5

Employing a heterogeneous catalyst using metal cluster complexes in zeolite and acetic acid-water shows that high paraxylene conversion can be obtained. But this resulted in a significantly higher pressure being used than commercially acceptable to deliver the yield. [8]

In another combination, palladium with antimony or gold can also be used to oxidise paraxylene to terephthalic acid. The ratios of palladium to antimony are 10:1 and water is used as solvent, with ratio to paraxylene 30:1. The operating temperature is 170 °C. [8] This process has the advantage that reactor corrosion is reduced, less hazardous reaction conditions are required and a yield of around 88.8 % is obtained in 5 hours. However, the problem is the use of expensive catalysts that make this process economically inefficient.

1.4.2 Carbon dioxide as co-oxidant

CO_2 is often used in process air to facilitate the catalytic oxidation process. It can be used with both heterogenous and homogeneous catalysts. It is introduced into the reaction to increase yields of terephthalic acid and maximize production. Another added advantage of this is that it can reduce the probability of a fire or explosion accident occurring when high temperature and explosive oxidants like hydrogen peroxide H_2O_2 and O_2 are used in high concentration. This is relevant when a flammable solvent is used as well. However, its main objective is to increase the oxidation activity because CO_2 it helps consume O_2. This is found to be due to the positive effect of solvent expansion of CO_2 as a soft cooxidant. It was found to be involved in the activation of paraxylene at temperatures lower than 400 ^{0}C. [8] Moreover, the presence of CO_2 can reduce the amount of impurities produced with terephthalic acid, which makes the purification process considerably less complicated. As a diluent oxidant, it can prevent oxidation of unwanted products because of a slow rate determining step which makes the process occur at a slower rate and because the CO formed during reaction partially blocks some active sites, preventing over oxidation.

While this property is useful for reducing impurities, it also results in deactivation or poisoning of active sites on the catalyst surface. This results in a dramatic decrease in the catalyst activity decreases.

1.4.3 The AMOCO Process

This process was commercialized in the late 1970’s. Before this, very few industrially acceptable methods were available to produce high quality terephthalic acid. Some of these processes were seriously hazardous, such as the oxidation of nitric acid at 200 °C and 13.5 bar of oxygen pressure. In another method, paraxylene oxidation was done solvent free with a cobalt catalyst but the p-toluic acid was found to be resistant to oxidation by the cobalt catalyst. [5] It also resulted in an increased operation cost due to the several steps in the esterification process. Hence the AMOCO process was more favorable In the AMOCO process, a temperature of 200 °C and 15 bar pressure is used to react paraxylene with oxygen in air. [6] A homogeneous catalyst, which is a combination of three ions; cobalt, manganese, and bromide ions; is used in solution. Acetic acid is used as solvent. Crude terephthalic acid is formed in a solution that can be precipitated, separated, and purified to give high quality pure terephthalic acid with an impurity content of 4-carboxybenzaldehyde (4-CBA) less than 25 ppm.

In this bromide-controlled air oxidation, the common sources of bromide ion are hydrobromic acid (HBr) and sodium bromide (NaBr). [7] Terephthalic acid formed initially is dissolved in solution at high temperature but can be easily precipitated out as a solid due to its low solubility in acetic acid. In the purification process, the crude terephthalic that has been crystallized and dried is dissolved in hot water to reduce 4-CBA to p-toluic acid using a palladium catalyst. [8]

1.4.4 Alternative Promoters

In the AMOCO process, the catalyst requires the use of harmful promoters such as HBr and NaBr. To eliminate this concern, other alternatives have been proposed. NHydroxyimides (NHPI) is an organic promoter used in terephthalic acid production, introduced around the same time as the AMOCO commercialisation process. [8] Its primary job is to generate peroxy radicals for further paraxylene oxidation. The additional advantage is the use of milder process conditions of around 100 °C temperature and 0.1 MPa of O_2 pressure. This results in a slightly lower selectivity yield than the AMOCO process of around 84%. [8] Hence with cobalt and manganese as catalysts and acetic acid solvent, it can give a good performance. However, NHPI needs to be added continuously to the reaction media for it to keep up with the oxidation rate of paraxylene because it is decomposed.

Another promoter that can be used is guanidine which has a positive effect on the selectivity of the desired product.

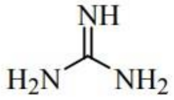
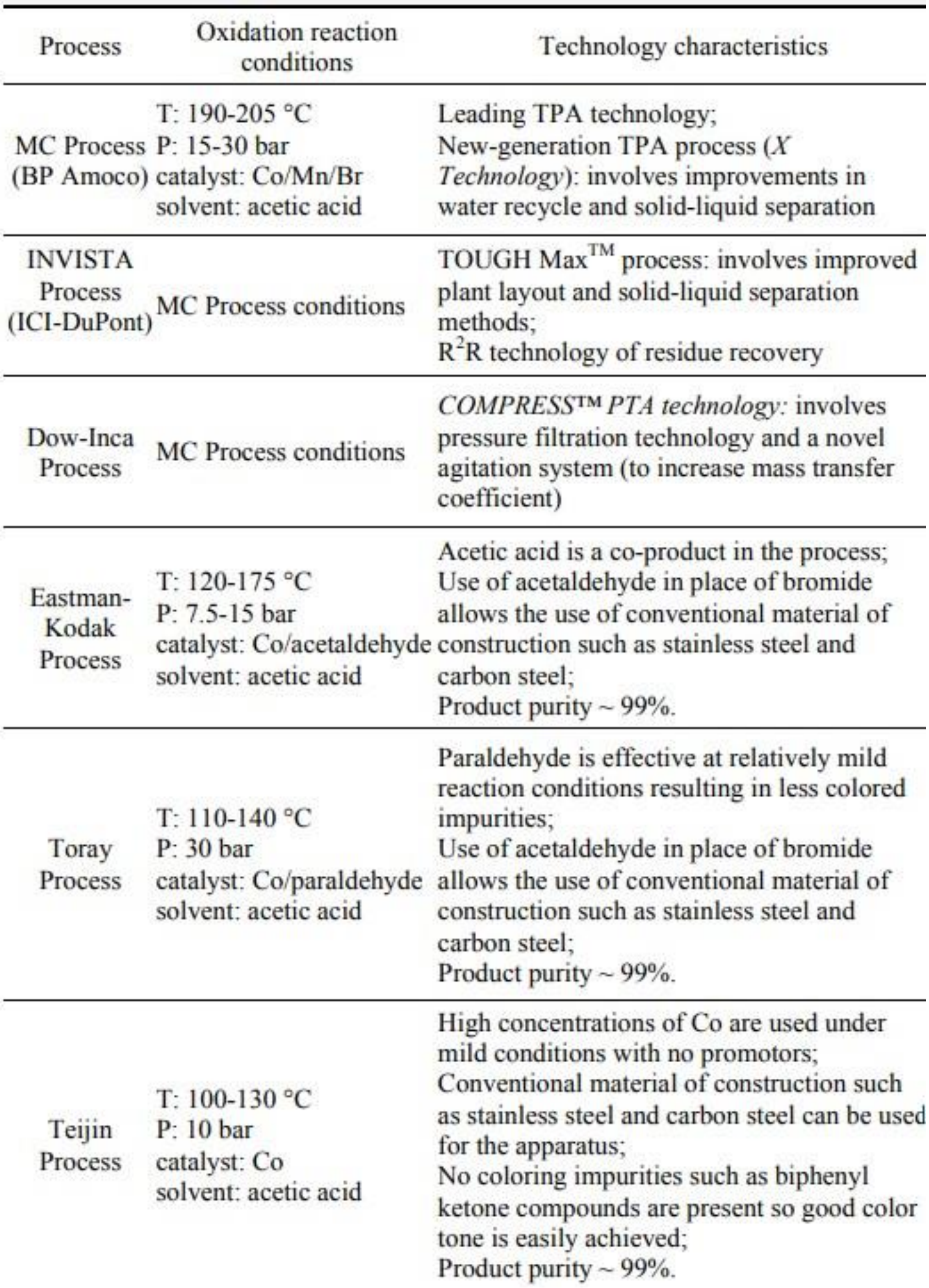


Figure 1.2: Guanidine structure

Ionic liquid promoters (example: 1-ethyl-3-methylimidazolium bromide) can also replace corrosive HBr. [15]

1.4.5 Summary of other processes to produce terephthalic acid Table

3: Terephthalic acid production processes [6]



Process	Oxidation reaction conditions	Technology characteristics
MC Process (BP Amoco)	T: 190-205 °C P: 15-30 bar catalyst: Co/Mn/Br solvent: acetic acid	Leading TPA technology; New-generation TPA process (*X Technology*): involves improvements in water recycle and solid-liquid separation
INVISTA Process (ICI-DuPont)	MC Process conditions	TOUGH Max^{TM} process: involves improved plant layout and solid-liquid separation methods; R^{2}R technology of residue recovery
Dow-Inca Process	MC Process conditions	*COMPRESS™ PTA technology:* involves pressure filtration technology and a novel agitation system (to increase mass transfer coefficient)
Eastman-Kodak Process	T: 120-175 °C P: 7.5-15 bar catalyst: Co/acetaldehyde solvent: acetic acid	Acetic acid is a co-product in the process; Use of acetaldehyde in place of bromide allows the use of conventional material of construction such as stainless steel and carbon steel; Product purity ~ 99%.
Toray Process	T: 110-140 °C P: 30 bar catalyst: Co/paraldehyde solvent: acetic acid	Paraldehyde is effective at relatively mild reaction conditions resulting in less colored impurities; Use of acetaldehyde in place of bromide allows the use of conventional material of construction such as stainless steel and carbon steel; Product purity ~ 99%.
Teijin Process	T: 100-130 °C P: 10 bar catalyst: Co solvent: acetic acid	High concentrations of Co are used under mild conditions with no promotors; Conventional material of construction such as stainless steel and carbon steel can be used for the apparatus; No coloring impurities such as biphenyl ketone compounds are present so good color tone is easily achieved; Product purity ~ 99%.

1.4 Advantages of the AMOCO process

The AMOCO process is a commercially dominant process which involves the oxidation of paraxylene to terephthalic acid and is employed by most industrial production units. It has a very high yield (~ 95%) of terephthalic acid production and can operate at a reasonable temperature and pressure. [8] This is known to be a promising process too, since around 98% of the paraxylene reacts and it has a reaction time of about 8–24 hours. The low solvent loss in a single reactor pass and relatively high yield is responsible for the near universal selection of this method.

The industry still has not found a replacement for the commercial AMOCO process and research is still undergoing to find processes with a high yield and less environment and safety problems. The above referenced methods cannot be used because all other methods suffer from problems such as the use of expensive chemicals like ethylene, expensive catalysts like noble metal catalysts and gold, unfriendly reaction conditions, and the use of another promoter to replace bromine like NHPI all increase the operational cost because sacrificial promoters are used and consumed in the reaction. [9] Additionally, this promoter has a poor level of solubility in acetic acid medium, which makes it less useful for commercial application.

1.5 Challenges and Obstacles

As discussed above, the AMOCO process has one of the highest yields of terephthalic acid production due to the use of bromine, without which the yields fall as below to less than 30%. But bromine also poses an environmental hazard and raises a safety concern over the formation of methyl bromide, CH_3Br. [15] This compound is severely toxic to human health as well as the environment becauses it leads to the destruction of stratospheric ozone.

Alternative methods have been proposed which include the use of a renewable source. Biomass is converted to 2,5-dimethylfuran (DMF) before being converted to para-xylene. The process is known as the Diels-Alder cycloaddition of ethylene. It uses $CuCI_2$ catalyst for paraxylene conversion which has an 88.3% yield. [15] Problems associated with this process include:

1. Complication in polymerisation which reduces the amount of DMF. Hence, the paraxylene yield becomes less which in turn affects terephthalic acid production as well.
2. Process requires a high cost due to the utilisation of ethylene.
3. Reaction is inconvenient.

The Mitsubishi decarbonylation and modification of the Henkel process can also be used for terephthalic acid production. It is carried out as a liquid phase air oxidation, with water as a solvent and a temperature of about 250–300 °C. [5] Palladium on carbon is the catalyst. Modification of the Henkel process is started once the formed dipotassium terephthalate undergoes crystallisation from its aqueous solution and finally, sulfuric acid is added to produce fine terephthalic acid crystals. However the use of more than two stages makes them intricate and complex, which is not economically feasible for the industry.

CHAPTER 2

LITERATURE REVIEW

2.1 Process Principles

Production of crude terephthalic acid occurs by an oxidation reaction, where paraxylene is reacted with air in given conditions. This section will explore the different mechanisms of the reaction and the chemistry involved.

2.1.1 Chemistry of Oxidation Process

Oxidation reaction is a reaction in which electrons are transferred from one species to another. The oxidized species is the one that loses electrons and gains oxygen, while the species that gains electrons is reduced and gains hydrogen.

The oxidation reaction of paraxylene is as follows:

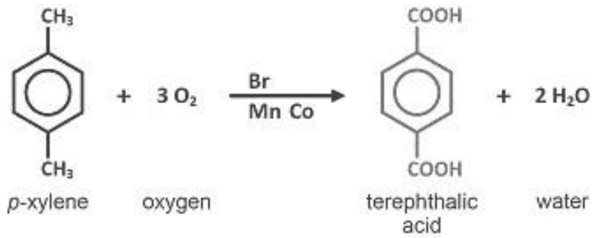


Figure 2.1: Reaction of paraxylene with oxygen [2]

Paraxylene is oxidized and the result is the formation of terephthalic acid and water. The reaction occurs in a series of stages as shown below.

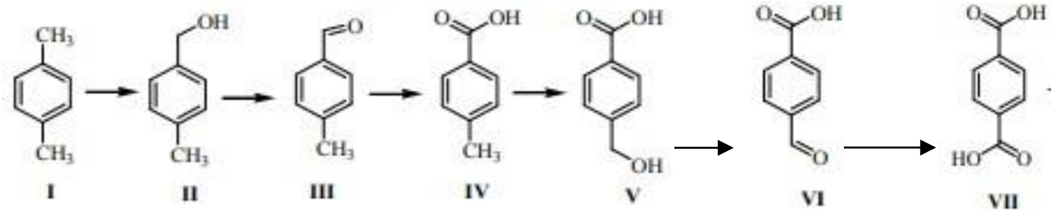


Figure 2.2: Intermediate compounds formed during oxidation reaction [8]

The reaction can be carried out at a certain range of temperatures and pressures. The reactor can be operated between 175–225 °C and 15–30 bar. Compressed air is fed to the reactor in excess. This is to provide measurable oxygen partial pressure for reaction and get high p-xylene conversion. This reaction is also highly exothermic and releases large amounts of energy (2×10^8 J/kg of reacted paraxylene). [11] Most of this heat of reaction is removed by evaporation of acetic acid solvent. Terephthalic acid has low solubility in acetic acid.

When the reaction is complete, terephthalic acid dissolved is cooled and the terephthalic acid precipitates out. About 98% of the paraxylene can be said to have reacted, and the selective yield of terephthalic acid is approximately 95%. Some of the paraxylene is lost as it is converted to intermediate compounds and may be completely oxidized to carbon oxides present in reactor effluent. Small amounts of acetic acid are lost too as converted to impurities such as methyl acetate. Oxidation of the methyl groups is approximately consecutive. This forms two main intermediates p-toluic acid and 4carboxybenzaldehyde (4-CBA). [6]

This results in a three-phase system being formed which yields solid terephthalic acid crystals, solvent with some dissolved terephthalic acid, and vapor that mostly consists of vaporized acetic acid, nitrogen, water, and smaller amounts of oxygen and carbon oxides.

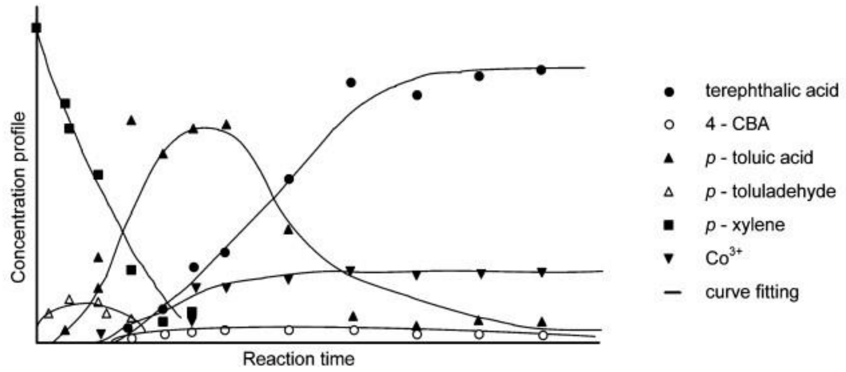


Figure 2.3: Reaction Profile [11]

The figure above shows the increase in concentration of terephthalic acid as the paraxylene is used up. It also depicts the increase in concentration of p-toluic acid and 4CBA, the major impurities.

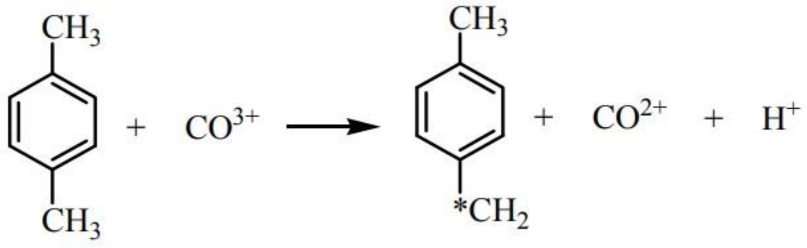
2.1.2 Reaction Mechanism

The reaction involves a homogeneous catalytic mechanism to convert para-xylene to terephthalic acid and is based on free radical generation. The three-ion complex of cobalt, manganese, and bromine is used in the liquid phase. Bromine from HBr is used as a promoter. This catalyst works by generating a radical species (denoted with *) through an electron transfer process. Bromine plays an important role as a promoter to generate radical compound species, along with the synergistic effect of cobalt and manganese to oxidize paraxylene. [8] This works by cobalt inducing the abstraction of the hydrogen atom at the start of the reaction. Manganese participates in further oxidation to aldehyde since cobalt catalyst cannot oxidise it any further.

The presence of acetic acid leads to an increase in radical species generation by reaction of acetic acid with water that produces acetate ions. Acetic acid acts as a Bronsted acid that donates protons to water. The acetate ions can then react with HBr to generate bromine radicals. These radicals are crucial in promoting reaction by abstracting the hydrogen atom from the methyl group. This leads to formation of the second radical of the substrate. The following oxidation then takes place in the presence of O_2 as an oxidant.

2.1.3 Chemistry of Reactions

Paraxylene first forms radical species by reaction with cobalt as shown in Equation 1. [8]

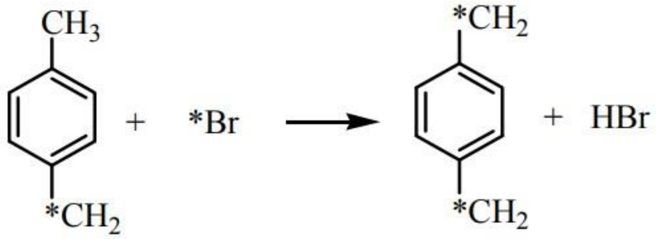


(1)

Acetic acid aids the reaction by donating protons to water resulting in the formation of acetate ions. These react with HBr to give bromide radicals that can react with paraxylene radical to give a more reactive specie. [8]

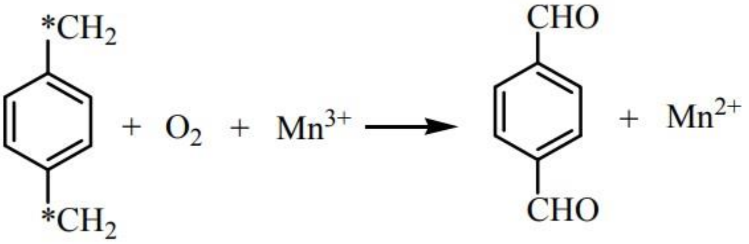
$$CH_3COOH + H_2O \longrightarrow CH_3COO^- + H_3O^+ \qquad (2)$$

$$CH_3COO^- + HBr \longrightarrow CH_3COOH + {}^*Br \qquad (3)$$



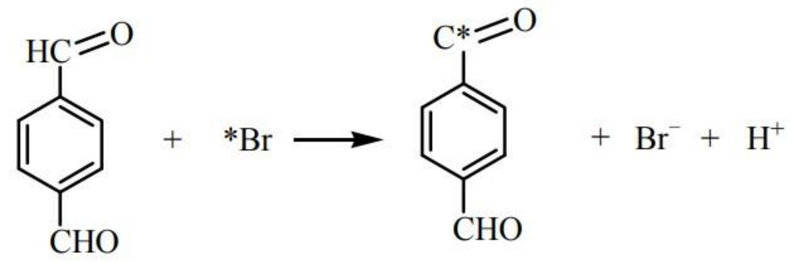
(4)

The paraxylene radical is now oxidized by oxygen in the presence of manganese ions as shown in Equation 5. [8]



(5)

The effect of bromide radicals is to cause further oxidation. In a series of stages, it reduces the aldehyde to a ketone by removing hydrogen. The ketone radical is further oxided with oxygen from air as shown in equation 8. [8]



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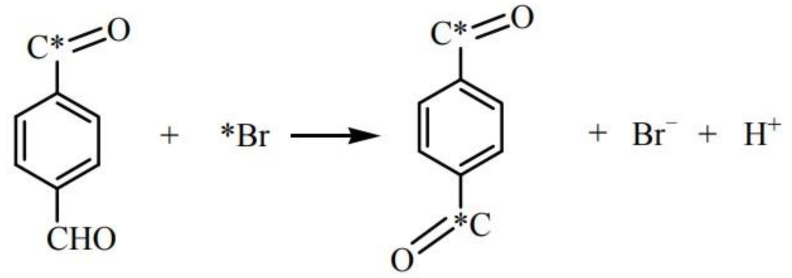

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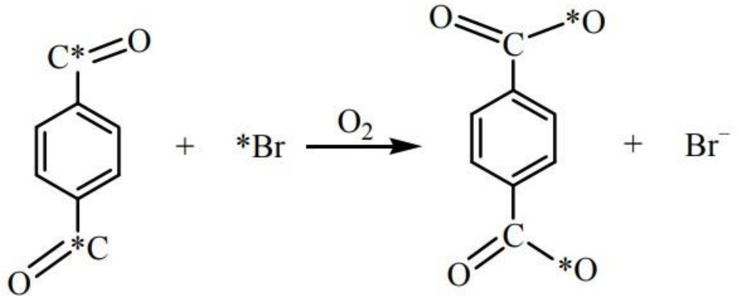
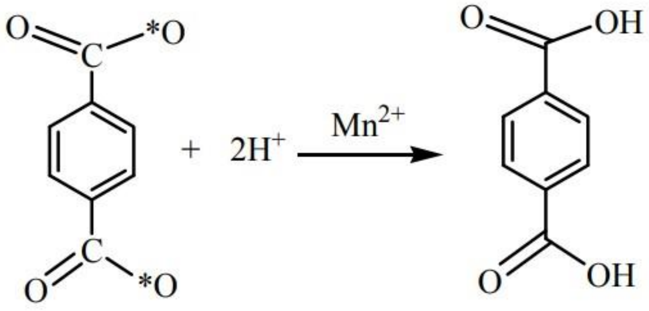


(8)

Lastly, protons are added to the radical in the presence of manganese ions to regenerate catalyst and form terephthalic acid. [8]



(9)

2.2 Process Conditions

Like all reactions, this reaction must operate under a specific set of conditions. These are detailed below.

2.1.4 Catalyst

The problem with the reaction without catalysts was the resistance of p-toluic acid toward oxidation. Thus, a catalyst breakthrough was required to overcome it and increase oxidation rates in aromatic hydrocarbons. Initial attempts were made to increase rates of oxidation by use of manganese bromide catalyst, but although few intermediates were found, oxidation yield did not significantly improve (77% terephthalic acid yield). The use of more metals was then implemented, and it was found that cobalt (Co) and manganese (Mn) together gave the highest terephthalic acid yields. Varying the concentrations and adding a bromide promoter increased both the yield and the rate of oxidation. [5] It was concluded that Co and Mn action in the Co/Mn/Br catalyst was synergistic, and the main discovery was bromine's ability to increase oxidation rate. Hence the most successful combination was proved to be bromine, cobalt, and manganese which are the main liquid phase homogenous catalysts of the AMOCO process.

Attempts to increase selectivity of catalyst are influenced or controlled by changing reaction conditions such as operating temperature, pressure, use of mild or strong oxidants, co-oxidant, reaction time and ensuring that catalyst is not deactivated by poisoning, leaching, or fouling.

2.1.5 Temperature and Pressure

The main objectives of the industrial optimisation of the oxidation of paraxylene are to minimise the impurity content, which includes 4-CBA in the crude terephthalic acid. Moreover, the production rate needs to be with an acceptable operational cost, and for this purpose temperature and pressure must be regulated strictly to ensure optimal reaction conditions in the reactor. [3]

For this, temperature is maintained at 200 ^{o}C and the reactor is operated isothermally. Since temperature directly affects the rate constant, it must be regulated. The Arrhenius plot below shows the rate constant vs temperature graph for conversion to terephthalic acid.

Figure 2.4: Temperature vs Rate constant for reaction [11]

As temperature increases, it has the effect of decreasing the amount of 4carboxybenzaldehyde by converting it to terephthalic acid.

In our continuously stirred reactor, the temperature is indirectly controlled by pressure which must be maintained at 15 bar, since there is a direct proportionality between both physical properties.

2.1.6 Solvent

Acetic acid used in the process is found to be the most stable solvent. [12] It shows good solubility for paraxylene and low solubility for terephthalic acid, so the product is easier to separate. There is an environmental issue related to its application, however, no replacement that would result in a good product yield has been found.

2.1.7 Impurities

The major impurity in crude terephthalic acid is 4-CBA, which has proved to be very troublesome. It has structural similarity to terephthalic acid, it co-crystallizes with terephthalic acid, and this makes its separation for purification extremely tedious and difficult. It also becomes trapped and inaccessible which makes completion of oxidation very difficult too.

Crude terephthalic acid as a feedstock for polyester is unsuitable. Although it is 99.7% pure, even the smallest impurities can decrease the quality of the subsequent polyester formed. [9] The deteriorating quality and strength of fibers make processing very difficult. Primarily, the 4-CBA impurity concentration acts as chain termination agent in PET manufacture, which is why the purification process is so vital. For this purpose, crude terephthalic acid is dissolved in hot water to reduce 4-CBA to p-toluic acid via catalytic hydrogenation to less than 25 ppm. The process conditions are 250 °C temperature over a palladium catalyst. [6]

Other colour-forming impurities and residual amounts of catalyst metals and bromine are also removed during purification to give a white powder from the light-yellow cake of crude terephthalic acid.

2.1.8 By-products

Methyl acetate, one of the main by-products in the terephthalic acid process, if formed by the oxidative decarboxylation of acetic acid as shown in the reaction below.

Decarboxylation is caused by peroxide interaction with the carboxylic or methyl groups of acetic acid. This is followed by degradation of the resulting radicals. Methyl acetate formation is a result of acetic acid degradation which causes solvent loss. This must be controlled to a certain extent. It is recovered and recycled to the reactor where a side reaction takes place to reconvert it to acetic acid by hydrolysis.

2.3 Selectivity in catalytic oxidation

Selectivity in paraxylene oxidation reaction can be defined in terms of selectivity to desired terephthalic acid product. The main problem arises due to the structural similarity of terephthalic acid and 4-CBA which results in problems with purification later since it is co-crystallised with terephthalic acid. To ensure that polyester quality is not questionable, the 4-CBA content in terephthalic acid must be less than 25 ppm. [7]

The problems with achieving good selectivity are:

1. Controlling the production of other by-products besides terephthalic acid. [14]
2. Controlling the over-oxidation of paraxylene to carbon dioxide is undesired. [14]
3. Controlling each situation individually, since they are interrelated. When 4-CBA impurity concentration is reduced, the tendency to form carbon dioxide increases. [14]

To get good selectivity, it is crucial that the proportion of the catalyst must be regulated. For the homogeneous bromine, cobalt, and manganese catalyst ratios of the three ions must be controlled to control oxidation. When the ratio of bromine to the metal ions is decreased, a significant decrease in 4-CBA production is noted. A smaller proportion of bromine in the catalyst reduces the activity of the catalyst.

However, if the metal content is higher than the bromine content, the catalyst is unable to performance well. One reason can be the hinderance of the catalytic activity for peroxide decomposition. One good solution can be to increase the cobalt and manganese ion ratio with the relative increase of bromine. [15] Thus, the free radical generation will be increased with the decomposition of peroxide, leading to higher catalyst activity. This must be controlled well or else it will result in unfavorable over-oxidation.

CHAPTER 3

UNIT PROCESSES

3.1 Process Equipment

The major equipment in the oxidation plant is as follows:

3.1.1 Feed Mix Drum

All fresh and recycle feed streams are fed to the feed mix drum is agitated by a paddle stirrer to mix paraxylene and acetic acid streams. The concentration of paraxylene in the feed mix drum must be maintained at 28% and for acetic acid at 72%. Catalyst stream from the catalyst recovery unit is also pumped into the feed mix drum. A stream from the feed mix drum is pumped to the reactor.

Figure 3.1: Feed Mix Drum

3.1.2 Reactor

A continuously stirred tank reactor is used for the reaction. A stream at room temperature containing paraxylene, acetic acid, along with catalyst and promoter, is pressurized and fed into the reactor. Pressurized oxygen is sparged from the bottom. The reaction conditions are maintained by a temperature and flow controller. Since the reaction is highly exothermic, there is enough heat to allow the CSTR to run isothermally at 200 oC. The reactor is cooled by a cooling water jacket. The reactor outlet is a slurry sent to crystallizers. It contains solid products, dissolved terephthalic acid, p-toluic acid, 4-CBA, and other unidentifiable impurities, acetic acid, and water. This vapor stream is sent to condensers for cooling down solvent, recovering and recycling it.

A reactor with a diameter of 4.01 m, a height of 12.03 m and volume of 180.2 m3 is employed for production. The reactor volume of the reactors is adjusted using a gas correction to account for the liquid expansion since air is sparged. The reactor is made of stainless steel material to withstand the high operating pressure and temperature and lined with titanium avoid corrosion due to corrosive catalyst.

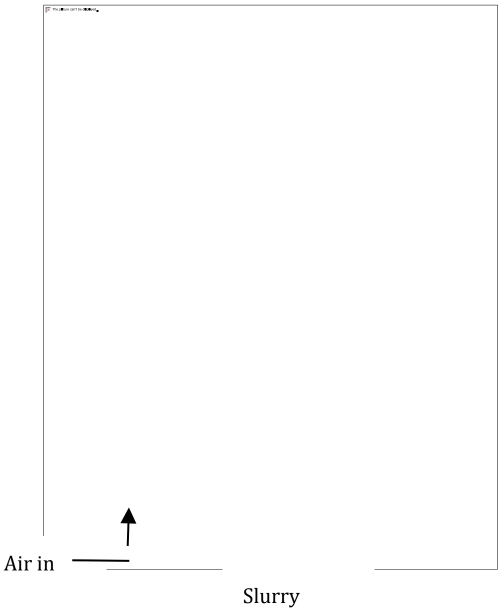


Figure 3.2: CSTR

3.1.3 Crystallization Unit

In this unit, the slurry stream from the reactor is depressurized in a series of crystallizers to a pressure close to atmospheric pressure. Due to this sudden drop in pressure, some of the liquid in the slurry stream vaporizes, which is separated out in a flash vessel and sent for solvent separation in the HP Absorber. The slurry then moves to the next crystallizer and then another. In three stages the mother liquor is separated from the solid product. The wet cake is sent to a rotary dryer. The product can be stored in silos until it is to be further purified.

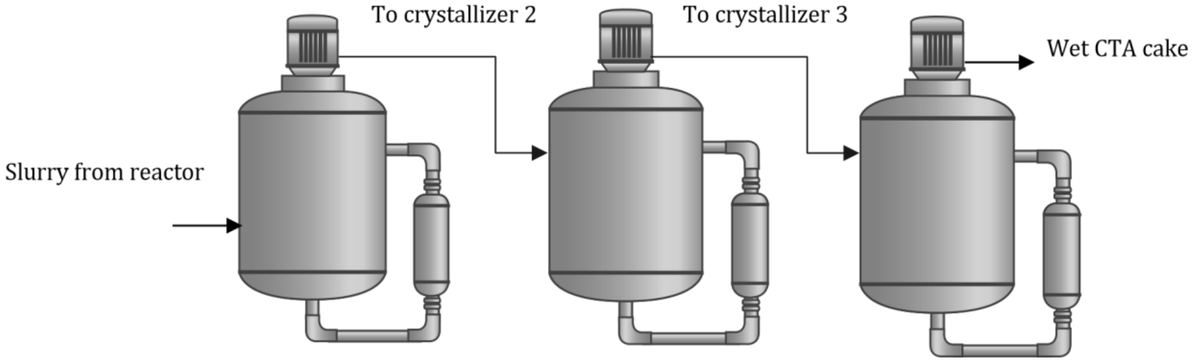


Figure 3.3: Crystallizer Unit

3.1.4 Reactor Condensers

To remove heat, the vaporized acetic acid solvent and water must be condensed in a series of condensers positioned after the reactor. Cooling coils could not be installed inside of the reactor to remove heat because they would interfere with the agitator and solid products would cake on top of them. In addition, an enormous area of cooling coils would be required to remove such a large quantity of heat, which would be impractical in a CSTR. Similarly, all the heat cannot be removed using just the cooling jacket. Hence three condensers in series are placed to condense the vapor and remove heat. The condenser is constructed using stainless steel to minimize corrosion. Water is on the shell side and hot corrosive vapor is on the tube side to allow maximum heat exchange.

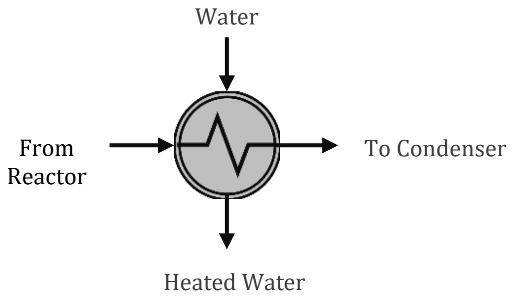


Figure 3.4: Shell and tube type condenser

3.1.5 HP Absorber

For the acetic acid to be recycled back, a series of separations must take place to purify it. A HP absorber column with three stages is used with silicon ball packing for this purpose. This column washes acetic acid vapor with liquid acetic acid and removes non-condensables and waste gases from acetic acid. Some of the purified stream is sent back to the feed mix drum. The remaining acetic acid in the bottoms is further purified in a second, smaller column to remove impurities so they can be safely disposed of.

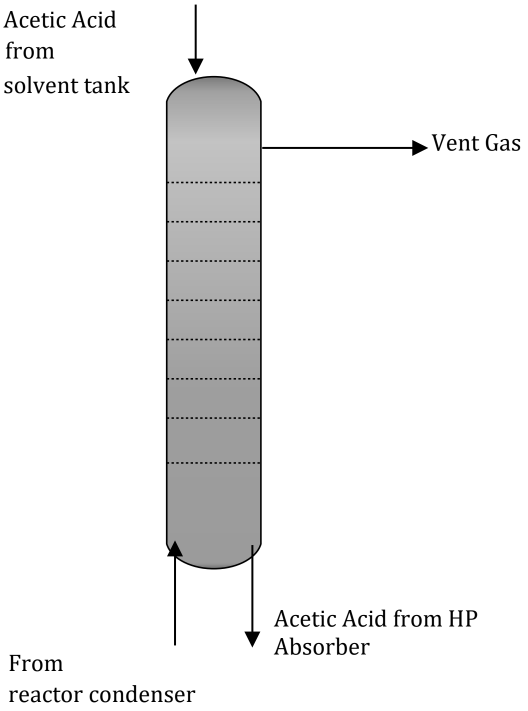


Figure 3.5: HP Absorber column

3.1.6 Dehydration Column

The purpose of the dehydration column is to remove water from the process. Drying is carried out by a stationary bed of absorbent. 75% of the water entering the tower is removed and can be treated for reuse.

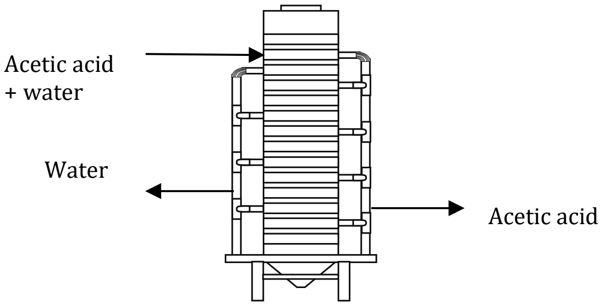


Figure 3.6: Dehydration column

3.1.7 Pump

The main objective of this pump is to increase the pressure of the feed stream from 7 bar to 15 bar before the stream enters the reactor. This is a centrifugal pump that develops a power of 2 kW.

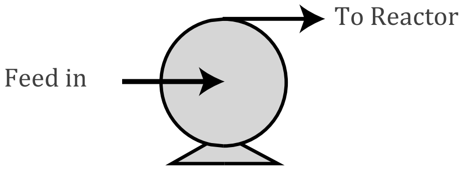


Figure 3.7: Feed pump to reactor

3.1.8 Compressor

Air must be compressed to 18 bar. Oxygen must be in excess for paraxylene oxidation, hence a mole ratio, as recommended by the industry, was to be 5:1 on a mole basis. To produce 100 tons of terephthalic acid per day, 105 tons of air per day was used. The compressor is the most energy intensive part of the plant, using up to 370 KW of power.

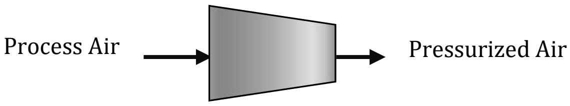


Figure 3.8: Compressor

3.2 Process Flow Diagram

This section will visualize the oxidation plant. The process flow diagram is presented to outline the relevant equipment, flow of materials and the control loops required for each equipment. The plant is largely divided into three sections; the reaction section, the product separation and processing section and lastly, the solvent recovery and recycle section.

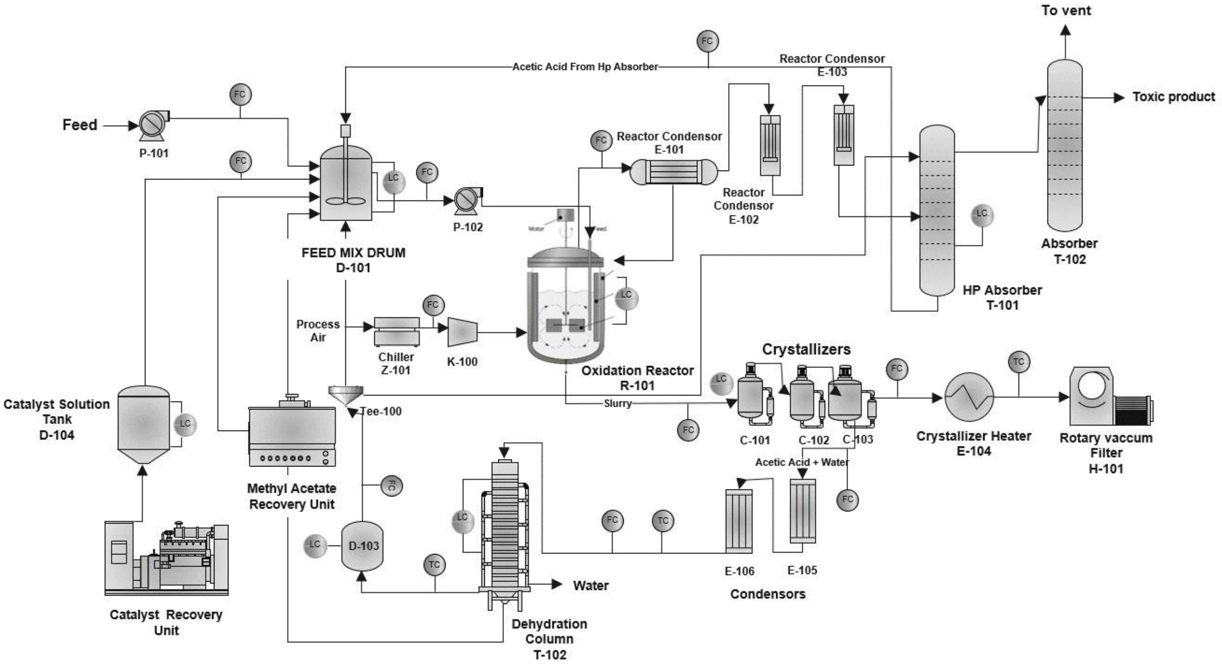


Figure 3.5: Process flow diagram to produce crude terephthalic acid

3.3 Process Description

Paraxylene feedstock, Co/Mn/Br catalyst and recycle streams containing paraxylene and acetic acid are pumped into feed mix drum. A stream is pumped into the oxidation reactor that contains 72% acetic acid and 28% paraxylene. A de-humidifier (chiller) is used to reduce the density of air before it is compressed and fed to the continuously stirred reactor. Paraxylene oxidizes into crude terephthalic acid at set conditions to minimize 4CBA production. Water, terephthalic acid, acetic acid and impurities are present after the reaction. Most of the acetic acid and water is vaporized due to the heat evolved in the reaction. The slurry containing terephthalic acid and water is sent through a series of crystallizers. CTA cake recovered after filtration from the mother liquor is washed and further purified. Acetic acid vapor is condensed in a series of condensers and is recovered in an HP Absorber and recycled back. Methyl Bromide is sent to the recovery unit for its safe disposal.

3.4 Objectives:

The AMOCO process used has the highest yield compared to any other method, hence our project is aimed at:

1. Dehumidifying process air to decrease compressor load and increase process efficiency.
2. Reduction in the amount of 4-CBA, an intermediate compound, produced to make CTA purification easier at an acceptable operational cost.
3. Design of a CSTR to ensure maximum yield.
4. Safe disposal of bromine derivatives because it causes reactor corrosion and environmental problems due to the formation of methyl bromide, a toxic compound.

CHAPTER 4

MATERIAL BALANCE

This chapter will discuss the law of conservation of mass for the entire process by considering material input and output through material flows into each equipment. Hence the component and overall balances will unknown streams. In this chapter, we will cover the material balance for feed mix drum, the reactor, the HP absorber, the dehydrator, the crystallizer unit, and the overall material balance.

4.1 Feed Mix Drum

Basis: 1-day operation

72% acetic acid and 28% paraxylene concentration must be maintained in the feed mix drum.

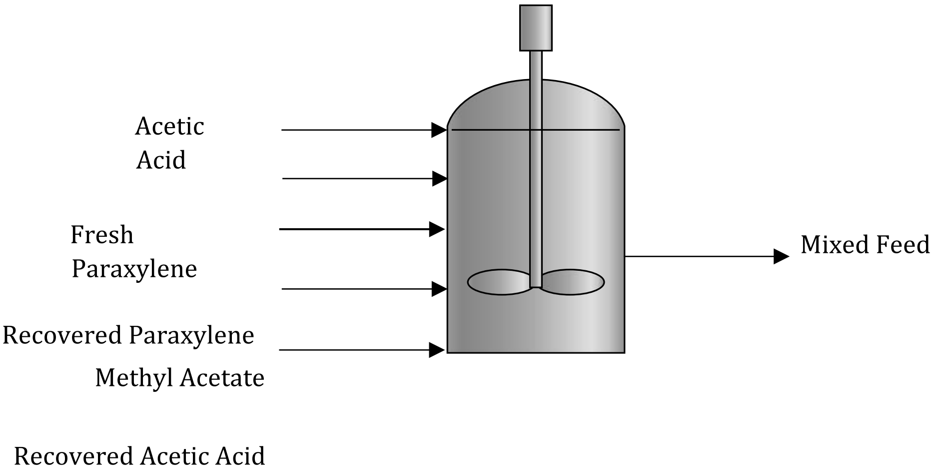


Figure 4.1: Feed mix drum material balance

4.1.1 Assumptions

It is a steady state process.

4.1.2 General Material Balance Equation

Accumulation = Input – Output + Generation – Consumption

Accumulation = 0

Generation = 0

Consumption = 0

Input = Output **Table 4**: FMD Material balance

	IN					**OUT**
Stream (kg/hr)	**Feed**	**Catalyst**	**Acetic Acid (HP Absorber)**	**Acetic Acid & Recycled Paraxylene**	**Methyl Acetate (Recovery)**	**Feed Mix to Reactor**

Paraxylene	1140.9	0	13.31	12.425	0	1166.67
Catalyst	0	0.804	0	0	0	0.804
Acetic Acid	150.02	0	2479.923	370.062	0	3000
Methyl Acetate	0	0	19.5	0	17.75	37.2
Water	0	0	304.2088	1.2187	0	305.43
TOTAL	**1290.95**	**0.804**	**2816.9168**	**383.7057**	**17.75**	**4490.64**

4.2 CSTR

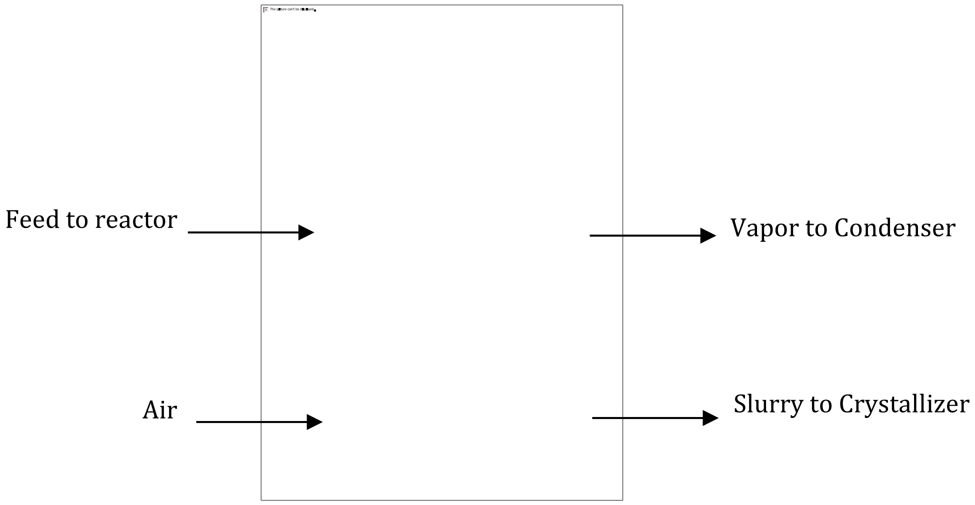


Figure 4.2: CSTR material balance

4.2.1 Assumptions

It is a steady state process.

4.2.2 General Material Balance Equation

Accumulation = Input - Output + Generation – Consumption

Accumulation = 0

Consumption = 0

Input = Output + Generation

$$C_8H_{10}+3O_2 \rightarrow C_8H_6O_4+2H_20$$

Paraxylene Terephthalic acid

Conversion = 90%

$C_8H_{10}+2.5O_2 \rightarrow C_8H_6O_3+2H_20$

Paraxylene 4-CBA

Table 5: Reactor Material Balance

	IN		**OUT**	
Stream (kg/hr)	**Feed to Reactor**	**Air from Compressor**	**To Crystallizer (Liquid slurry)**	**To Condenser (vapors)**
Paraxylene	1166.67	0	17.75	8.5
Catalyst	0.804	0	-	0.804
Acetic Acid	3000	0	556.49	2443.5
Methyl Acetate	37.2	0	17.75	20.5
Air	0	4376.19	-	3804.5
Water	305.43	0	36.7	319.7
Crude Terephthalic Acid (CTA)	0	0	1639.18	1.5
TOTAL	**4490.64**	**4376.19**	**2267.83**	**6599**

4.3 Crystallizer Unit

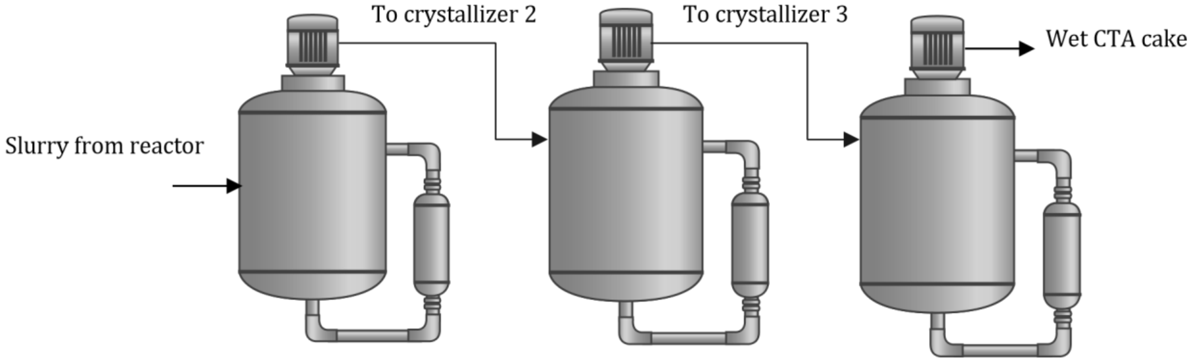


Figure 4.3: Crystallizer Unit

Table 6: Reactor Material Balance

	IN	**OUT**
Stream (kg/hr)	From Reactor	To Crystallizer 2
Paraxylene	17.75	17.75
Acetic Acid	556.5	556.5
Methyl Acetate	17.75	17.75
Water	36.66	36.66
Crude Terephthalic Acid (CTA) (Liquid)	1639.18	163.918
Crude Terephthalic Acid (CTA) (Solid)	0	1475.3
TOTAL	**2267.8**	**2267.8**

Table 7: Crystallizer 2 Material Balance

	IN	**OUT**
Stream (kg/hr)	To Crystallizer 2	To Crystallizer 3
Paraxylene	17.75	17.75
Acetic Acid	556.5	556.5
Methyl Acetate	17.75	17.75
Water	36.66	36.66
Crude Terephthalic Acid (CTA) (liquid)	163.918	81.9
Crude Terephthalic Acid (CTA) (solid)	1475.3	1557.2
TOTAL	**2267.8**	**2267.8**

Table 8: Crystallizer 3 Material Balance

	IN	OUT	
Stream (kg/hr)	To Crystallizer 3	To Heater E-102	To Condenser E103
Paraxylene	17.75	-	17.75
Acetic Acid	556.5	27.8	528.66
Methyl Acetate	17.75	-	17.75
Water	36.66	1.84	34.82
Crude Terephthalic Acid (CTA) (liquid)	81.9	-	-
Crude Terephthalic Acid (CTA) (solid)	1557.2	1639.18	-
TOTAL	**2267.8**	**1668.85**	**598.98**

4.4 Dehydrator

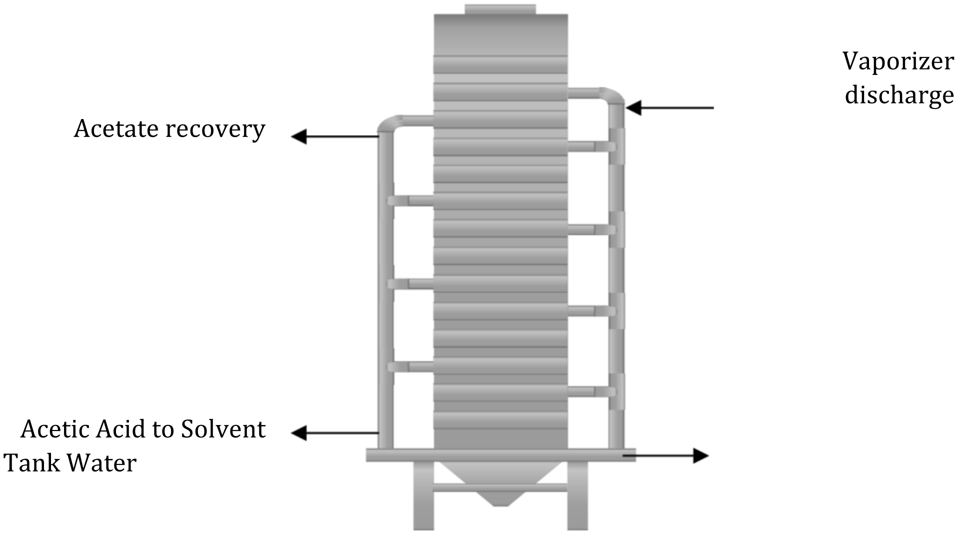


Figure 4.4: Dehydration column

Table 9: Dehydrator Material Balance

	IN	OUT		
Stream (kg/hr)	From Condenser	To Solvent Drum	To Acetate Recovery Unit	Excess Water
Paraxylene	17.75	17.75	-	-
Acetic Acid	528.6	528.6	-	-
Methyl Acetate	17.75	-	17.75	-
Water	34.8	1.74	-	33.1
TOTAL	**598.9**	**548.2**	**17.75**	**33.1**

4.5 Tee

Acetic Acid to

Acetic Acid

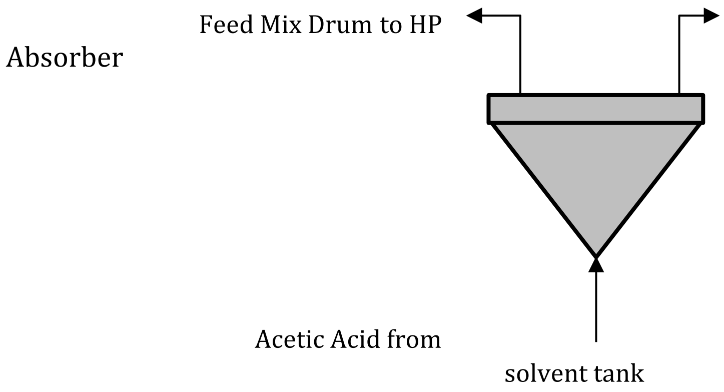


Figure 4.5: TEE

Table 10: Tee Material Balance

	IN	OUT	
Stream (kg/hr)	Acetic Acid from tank	To HP Absorber	To Feed Mix Drum
Paraxylene	17.75	5.33	12.42
Acetic Acid	528.6	158.6	370.1
Water	1.74	0.52	1.22
TOTAL	**548.2**	**164.4**	**383.7**

4.6 HP Absorber

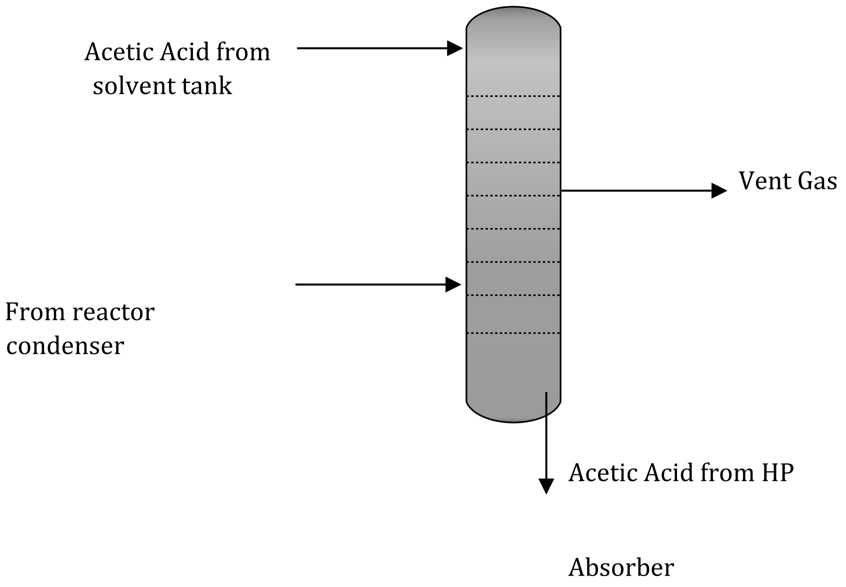


Figure 4.6: HP absorber

	IN		OUT	
Stream (kg/hr)	**Acetic Acid Solvent Tank**	**From Reactor Condenser**	**AA from HP Absorber**	**Vent Gas**
Paraxylene	5.2	8.5	13.31	0.43
Acetic Acid	158. 6	2443.5	2479.9	122.2
Methyl Acetate	-	20.5	19.5	1.02
Air	0.5223	3804.5	0	3804.5
Water	-	319.67	304.2	15.9
Crude Terephthalic Acid (CTA)	-	1.5	-	1.5
TOTAL	**164.4**	**6599**	**2816.9**	**3945.6**

4.7 Overall Material Balance

Table 11: Overall Material Balance

	IN			OUT	
Stream (kg/hr)	**Feed Stream**	**Catalyst Stream**	**Air In**	**Vent Gas**	**CTA to Heater**
Paraxylene	1140.9	-	-	0.43	
Catalyst	-	0.804	-	-	
Acetic Acid	150.02	-	-	122.2	27.8

Methyl Acetate	-	-	-	1.02	
Air	-	-	4376.19	3804.5	
Water	-	-	-	15.9	1.84
Crude Terephthalic Acid (CTA)	-	-	-	1.5	1639.18
TOTAL	**1290.5**	**0.804** **5667.494**	**4376.19**	**3945.6** **5667.494**	**1668.15**

CHAPTER 5

ENERGY BALANCE

The energy balance of a system revolves around the law of conservation of energy; that energy can neither be created nor destroyed, it can only change forms. Hence for a steady system, it can simply be expressed as Energy Input = Energy Output. In this chapter we will discuss the energy balance around pumps, condenser, compressor, vaporizers, reactor, and crystallizers.

5.1 Pumps

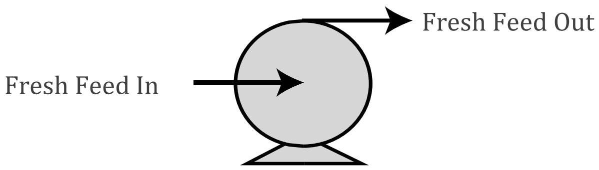


Figure 5.1: Pump

Energy balance over pump is given by the Bernoulli’s equation: [13]

$$\eta Q_{pump} = \dot{m}\left(\Delta Z + \frac{\Delta P}{\rho g} + \frac{v^2}{2g}\right) + Q_{losses}$$

$$\eta Q_{pump} = \dot{m}\left(\frac{\Delta P}{\rho g}\right)$$

$$Q_{pump} = \frac{\dot{m}}{\eta}\left(\frac{\Delta P}{\rho}\right)$$

An isentropic efficiency of 75% is assumed for calculations.

Table 12: Feed pump Energy Balance

P-101		IN	OUT
Temperature	**°C**	60	60
Pressure	**bar**	1	7
Density	**g/cm³**	0.86	0.86
Mass Flow Rate	**kg/h**	1290.9	1290.9
Duty	**kW**	**1**	

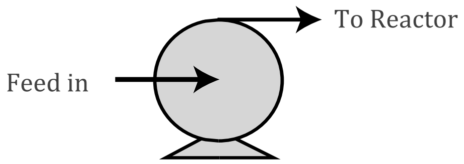


Figure 5.2: Pump to Reactor

Table 13: Pump to Reactor Energy Balance

P-102		IN	OUT
Temperature	**°C**	60	60.7
Pressure	**bar**	7	15
Density	**g/cm³**	0.98	0.98

Mass Flow Rate	**kg/h**	4166.67	4166.67
Duty	**kW**	**2**	

5.2 Condensers

5.2.1 Condenser 1

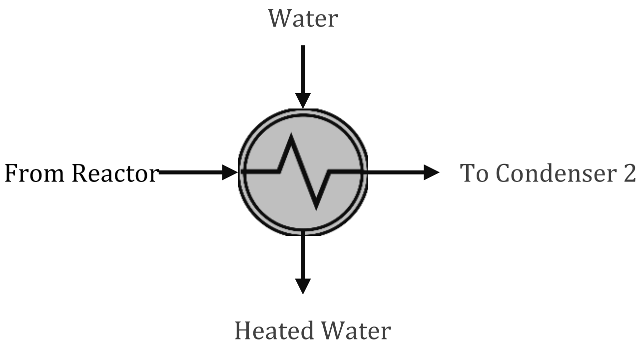


Figure 5.3: Reactor condenser 1

The following heat balance equation is used: [13]

$$Q = \dot{m}\,(\Delta H)$$

$$Q = \dot{m}\,C$$

$$p(\Delta T) + Hl$$

Table 14: Condenser 1 Energy Balance

E-101					
		Shell Side		**Tube Side**	
	Units	**In**	**Out**	**In**	**Out**
Vapor fraction		0	0	1	0.97
Temperature	**^{o}C**	25	94	200	130

Pressure	**bar**	1	1	15	5
Mass flow	**kg/h**	2500	2500	6598.2	6598.2
Heat capacity	**kJ/kmol.K**	4.2		44.8	
Latent Heat	**kJ/kg**	–		1273	
Energy (Q)	**kW**	**202.7**		**-202.7**	

5.2.2 Condenser 2

Table 15: Condenser 2 Energy Balance

E-102					
		Shell Side		**Tube Side**	
	Units	**In**	**Out**	**In**	**Out**
Vapor fraction		0	0	0.97	0.85
Temperature	**ºC**	25	86.1	130	105
Pressure	**bar**	1	1	5	4.5

Mass flow	**kg/h**	4500	4500	6598.2	6598.2
Heat capacity	**kJ/kmol.K**	4.2		44.93	
Energy (Q)	**kW**	**322**		**-322**	

5.2.3 Condenser 3

Table 16: Condenser 3 Energy Balance

E-103					
		Shell Side		**Tube Side**	
	Units	**In**	**Out**	**In**	**Out**
Vapor fraction		0	0	0.85	0.81
Temperature	**ºC**	25	86	105	80
Pressure	**bar**	1	1	4.5	4
Mass flow	**kg/h**	2200	2200	6598.2	6598.2
Heat capacity	**kJ/kmol.K**	4.2		44.93	
Energy (Q)	**kW**	**157.1**		**-157.1**	

5.2 Vaporizers

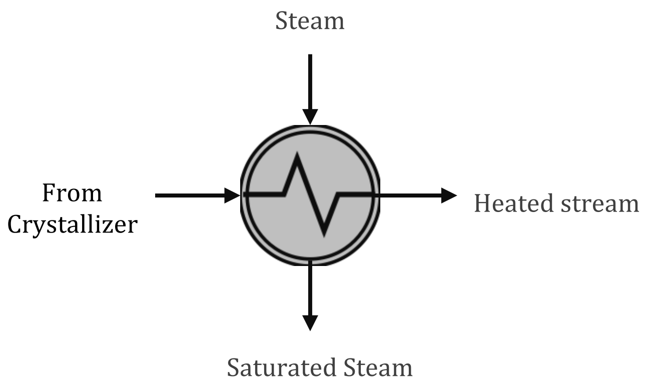


Figure 5.4: Vaporizer

The heat balance of a vaporizer is given by:

$$Q = \dot{m}\,(\Delta H)$$

For steam = Hl

Table 17: Vaporizer 1 Energy Balance

E-105					
		Shell Side		**Tube Side**	
	Units	**In**	**Out**	**In**	**Out**
Vapor fraction		1	0	0	0.3
Temperature	**^oC**	159	159	30	91.8
Pressure	**bar**	5	5	1	1
Mass flow	**kg/h**	134	134	598.98	598.98
Latent Heat	**kJ/kg**	2610		531.9	
Energy (Q)	**kW**	**- 97.2**		**97.2**	

Table 18: Vaporizer 2 Energy Balance

E-106					
		Shell Side		**Tube Side**	
	Units	**In**	**Out**	**In**	**Out**
Vapor fraction		1	0	0.3	1
Temperature	**^oC**	159	159	91.8	128
Pressure	**bar**	5	5	1	1

Mass flow	**kg/h**	13.8	13.8	598.98	598.98
Latent Heat	**kJ/kg**	2610		531.9	
Energy (Q)	**kW**	**-10**		**10**	

5.3 **Compressor**

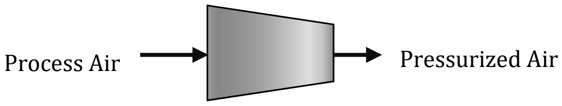


Figure 5.5: Compressor

The energy of a compressor is given by: $W = \dot{m}\ (\Delta H)$

Table 18: Compressor Energy Balance

K-100			
	Units	**In**	**Out**
Vapor fraction		1	1
Temperature	**^{o}C**	25	200
Pressure	**bar**	1	18
Mass flow	**kg/h**	4376.19	4376.19
Molar enthalpy	**kJ/kg**	-0.56	358.7

Work (W)	**kW**	**70**

5.4 Material and Energy Balance

5.5.1 Reactor

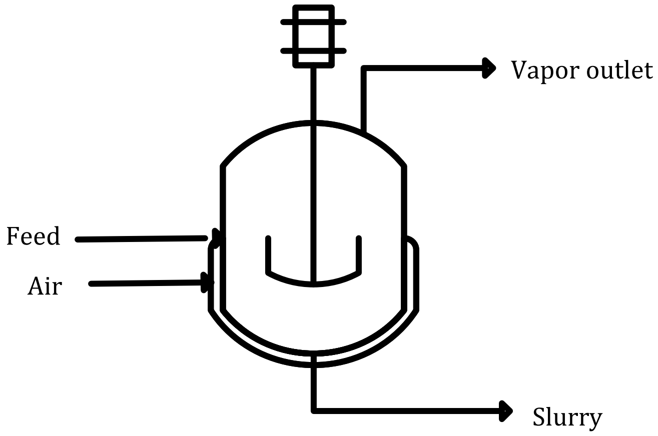


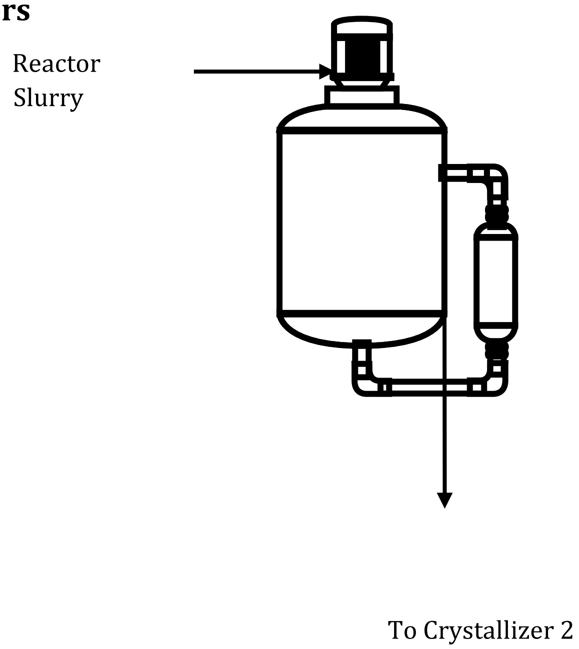
Figure 5.6: Continuously stirred tank reactor

Table 19: Reactor Material and Energy Balance

R-101		IN		OUT	
		Feed	**Air**	**Reactor Slurry**	**To Reactor Condenser**
Temperature	**°C**	60.7	200	200	200
Pressure	**bar**	15	18	15	15
Latent Heat	**kJ/kg**	425.5	29.2	322.2	30.6
Enthalpy	**kJ/kg**	-5253	$-2.6\text{x}10^{-14}$	-4504	–

Mass Flow Rate	**kg/h**	4490.64	4376.19	2267.8	6598.2
Heat of reaction	**kJ/mol**	**624**			
Duty	**kW**	**749**			

5.5.2 Crystallizers



Data for crystallizer energy balance:

Heat of crystallization: – 816.3 kJ/mol

Cp of solid: 199.6 J/mol.K

Energy Balance of crystallizer is carried out using the following equation:

$$Q = \dot{m}\ (\Delta H)$$

Table 20: Crystallizer 1 Material and Energy Balance

C-101		IN	OUT
		Reactor Slurry	**To Crystallizer 2**
Temperature	**^{o}C**	200	150

Pressure	**bar**	15	12
Enthalpy	**kJ/kg**	-4610.07	-4789.07
Mass Flow Rate	**kg/h**	2267.8	2267.8
Duty	**kW**	**179**	

Table 21: Crystallizer 2 Material and Energy Balance

C-102		IN	OUT
		To Crystallizer 2	**To Crystallizer 3**
Temperature	**^{o}C**	150	90
Pressure	**bar**	12	4.5
Enthalpy	**kW**	-4789.07	-4965.6
Mass Flow Rate	**kg/h**	2267.8	2267.8
Duty	**kW**	**176.5**	

5.7 Overall Energy Balance

Table 22: Overall Energy Balance

	Out

		Reactor Condenser 1	Reactor Condenser 2	Reactor Condenser 3	Crystallizer 1	Crystallizer 2	Crystallizer 3
Temp	°C	130	105	80	150	90	30
Pressure	**bar**	5	4.5	4	12	4.5	1
Heat Capacity	**kJ/kmol.K**	44.8	44.93	44.93	199.6	199.6	199.6
Mass Flow Rate	**kg/h**	6598.2	6598.2	6598.2	2267.8	2267.8	2267.8
Duty	**kW**	**202.7**	**322**	**157.1**	**179**	**176.5**	**66.9**

CHAPTER 6

EQUIPMENT DESIGN

This chapter will discuss the design calculations for the major equipment in the paraxylene oxidation plant.

6.1 Design of a reactor

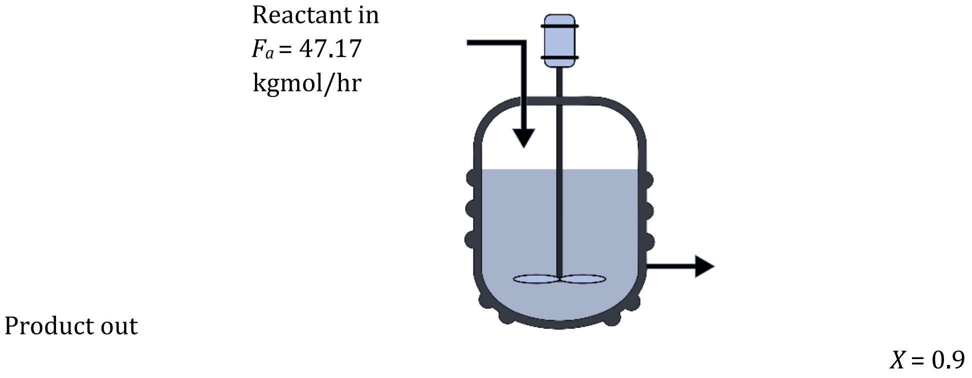


Figure 6.1: CSTR

A continuously stirred tank reactor is employed for the oxidation reaction. The first step is to calculate the rate of reaction, –rA using the rate equation for the oxidation of paraxylene by the AMOCO process. The exact rate equation may vary depending on the specific catalyst and conditions used, a simplified rate equation for this reaction is as follows: [10]

$$-rA = k * C_p * (1 - X)^n$$

Where: k is the rate constant

C_p is the concentration of paraxylene

n is the reaction order

(1-X) is the fraction of unreacted paraxylene

The following data is available from literature:

$X = 0.9$

$C_p = 2.06$ kgmol/m^3 $k = 0.52$/hr for

1200 rpm and 200 ^oC $n = 0.65$

Result:

$-rA = 0.52 * 2.06 * (1 - 0.9)^{0.65}$

$-rA = 0.2358$ kgmol/m^{3}hr

The next step is to calculate reactor volume. The design equation for a CSTR is as follows: $V = \frac{F \times X}{-rA}$

Where, V is the reactor volume

F is the flow rate of paraxylene

X is the fractional conversion of paraxylene

–rA is the rate of reaction per unit volume of the reactor

Data available from literature:

$X = 0.9$

$-rA = 0.2358$ kgmol/m^{3}hr

$F_a = 47.17$ kgmol/hr

Result:

$$\mathbf{V = 180.2\,m^3}$$

The final step is to calculate reactor parameters.

Assuming an optimum height to diameter ratio of 3:1, we can calculate the dimensions of the CSTR as follows: [10]

$$V = \frac{\pi}{4}(D^2)(H)$$

$$\frac{H}{D} = 3$$

$V = 0.75 * \pi * D^3$

$D^3 = (180.2) / (0.75 * \pi) = 76.468\ \mathrm{m}^3$

$D = (76.468\ \mathrm{m}^3)^{(1/3)} = 4.011\ \mathrm{m}$

$H = 3D = 12.033\ \mathrm{m}$

Table 23: Summary of Reactor Design

Reactor type	Continuously stirred tank reactor
Operation	Continuous
Catalyst	Co/Mn/Br
Material	Stainless steel with titanium lining
Stirring rate	1200 rpm
Height	12.03 m
Diameter	4.011
Volume	180.2 m^3
Flow	8866.3 kg/hr

6.2 Design of heat exchanger

Design of heat exchanger is as follows:

Table 24: Shell-side Specifications

Inlet temp (t1) °C	25
Outlet temp (t2) °C	84.65
Mass flow Rate kg/h	2500
Specific heat kJ/(kg.K)	4.18
Thermal Conductivity W/(m.K)	0.6370
Viscosity (cP)	0.39
Shell diameter (in)	8.07
Segmented Cut	25
Baffle Spacing (in)	6.75

Table 25: Tube-side Specifications

Inlet temp (t1) °C	200
Outlet temp (t2) °C	130.12
Mass flow Rate kg/h	6598
Specific heat kJ/(kg-K	1.165
Thermal Conductivity W/(m-K)	0.039
Viscosity (cP)	0.0223
tube diameter (in)	0.75
BWG	14
Pitch (in)	0.937
No of tubes	55
Length (in)	72

The shell and type exchanger is BEM type. Therefore, this exchanger typically has two passes on shell side and one pass on tube side.

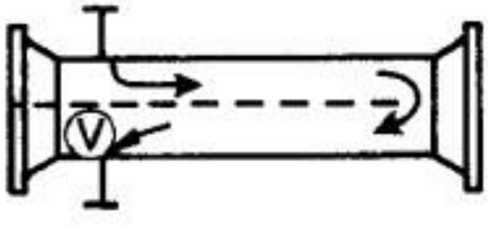


Figure 6.2: Passes in a BEM type exchanger [10]

This exchanger is designed by Kern's method comprising of fourteen steps.

Heat balance *Equation*

1:

$$\boldsymbol{Q = mC_P\Delta T}$$

This is the most fundamental equation used in heat exchanger design.

Hot stream:

$$Q = 6598 * 1.1615(69.88)$$

$$Q = 535530.76\ kJ/hr$$

Cold stream:

$$Q = 2500 * 4.12(59.65)$$

$$Q = 535530.76\ kJ/hr$$

LMTD:

Equation 2:

$$LMTD = (\Delta T_2 - \Delta T_1)/\ ln(\Delta T_2/\Delta T_1)$$

Table 26 LMTD

Uncorrected	111.27
True LMTD	110.01

R= 1.17

S=0.399

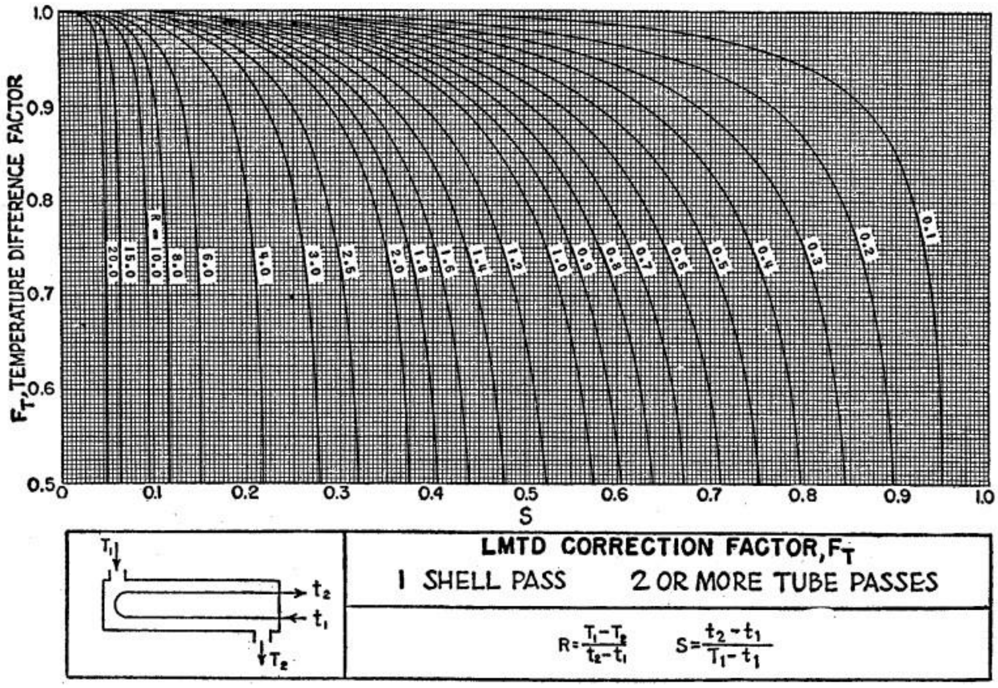


Figure 6.3: LMTD Correction factor

From the figure

$$F_T = 0.744$$

$$\Delta t = F_T * LMTD$$

$$\Delta t = 82.04°\text{C}$$

$$\frac{\Delta t_c}{\Delta t_h} = 0.91$$

$$k_c = 0.398$$

$$F_c = 0.841$$

$$T_c = 188.88°\text{C}$$

$$\Delta t_c = 75.16°\text{C}$$

Shell side calculations:

Flow area

$$\alpha_s = \frac{ID* \quad *C''B}{144P_t}$$

$$\alpha_s = \frac{8.07 * 0.187 * 6.75}{144x\ 0.937}$$

$$\alpha_s = 0.07(ft^2)$$

Mass velocity

$$G = \frac{W}{\alpha_S}$$

$$G = 35714.28 \frac{Kg}{ft^2 . Hr}$$

Reynolds number

$$Re = \frac{DeG}{\mu}$$

$$Re = 4172$$

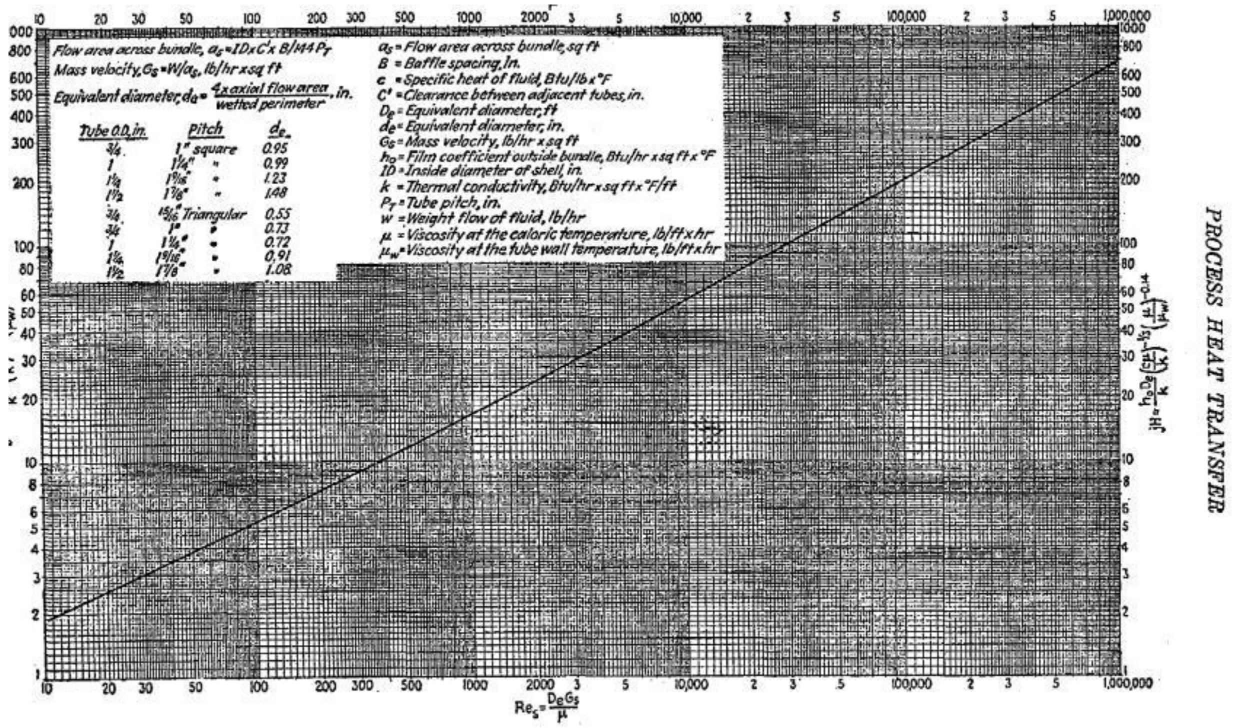


Figure 6.4: jH factor for shell side calculations

From the graph

$$Jh = 27$$

$$\left(\frac{c\mu}{k}\right)^{\frac{1}{3}} = 1.41$$

$$\frac{h_0}{\varphi_S} = jh \frac{K}{D_e} \left(\frac{c\mu}{k}\right)^{\frac{1}{3}}$$

$$\frac{h_0}{\varphi_s} = 532.21\left(\frac{KJ}{Hr.ft^2.°C}\right)$$

$$tw = tc + \frac{ho/\varphi s}{hio/\varphi t + ho/\varphi s}(Tc - tc)$$

$$t_w = 158.6°C$$

Tube side calculations:

Flow area

$$\alpha_t = \frac{N_t\alpha_t}{144n}$$

$$\alpha_t = 0.09ft^2$$

Mass velocity

$$W = G/\alpha_t$$

$$W = 73311.11\,\frac{Kg}{ft^2.Hr}$$

Reynolds number

$$Re = \frac{DeG}{\mu}$$

$$Re = 122185.18$$

$$\frac{L}{D} = 150$$

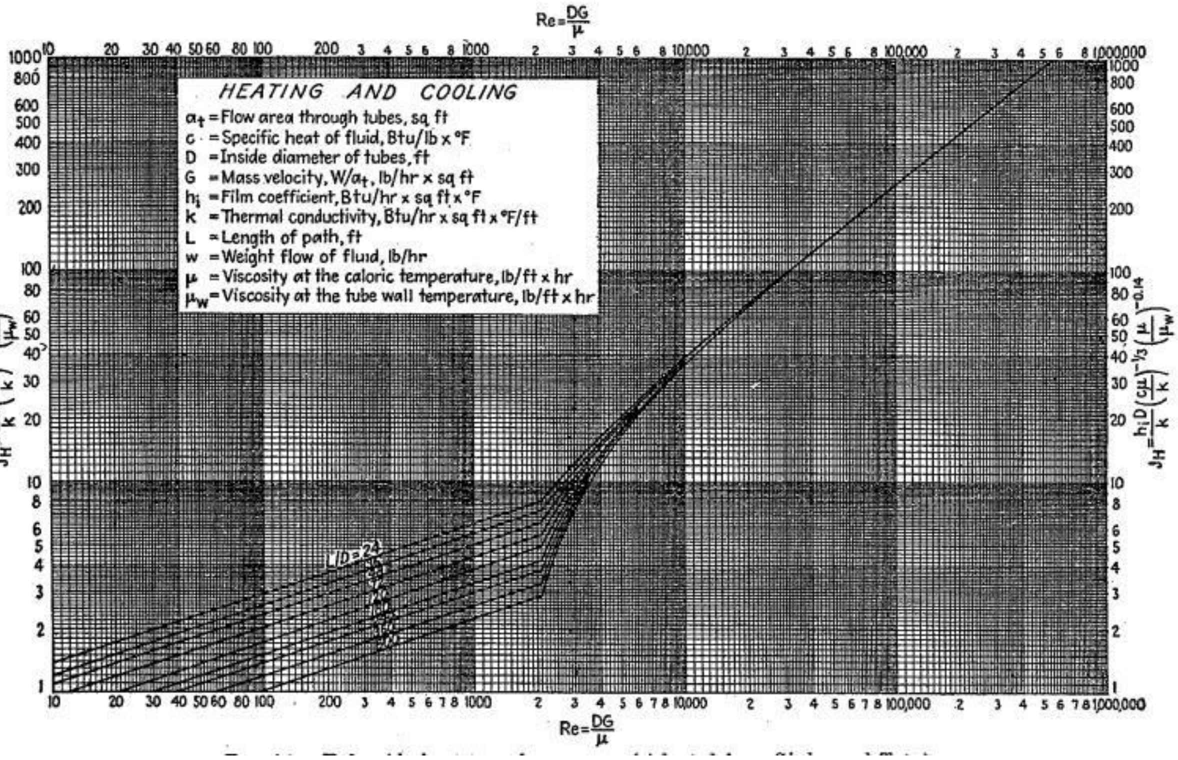


Figure 6.5: jH factor for tube side calculation

From the graph

$$jH = 280$$

$$\left(\frac{c\mu}{K}\right)^{\frac{1}{3}} = 0.89$$

$$\frac{h_i}{\varphi_t} = jh\,\frac{K}{D}\left(\frac{c\mu}{k}\right)^{\frac{1}{3}}$$

$$\frac{h_i}{\varphi_t} = 249.2\left(\frac{kJ}{hr\,.\,ft^2.℃}\right)$$

$$\frac{h_{io}}{\varphi_t} = \frac{h_i}{\varphi_t} * \frac{ID}{OD}$$

$$\frac{h^{io}}{\varphi_t} = 192.7(\frac{KJ}{Hr.ft^2.°C})$$

Overall exchanger calculations

Clean overall coefficients

$$U_c = \frac{hio + ho}{hioho}$$

$$Uc = 157.1(\frac{KJ}{.ft\,Hr}{}^2.°C)$$

Cross-sectional area

$$A = 64.779ft^2$$

Dirt overall coefficient

$$\frac{1}{U_D} = \frac{1}{U_C} + R$$

$$\frac{1}{U_D} = 100.7(\frac{KJ}{Hr.ft^2.°C})$$

Dirt factor

$$R = 0.003$$

Pressure drop calculations

Shell side

$$Number\ of\ crosses = N + 1 = 12L/B$$

$$N + 1 = 10.66$$

$$\Delta P_s = fG_s^2D_s(N + 1)/5.22 \times 10^{10}D_es\varphi_s$$

$$\Delta P_s = 2.59psi$$

Tube side

$$\Delta P_t \quad \underline{\qquad\qquad} \quad = f G_{t2} L n \quad {}_{10} D_e s \varphi_t$$

$$\times 10$$

$$5.22$$

$$\Delta P_t = 0.01$$

$$P_t = 1.42\ psi$$

$$\Delta P = 1.43 Psi$$

6.3 Designing of an HP Absorber

An absorption column is a crucial unit operation used in chemical engineering to separate components of a gas mixture based on their differing solubilities in a liquid phase. It is commonly employed in various industrial processes, such as gas purification, air conditioning, and acid gas removal.

Working Principle of an Absorption Column in Chemical Engineering

The absorption column consists of a vertical tower packed with suitable packing material or with trays. Installation of packing and trays divides the column into two major types. The gas mixture, which contains the desired component to be absorbed, enters the bottom of the column, while a liquid solvent or absorbent is introduced at the top. As the gas rises through the column, it meets the descending liquid stream. Mass transfer occurs between the gas and liquid phases, allowing the desired component to dissolve or be absorbed into the liquid phase. [10]

In terms of process control, absorption columns are typically operated in either a cocurrent or counter-current flow arrangement. In co-current flow, the gas and liquid flow in the same direction, while counter-current flow involves opposing directions. Countercurrent flow is often preferred due to its higher efficiency, allowing for greater separation between components.

The design of an absorption column aims to maximize the contact between the gas and liquid phases to enhance mass transfer. This is achieved by choosing suitable packing materials or tray designs that provide a large interfacial area for effective interaction between the phases. The column may also incorporate additional features such as redistributors and liquid or vapor distributors to ensure uniform flow distribution.

Efficiency

The efficiency of the absorption process depends on several factors:

- Physical properties of the gas and liquid phases.
- Choice of absorbent.
- Design and operating parameters of the column.

Selection of solvent

The selection of an appropriate absorbent is crucial to achieve high separation efficiency. Commonly used absorbents include water, amines, glycols, and various organic solvents, depending on the specific application.

Examples:

- Acid gas removal
- Solvent recovery
- Air pollution control
- Dehydration of natural gas
- Refrigeration and air conditioning

An absorption column was used for the recovery of air and other gases. Packings were installed for the following reasons:

1. Small trays are expensive to fabricate; packed towers are more frequently used for columns with diameters less than or equal to 8 feet.
2. The pressure drop experienced in a packed column is generally lower compared to a plate column. This is because plate columns have additional friction caused by vapor passing through the liquid on each tray. When the tower contains a significant number of plates, the pressure drop can become considerable. In such cases, opting for a packed column can result in substantial cost savings. [10]
3. The presence of liquid on each plate in a plate column can result in a significant accumulation of liquid. In contrast, a packed tower allows the liquid to flow as a thin film over the packing material. This difference in liquid distribution between plate and packed columns leads to distinct hydrodynamic characteristics in the two types of columns. [10]

Designing steps of the absorption column

The design includes several fundamental steps:

- Selection of packing material/trays

- Size of packing
- Number of stages (trays/packings)
- Calculation of column diameter
- Height of packing
- Degree of wetting
- Calculation of pressure drop at flooding region
- Calculation of liquid holdup

The packed bed absorption tower was based on the solubility of oxygen in acetic acid since the solubility statistics for oxygen, nitrogen, and water reveal that oxygen is the least soluble among the three components in acetic acid.

Calculations

Basis: 1 hour operation

Selection of packing material/trays: Silicon; ball type packing.

Size of packing Packing size = $\frac{1*D}{15} = 1 * 1/15 = 0.0666\ m$

Number of packings:

*Columns X and Y refers to mole fractions of oxygen in liquid and gas respectively.

The Mc-Cabe Thiele method was used to calculate the number of packings.
National University of Sciences and Technology

Mass Balance:

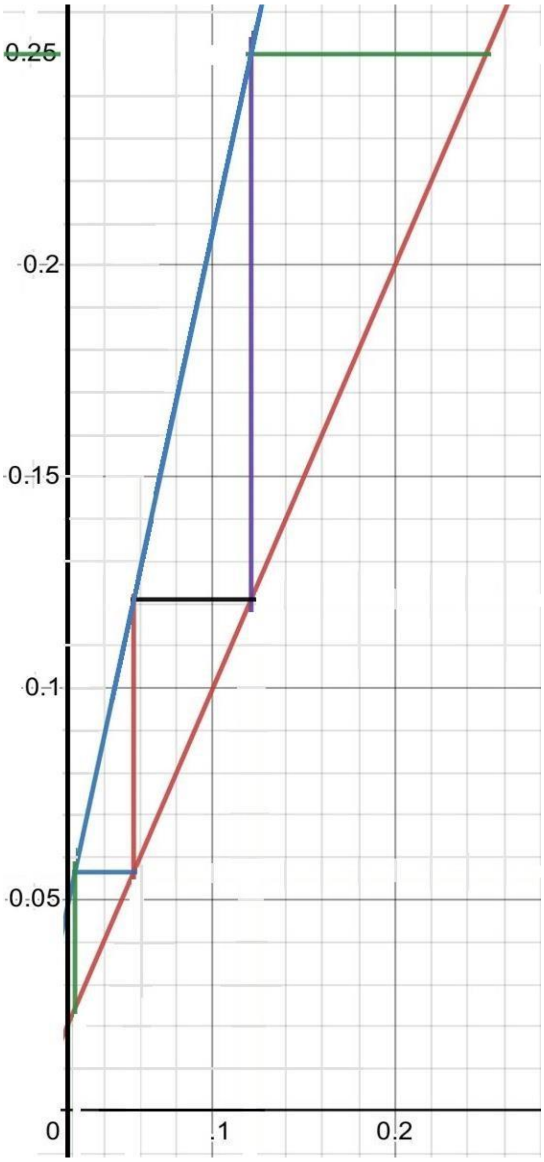
$$Gm\ (Y - Y2) = Lm\ (X - X2)$$

$$107.64(\mathrm{Y} - 0.046) = 215.97(\mathrm{X} - 0.019)$$

$$X = 0.5Y - 0.004$$

Figure 6.6: Plot to find number of stages.

Desmos software was used to plot a graph to find number of packings.



From the graph:

$$N_{OG} = 3$$

Column diameter:

The sizing of randomly packed towers is often based on Sherwood correlations, which provide useful methods for determining tower dimensions. These correlations are commonly utilized to calculate the absorber diameter, taking into account factors such as mass transfer and fluid flow characteristics. *Data was taken at 42°C and 400 kN/m^2

abscisox = $L/G \times \square_v/\square_l$

L = Flow rate of water = 291.463 kg/hr G =

Flow rate of a gas mixture = 11617.6 kg/hr ρ_v

= density of gas stream = 3.979 kg/m^3 ρ_l =

density of acetic acid = 7.573 kg/m^3

$$\frac{\rho_v}{\rho_l} = 0.52$$

$$\frac{L}{G} \times \frac{\rho_v}{\rho_l} = 0.011$$

For silicon packing;

F_p = 1076 m^{-1} K_4 = 1.5 μL = viscosity of

acetic acid = 1.15 kg/m^3

$$G^{*} = \left[\frac{K_4 \rho_v(\rho_l - \rho_v)}{13.1\, F_p\, (\mu L / \rho_l)}\right]^{1/2}$$

G* = 3.979 kgm²/s

A = area of cross-section

A = G/G*

A = 0.8 m²

D = diameter of cross-section

$$D = [4 \times \frac{A}{\pi}]^{1/2}$$

D = 1m

By calculations area and diameter comes out to be **0.8 m²** and **1 m** respectively.

Height of packing

For silicon-ball-type packing:

$$H_{OG} = 1.03 \frac{(G_m)_{0.426}}{(L_m)^{0.425}}$$

Where,

H_{OG} = height of a transfer unit

G_m = gas flow rate, = 0.129 kg.mol/hr.ft^2

L_m = liquid flow rate = 0.04 kg.mol/hr.ft^2

$$\mathbf{H_{OG} = 1.63\ m}$$

$$Z = H_{OG} \overset{*}{N}_{OG}$$

Where,

Z is the height of packing

$$\mathbf{Z = 4.89\ m}$$

Using,

Allowance for liquid distribution = 1.00 m

Allowance for liquid redistribution = 1.00 m

$$\text{Total height of column} = 1.00+1.00+4.89$$

$$\textbf{Total height of column} = \mathbf{6.89 \approx 7}\boldsymbol{m}$$

Degree of wetting

The degree of wetting in an absorption column refers to the extent to which the packing or trays within the column are covered with a liquid film. In the context of chemical engineering, it is a crucial factor that influences the efficiency of mass transfer between the gas and liquid phases.

The design and selection of appropriate column internals, such as trays or packing materials, are crucial for achieving and maintaining a desirable degree of wetting. The geometry and surface properties of the internals influence the liquid distribution and film formation on the packing or trays. Efficient liquid distribution systems, such as liquid distributors and weirs, are employed to ensure uniform coverage of the packing or trays, thus promoting optimal wetting.

It is important to note that achieving an optimal degree of wetting is a balance between providing enough liquid for effective absorption while avoiding flooding or excessive pressure drop. Flooded conditions occur when there is too much liquid, hindering gas flow and compromising mass transfer efficiency.

$$LP = Liquid\ rate/surface\ area\ of\ packing$$

Where,

Liquid rate = 291.463 kg/hr = 0.08 kg/s

Surface area of packing = 69 m^2/m^3

$$LP = 1.2 * 10^{-3} \frac{kg}{msec}$$

Pressure drop at flooding region:

$$\Delta Pflood = 0.108 psi/\, ft\ of\ packing \times height\ of\ packing\ \ \boldsymbol{\Delta Pflood = 1.7 psi = 0.12\ bar}$$

Liquid hold-up:

*4% of packing weight was taken as the liquid hold up for silicon packing.

$$Liquid\ Holdup = 0.04 * \quad * V\rho_B$$

Where,

V = Volume of Packing ρ_B = Bulk density

of packing = 500 kg/m^3

$$V = \frac{\pi}{4} D^2 \times Hp$$

$$V = 3.84 m^3$$

$$Liquid\ Holdup = 0.04 * 3.84 * 500$$

$$\boldsymbol{Liquid\ Holdup = 76.8\ kg\ of\ acetic\ acid}$$

Table 27: Design parameters for absorption column

Design parameter	Specifications
Packing type	Silicon-ball-type packing
Packing size	0.066m

No. of stages	3
Cross section area	0.8 m^2
Column diameter	1m
Height of packing	4.89m
Column height	7m
Degree of wetting	$1.2 * 10^{-3} \frac{kg}{msec}$
Pressure drop	1.7 psi
Liquid hold up	76.8 kg of acetic acid

6.4 Design of a crystallizer

The basic design of a crystallizer requires some data which is summarized in the table below.

Table 28: Crystallizer Data [13]

Feed Rate	2267.5 kg/h
Terephthalic Acid	1639.18 kg/h
Crystals formed	1475.3 kg/h
Solute leaving with mother liquor	163.9 kg/h
Feed Temperature	194 ^{0}C
Feed Pressure	12.6 barg
Feed density	1070 kg/m^3
Feed Volume	2.119 m^3
Ideal size of crystals L_D	100 μm
Crystal growth rate G_c	4.67 x 10^{-9} m/s

The first step in the process is to find required holding time. Required holding time is given by the equation: [10]

$$T_h = \frac{L_D}{3G} = \frac{100\times10^{-6}}{3\times4.67\times10^{-9}}$$

$$T_h = 7137.75 \text{ s} = 1.98 \text{ hours}$$

Next, the working volume of crystallizer is found.

Volume of suspension in the crystallizer at any time = (2.119m^3/h)*(1.98 h) = 4.02 m^3

This is the "working volume" of the crystallizer. Add 60% to account for vapour bubbles and froth.

Effective suspension volume in the crystallizer = (4.02 m^3)*(1.6) = 6.72 m^3

Now to find the diameter of the vessel, an assumption will be made.

Select a **1.5 m** diameter vessel (this will be checked and changed if necessary) with a conical bottom.

Take a cone angle of 45 degrees for the conical bottom.

Volume of the conical part (radius = 0.75 m) of the tank = (π/3)(0.75)^2(1.5) = 0.88 m^3

Volume of the cylindrical part = 6.72 - 0.88 = 5.87 m^3

Height = $\frac{5.87}{(\pi)(0.75)^2}$ = 3.321 m

Add 0.67 m space above the boiling liquid for disengagement of the entrained droplets.

Total length of the cylindrical part of the tank = 3.321 m + 0.67 m = 4 m

Lastly the assumed diameter of the tank is validated.

Data available from literature:

- Absolute pressure in the vapor space = 4.99 atm
- Boiling point of the solution = 380K
- Density of vapor at this temperature and pressure, ρ_v = 0.0957 kg/m^3

Volumetric rate of vapor generation = (6520 kg/h)/(0.0957 kg/m^3) = 6.8 x 10^5 m^3/h

To determine allowable velocity of vapor without risking entrainment, the vapor velocity is found using the following equation:

$$u_v = C_v\left(\frac{\rho_l - \rho_v}{\rho_v}\right)^{1/2} \approx C_v\left(\frac{\rho_l}{\rho_v}\right)^{1/2}$$

For evaporation under vacuum, a conservative value of C_v = 0.0401 m/s is used.

Allowable velocity, u_v = $\frac{0.0401}{(\quad}1071/0.0957)_2$ = 4.4880 m/s

Area required for evaporation = $\frac{6.8 \times 10^5}{(3600)(4.488)_2}$ = 8.38 m^2

Cross-section of the tank = 8.38 m^2. Hence a tank of **1.5 m** diameter is suitable.

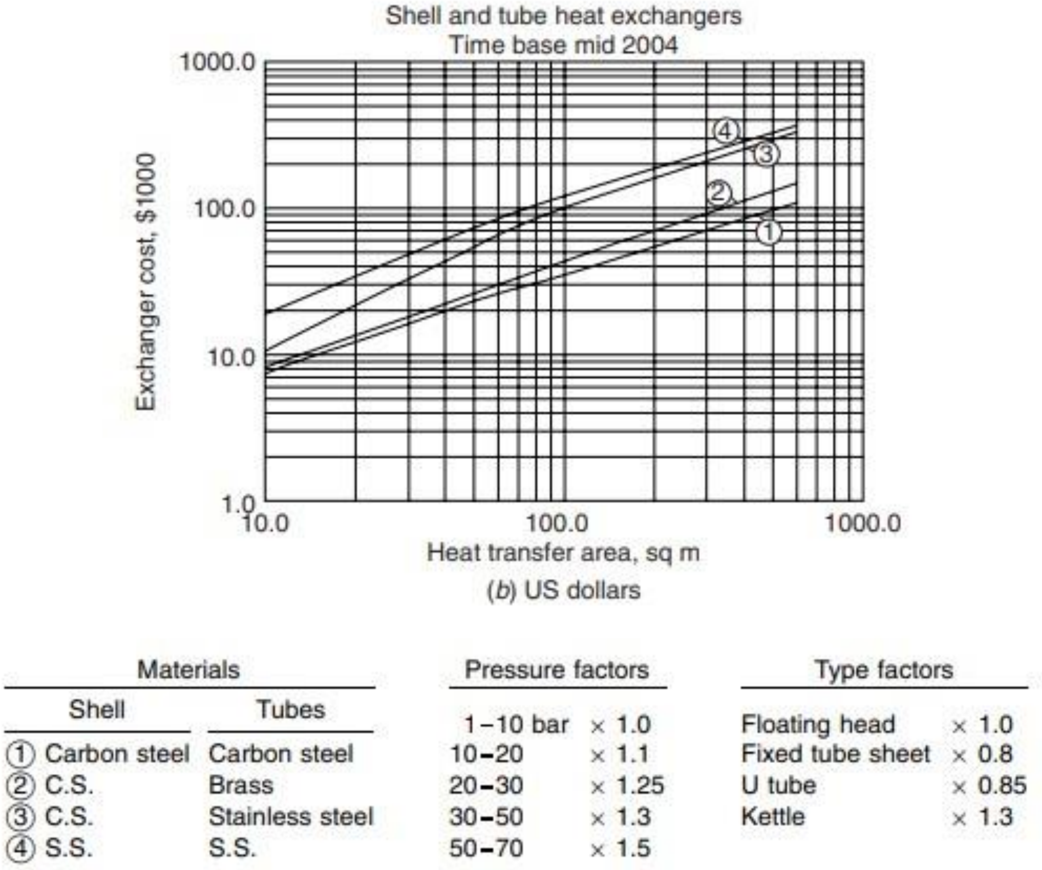
CHAPTER 7

COST ANALYSIS

The economic analysis of the plant is as follows:

7.1 Condensers

This graph below is used for heat exchangers cost estimation.



Materials	
Shell	Tubes
① Carbon steel	Carbon steel
② C.S.	Brass
③ C.S.	Stainless steel
④ S.S.	S.S.

Pressure factors	
1−10 bar	× 1.0
10−20	× 1.1
20−30	× 1.25
30−50	× 1.3
50−70	× 1.5

Type factors	
Floating head	× 1.0
Fixed tube sheet	× 0.8
U tube	× 0.85
Kettle	× 1.3

Figure 7.1: Shell Heat Exchanger Cost Graph [10]

Shell and tube heat exchanger of floating head type.

- Heat transfer area of 64.29 m^2.
- The bare equipment cost is $47,385.
- Using Graph 1, the pressure factor is determined to be 1.3, and the type factor is 1.0.
- To calculate the total cost, we multiply the bare equipment cost by the pressure factor and the type factor:
- Cost = Bare equipment cost * Pressure factor * Type factor

- Cost = $47,385 * 1.3 * 1.0
- Cost = $61,810.50
- Therefore, the total cost of the shell and tube heat exchanger is approximately $61,810.50.
- Since the top three condensers have the same specifications, the cost of each condenser unit would be the total cost multiplied by the number of units:
- Cost of condenser unit = 3 x $61,810.50
- Cost of condenser unit = $185,431.50

Hence, the cost of the condenser unit for the top three condensers would be approximately $185,431.50.

Indexing

To convert a cost from 2004 to 2023 using indexing, appropriate index values for each year are required.

- The index value for the base year (2004) is 100.
- The index value for the target year (2023) is 490.
- Calculate the cost in the target year by dividing the target year index by the base year index and multiplying it by the original cost:
- Cost in 2023 = (Target Year Index / Base Year Index) * Original Cost
- Cost in 2023 = (490 / 100) * 150,500
- Cost in 2023 = $ 61,600

7.2 Pump

The cost of a centrifugal pump with a 1 kW power rating was estimated to be $2500 using the relevant graph from the Colson book, indicating its capital cost. This estimation assumes the accuracy and applicability of the graph within the given context.

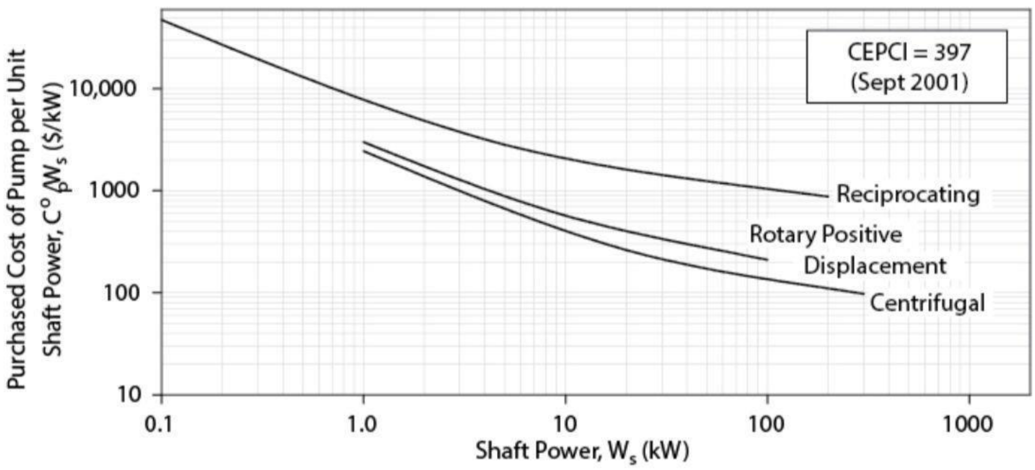


Figure 7.2: PUMP Cost Graph [10]

7.3 HP Absorber

To calculate the cost of an absorber column using the Coulson graphs and table shown below, these steps would be followed:

- Determine the column diameter (D) and packing height (H) based on the given values:

D = 1 m, H = 4.89 m.

- Locate the appropriate row in the Colson table for the equipment type (Absorber) and material of construction.
- Identify the cost factor (CF) based on the operating conditions and the column size parameters (D and H).
- Determine the power values (m and n) for the size parameters (D and H) from the table.
- Calculate the capital cost (C) using the formula: C = CF * (D^m) * (H^n)
- Substitute the given values into the formula: C = CF * (1^m) * (4.89^n)
- Apply the specific values of m and n from the table to the formula.
- Calculate the final capital cost by multiplying the cost factor (CF) by the appropriate size parameters raised to the respective power values.
- For example, if the cost factor (CF) obtained from the table is 10, and the power values are m = 0.5 and n = 0.7, you would calculate the capital cost as follows:
- C = 10 * (1^0.5) * (4.89^0.7) C = 10 * 1 * $2394 (approximately) C = $ 23,940 (approximately)

Thus, the calculated capital cost for the Absorber is approximately $23,940, based on the given column diameter of 1 m and packing height of 4.89 m.

After indexing it comes out to be $ 25,940.

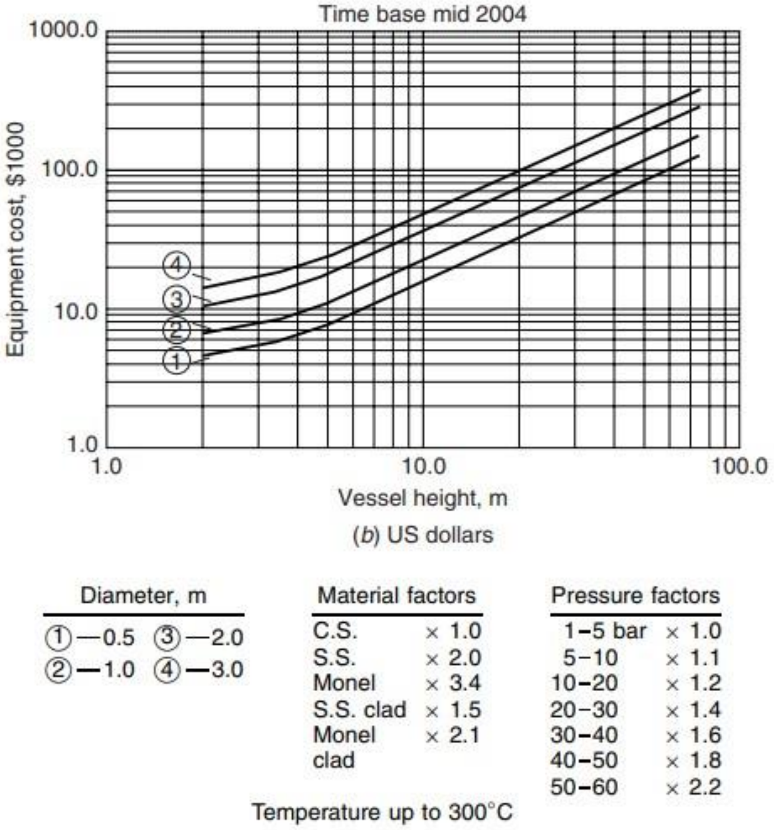
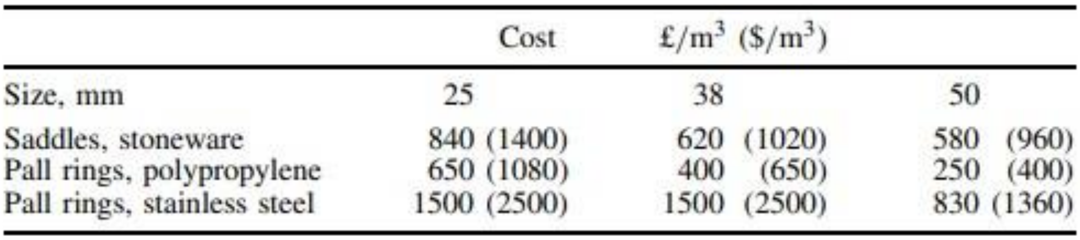


Figure 7.3: Column Cost Graph [10]



	Cost	£/m³ ($/m³)	
Size, mm	25	38	50
Saddles, stoneware	840 (1400)	620 (1020)	580 (960)
Pall rings, polypropylene	650 (1080)	400 (650)	250 (400)
Pall rings, stainless steel	1500 (2500)	1500 (2500)	830 (1360)

Figure 7.4: Packing Cost Graph [10]

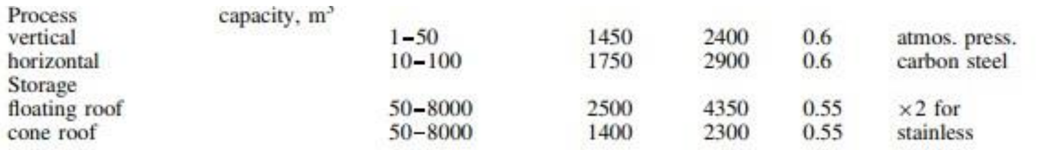
7.4 Reactor

To calculate the cost of a reactor made of stainless steel (SS) with a diameter of 4 m and a height of 12 m, resulting in a total cost of $150,500, follow these steps:

- Determine the reactor diameter (D) and height (H) based on the given values: D = 4 m, H = 12 m.
- Locate the relevant row in the Coulson economic analysis table for reactors made of stainless steel (SS).
- Identify the cost factor (CF) based on the operating conditions and the reactor size parameters (D and H).
- Determine the power values (m and n) for the size parameters (D and H) from the table.
- Calculate the capital cost (C) using the formula: C = CF * (D^m) * (H^n)
- Substitute the given values into the formula: C = CF * (4^m) * (12^n)
- Apply the specific values of m and n from the table to the formula.
- Calculate the final capital cost by multiplying the cost factor (CF) by the appropriate size parameters raised to the respective power values.
- For example, if the cost factor (CF) obtained from the table is 100, and the power values are m = 0.6 and n = 0.8, you would calculate the capital cost as follows:
- C = 100 * (4^0.6) * (12^0.8) C = 100 * 2.297 * 8.859 (approximately) C = $150,500 (approximately)

Thus, the calculated capital cost for the stainless-steel reactor with a diameter of 4 m and a height of 12 m is approximately $150,500

Vessel Cost Graph [10]



Process	capacity, m^3					
vertical		1–50	1450	2400	0.6	atmos. press.
horizontal		10–100	1750	2900	0.6	carbon steel
Storage						
floating roof		50–8000	2500	4350	0.55	×2 for
cone roof		50–8000	1400	2300	0.55	stainless

Using the above table, cost of a feed mix drum comes out to be $ 5,513 and the cost of a solvent tank comes out to be $ 3,166.

7.5 Purchased cost of equipment

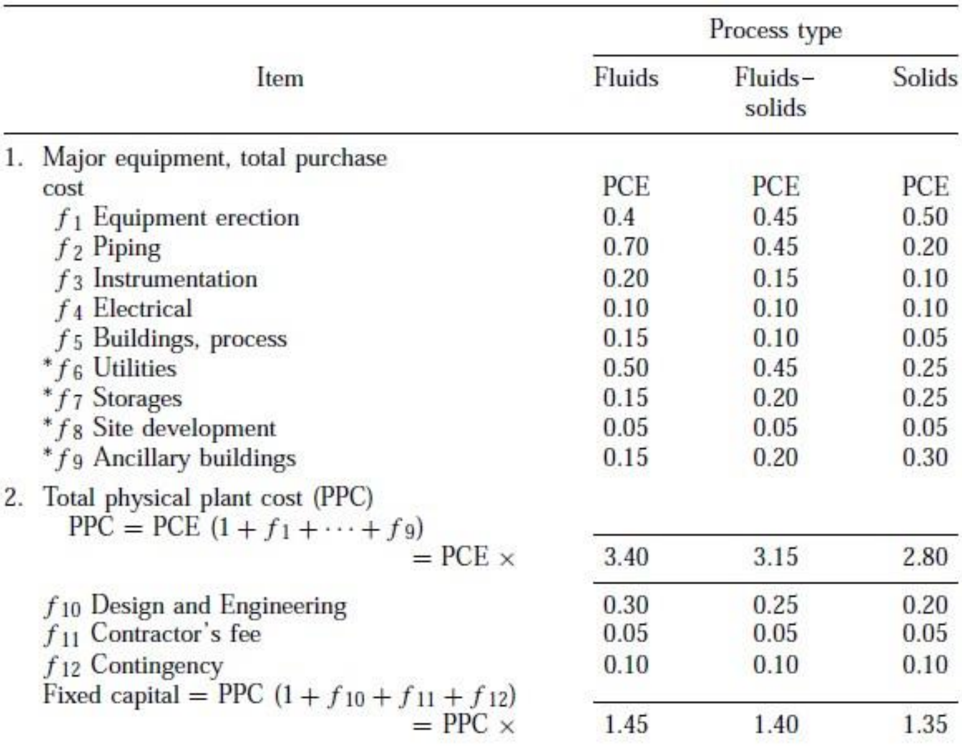
Table 29: Purchased cost of equipment

Pump	$ 2,500
Pump to Reactor	$ 1,500
Compressor	$ 21,770
Dehumidifier	$ 10,000

Feed Tank	$ 5,513
Reactor	$ 209,500
Condenser 1	$ 61,600
Condenser 2	$ 61,600
Condenser 3	$ 61,600
Crystallizer 1	$ 25,000
Crystallizer 2	$ 25,000
Crystallizer 3	$ 25,000
Vaporizer 1	$ 35,200
Vaporizer 2	$ 35,200
HP Absorber	$ 25,940
Waste Absorber	$ 11,370
Dehydration Column	$ 8,600
Solvent Tank	$ 3,166
Total PCE	**$ 6.3 million**

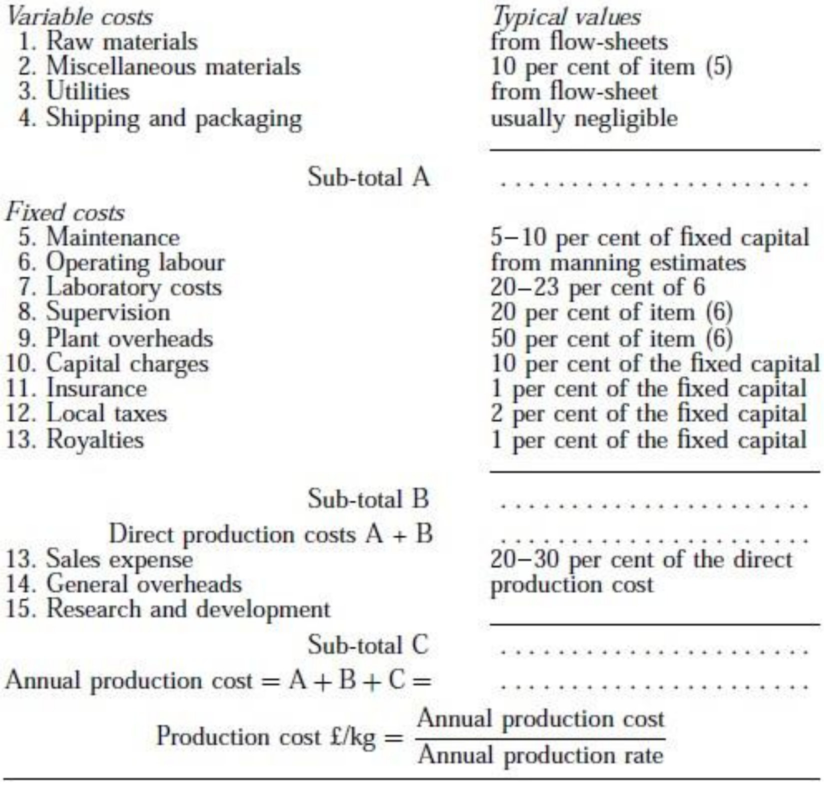
7.6 Physical Plant Cost

Table 30: Physical plant Cost [10]



Item	Process type		
	Fluids	Fluids–solids	Solids
1. Major equipment, total purchase cost	PCE	PCE	PCE
f_1 Equipment erection	0.4	0.45	0.50
f_2 Piping	0.70	0.45	0.20
f_3 Instrumentation	0.20	0.15	0.10
f_4 Electrical	0.10	0.10	0.10
f_5 Buildings, process	0.15	0.10	0.05
*f_6 Utilities	0.50	0.45	0.25
*f_7 Storages	0.15	0.20	0.25
*f_8 Site development	0.05	0.05	0.05
*f_9 Ancillary buildings	0.15	0.20	0.30
2. Total physical plant cost (PPC) PPC = PCE $(1 + f_1 + \cdots + f_9)$ = PCE ×	3.40	3.15	2.80
f_{10} Design and Engineering	0.30	0.25	0.20
f_{11} Contractor's fee	0.05	0.05	0.05
f_{12} Contingency	0.10	0.10	0.10
Fixed capital = PPC $(1 + f_{10} + f_{11} + f_{12})$ = PPC ×	1.45	1.40	1.35

Table 31: Summary of Production costs [10]



Variable costs	*Typical values*
1. Raw materials	from flow-sheets
2. Miscellaneous materials	10 per cent of item (5)
3. Utilities	from flow-sheet
4. Shipping and packaging	usually negligible
Sub-total A	....
Fixed costs	
5. Maintenance	5–10 per cent of fixed capital
6. Operating labour	from manning estimates
7. Laboratory costs	20–23 per cent of 6
8. Supervision	20 per cent of item (6)
9. Plant overheads	50 per cent of item (6)
10. Capital charges	10 per cent of the fixed capital
11. Insurance	1 per cent of the fixed capital
12. Local taxes	2 per cent of the fixed capital
13. Royalties	1 per cent of the fixed capital
Sub-total B	....
Direct production costs A + B	....
13. Sales expense 14. General overheads 15. Research and development	20–30 per cent of the direct production cost
Sub-total C	....
Annual production cost = A + B + C =	....

$$\text{Production cost £/kg} = \frac{\text{Annual production cost}}{\text{Annual production rate}}$$

Table 32: PPC

Equipment Erection	0.45
Piping	0.45
Instrumentation	0.15
Electrical	0.10

Process	0.10
Storages	0.20
Utilities	0.45
Physical Plant Cost	**$ 18.2 million**

7.7 Fixed Capital

Table 33: Fixed cost

Design and Engineering	0.3
Contingencies	0.1
Contractor's fees	0.05
Total	**$ 26.5 million**

Raw Materials

The two main reactants are paraxylene and oxygen. Paraxylene is available at a cost of \$0.45/lb while compressed oxygen at a pressure of 2.0 MPa is available at a cost of \$.07/lb. Acetic acid, is bought at \$0.23/lb and recycled throughout the process to minimize the amount of free acetic acid needed

Variable operating cost

Table 34: Variable operating cost

Raw material	$ 14.2 million
Miscellaneous	$ 0.133 million
Utilities	$ 8.5 million
Total	**$ 22.8 million**

7.8 Fixed operating Cost

Table 35: Fixed operating cost

Maintenance	$ 1.3 million
Operating Labor	$ 2 million
Supervision	$ 0.265 million

Laboratory	$ 0.265 million
Plant Overheads	$ 0.663 million
Capital Charges	$ 2.65 million
Insurance	$ 0.265 million
Local Taxes	$ 0.265 million
Total	**$ 7.67 million**

The plant incurs an annual operating cost of $7.67 million.

Crude terephthalic acid is produced and transported as a solid at a price of $0.60/lb.

7.9 Economic Analysis Summary

Table 36: Whole Plant Summary

Purchased Equipment Cost (PCE)	$ 6.3 million
Physical Plant Cost (PPC)	$ 18.2 million
Fixed Capital	$ 26.6 million
Fixed Operating Cost	$ 7.67 million
Variable Operating Cost	$ 22.8 million
Annual Operating Cost	$ 30.47 million
Annual Revenue	$ 73 million
Annual profit	$ 16.3 million
Payback Time	**3.5 years**

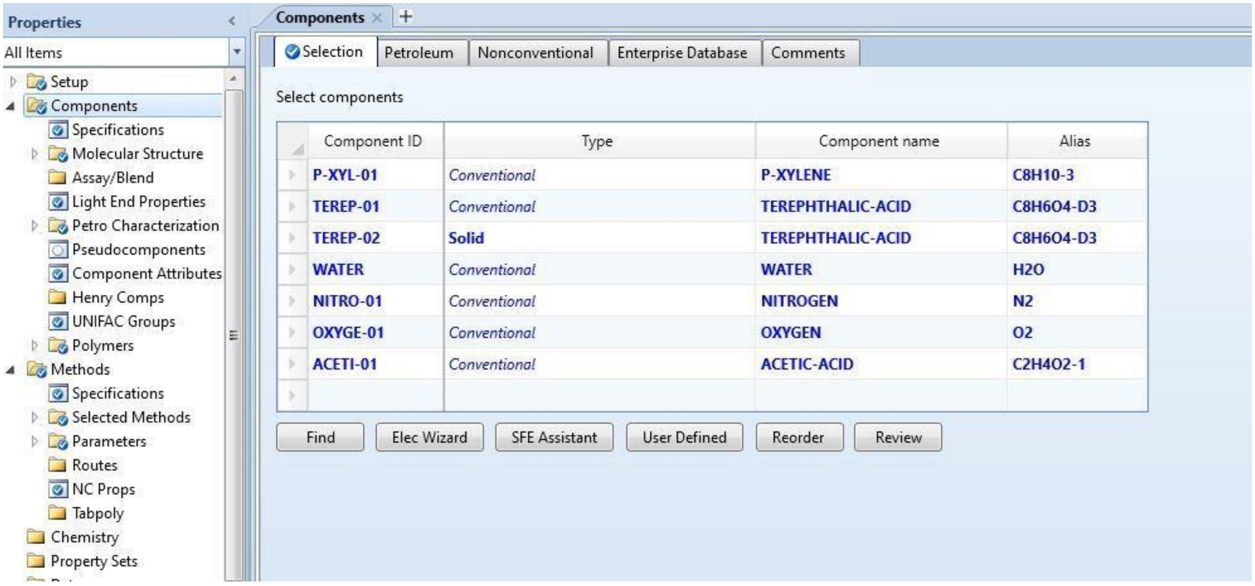
CHAPTER 8

SIMULATION

To simulate and analyze the production process of CTA (terephthalic acid) from paraxylene in our project, we utilized Aspen Plus software. The simulation incorporated a crystallizer unit to accurately model the crystallization step. By employing Aspen Plus, we were able to study the process parameters, optimize operating conditions, and evaluate the overall performance of the CTA production plant.

8.1 COMPONENT LIST

The provided screenshot displays the list of components that have been included in the simulation.



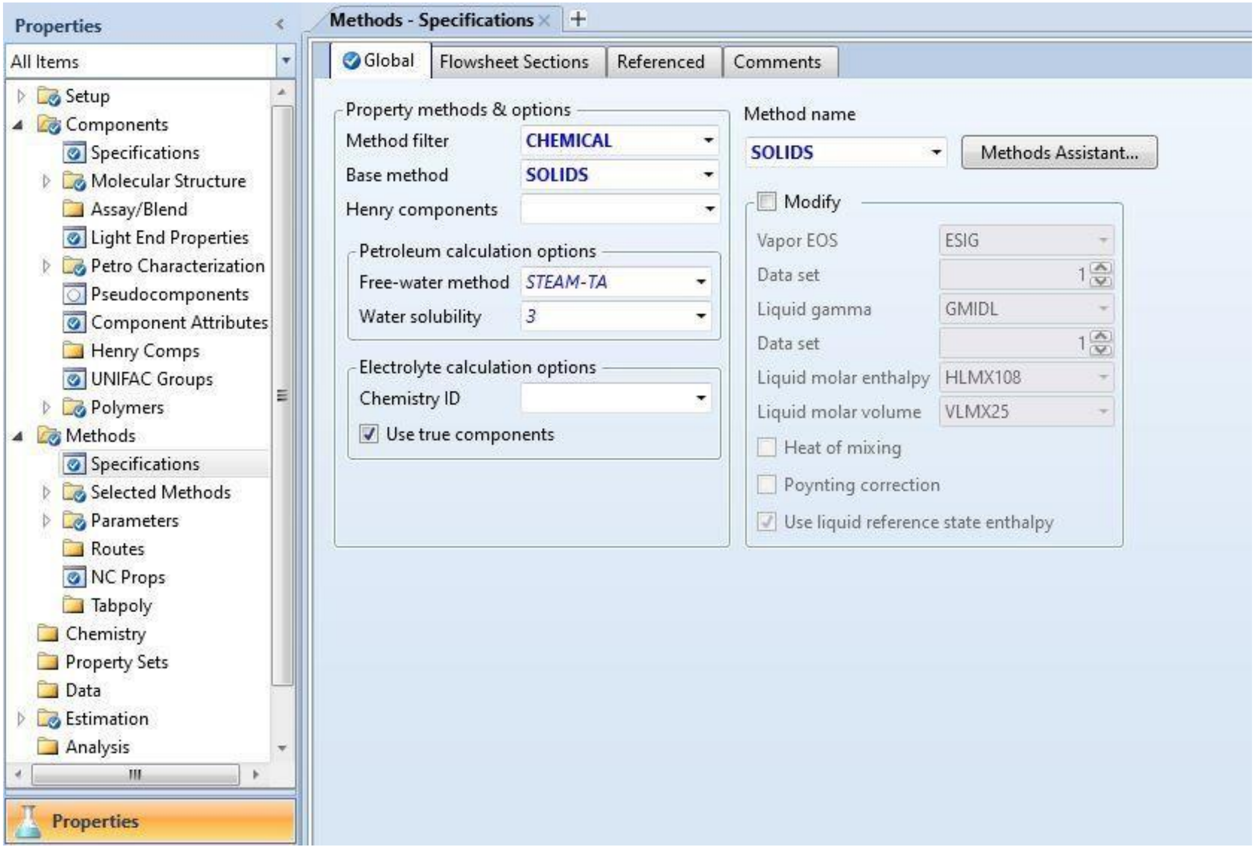
Select components

Component ID	Type	Component name	Alias
P-XYL-01	Conventional	P-XYLENE	C8H10-3
TEREP-01	Conventional	TEREPHTHALIC-ACID	C8H6O4-D3
TEREP-02	Solid	TEREPHTHALIC-ACID	C8H6O4-D3
WATER	Conventional	WATER	H2O
NITRO-01	Conventional	NITROGEN	N2
OXYGE-01	Conventional	OXYGEN	O2
ACETI-01	Conventional	ACETIC-ACID	C2H4O2-1

Figure 8.1: Component List

8.2 Property Package

In the subsequent step, we opted for the property package specifically designed for solids within Aspen Plus. This decision was made to account for the presence of a crystallizer unit in our process. By selecting the appropriate property package, we were able to accurately model and analyze the behavior of solid components during the crystallization process, ensuring a comprehensive and realistic simulation of the overall system.



Property methods & options

Method filter: CHEMICAL

Base method: SOLIDS

Henry components:

Petroleum calculation options

Free-water method: STEAM-TA

Water solubility: 3

Electrolyte calculation options

Chemistry ID:

☑ Use true components

Method name: SOLIDS

☐ Modify

Vapor EOS: ESIG

Data set: 1

Liquid gamma: GMIDL

Data set: 1

Liquid molar enthalpy: HLMX108

Liquid molar volume: VLMX25

☐ Heat of mixing

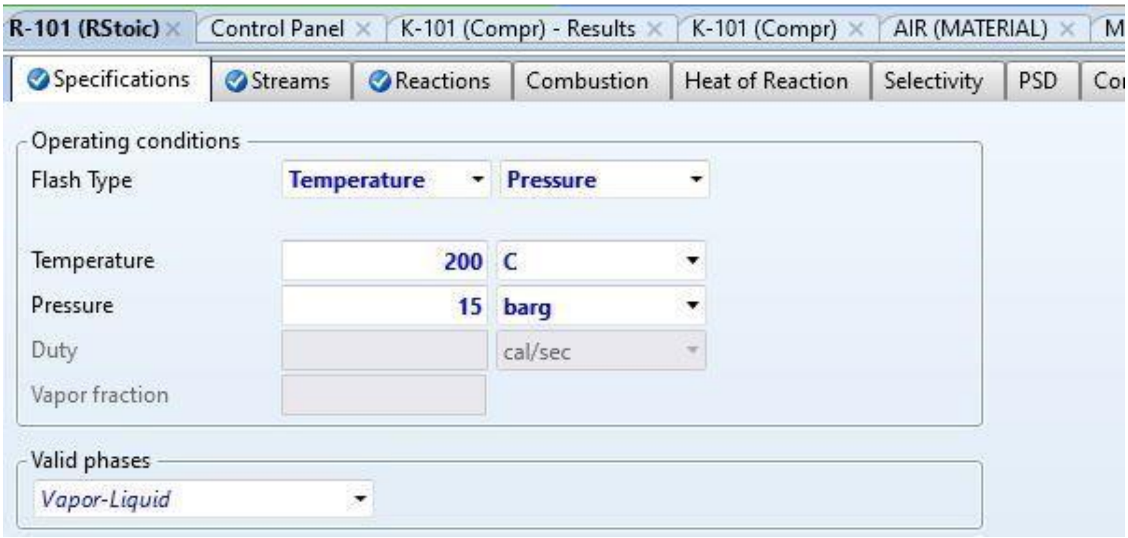
☐ Poynting correction

☑ Use liquid reference state enthalpy

Figure 8.2: Property package for simulation

8.3 Reactor

The reactor in our simulation is designed with specific specifications and parameters, as indicated in the provided screenshot. These specifications include a high conversion rate of 90 percent, demonstrating the efficiency of the reaction taking place within the reactor.



Operating conditions

Flash Type: Temperature, Pressure

Temperature: 200 C

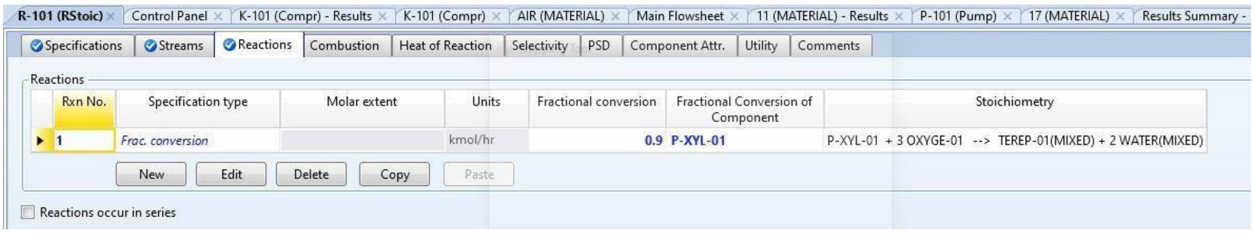
Pressure: 15 barg

Duty: cal/sec

Vapor fraction:

Valid phases: Vapor-Liquid

Figure 8.3: Specifications for reactor



Reactions

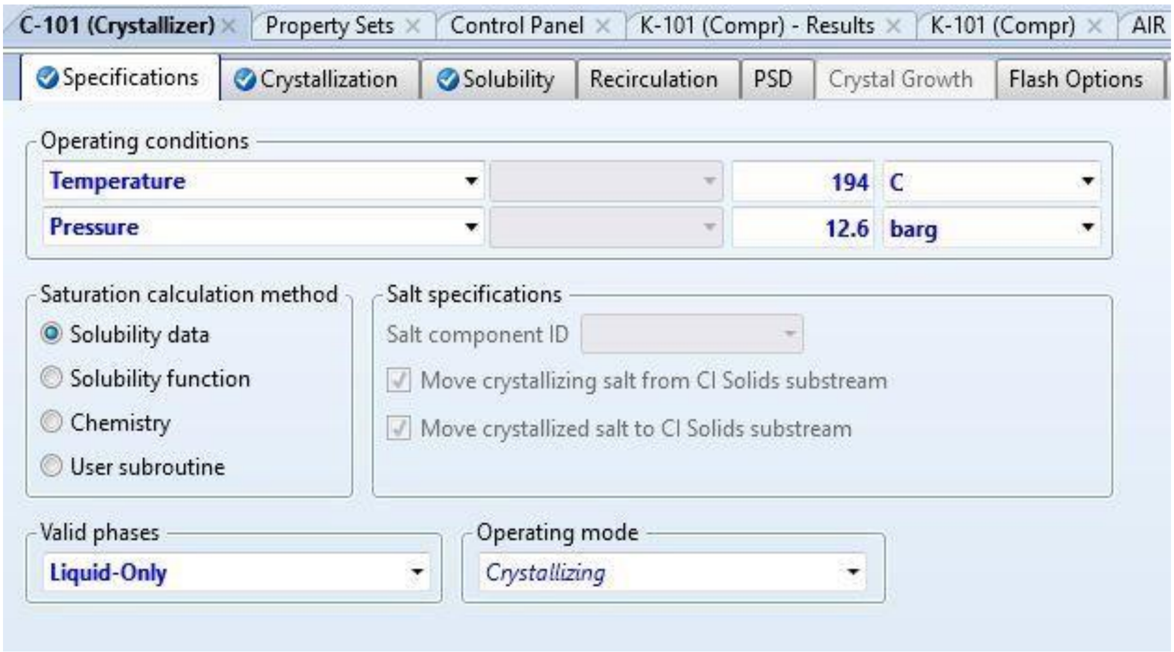
Rxn No.	Specification type	Molar extent	Units	Fractional conversion	Fractional Conversion of Component	Stoichiometry
1	*Frac. conversion*		kmol/hr	0.9	**P-XYL-01**	P-XYL-01 + 3 OXYGE-01 --> TEREP-01(MIXED) + 2 WATER(MIXED)

☐ Reactions occur in series

Figure 8.4: Reaction and conversion for simulation

8.4 Crystallizer

In our simulation, the crystallizer unit is configured with the specifications shown in the provided screenshot. Additionally, we have incorporated solubility curve data to accurately model the crystallization process at the specified operating parameters. By utilizing this data, we can effectively simulate and analyze the formation and growth of crystals within the crystallizer, enabling a comprehensive evaluation of the crystallization process in our project.



Operating conditions

Temperature 194 C

Pressure 12.6 barg

Saturation calculation method

● Solubility data

○ Solubility function

○ Chemistry

○ User subroutine

Salt specifications

Salt component ID

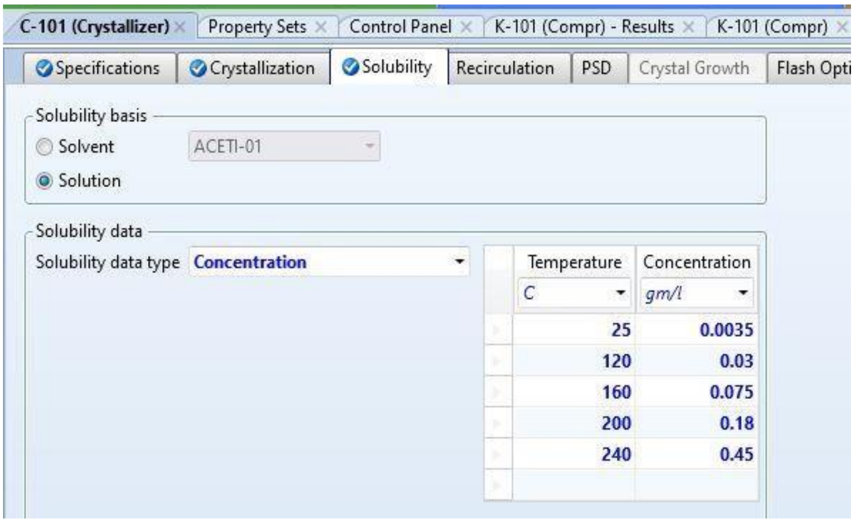
☑ Move crystallizing salt from CI Solids substream

☑ Move crystallized salt to CI Solids substream

Valid phases: **Liquid-Only**

Operating mode: *Crystallizing*

Figure 8.5: Specifications for crystallizer for simulation



Solubility basis

○ Solvent ACETI-01

● Solution

Solubility data

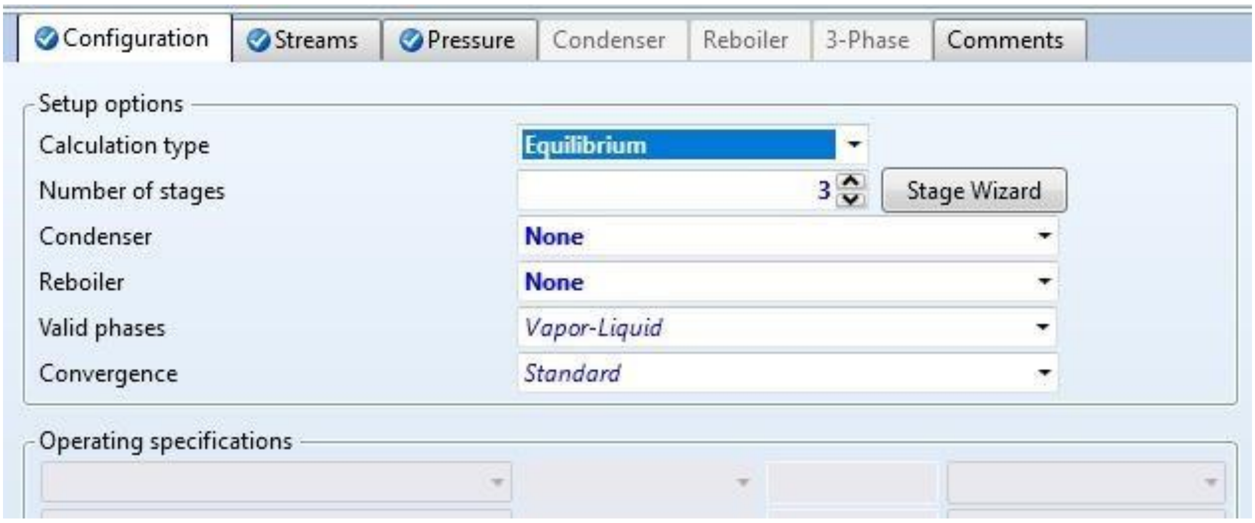
Solubility data type: Concentration

Temperature	Concentration
C	gm/l
25	0.0035
120	0.03
160	0.075
200	0.18
240	0.45

Figure 8.6: Solubility curve data for crystallizer for simulation

8.5 HP Absorber

The HP absorber unit in our simulation is configured with the specifications depicted in the provided screenshot. These specifications include the number of plates utilized in the absorber and the corresponding operating parameters. By incorporating this information into the simulation, we can accurately model the absorption process occurring within the HP absorber. This allows us to analyze the efficiency and performance of the unit based on the given operating conditions and plate configuration.



Setup options

Calculation type: Equilibrium

Number of stages: 3

Condenser: None

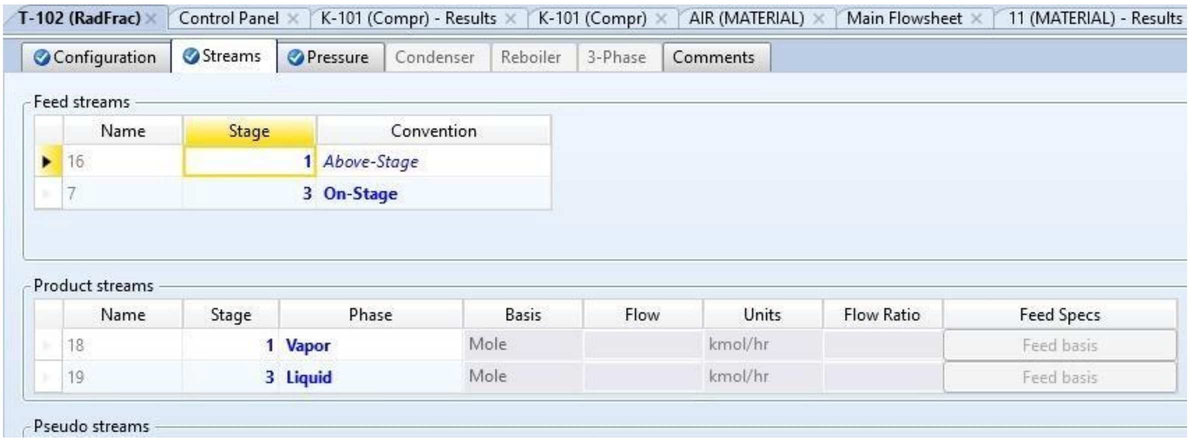
Reboiler: None

Valid phases: Vapor-Liquid

Convergence: Standard

Operating specifications

Figure 8.7: Type of HP Absorber selection for simulation



Feed streams

Name	Stage	Convention
16	1	*Above-Stage*
7	3	**On-Stage**

Product streams

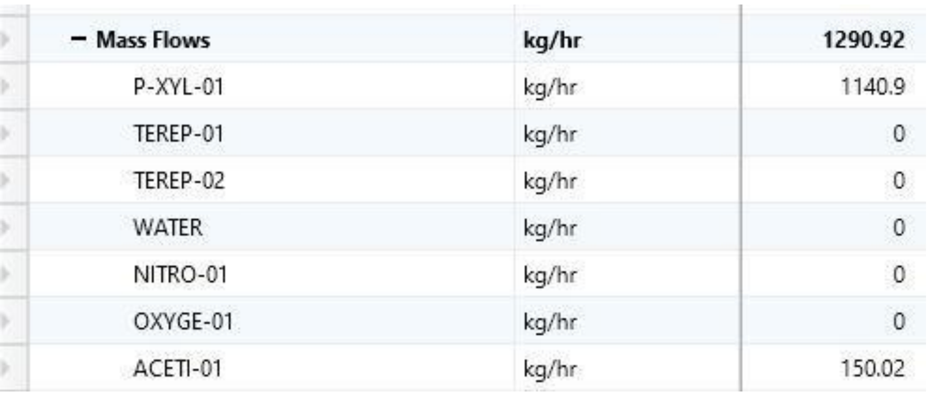
Name	Stage	Phase	Basis	Flow	Units	Flow Ratio	Feed Specs
18	1	**Vapor**	Mole		kmol/hr		Feed basis
19	3	**Liquid**	Mole		kmol/hr		Feed basis

Pseudo streams

Figure 8.8: Stream data for HP absorber for simulation

8.6 Results

The provided screenshots illustrate the composition of the feed and product streams, indicating the production of CTA (terephthalic acid) from paraxylene. The screenshots serve as visual representations of the transformation of paraxylene into CTA within our simulation, highlighting the changes in composition throughout the process.



− Mass Flows	**kg/hr**	**1290.92**
P-XYL-01	kg/hr	1140.9
TEREP-01	kg/hr	0
TEREP-02	kg/hr	0
WATER	kg/hr	0
NITRO-01	kg/hr	0
OXYGE-01	kg/hr	0
ACETI-01	kg/hr	150.02

Figure 8.9: Feed stream data entering the process for simulation

+ Mole Fractions		
− Mass Flows	**kg/hr**	**1780.26**
P-XYL-01	kg/hr	0
TEREP-01	kg/hr	0
TEREP-02	kg/hr	1780.26
WATER	kg/hr	0
NITRO-01	kg/hr	0
OXYGE-01	kg/hr	0
ACETI-01	kg/hr	0

Figure 8.9: Product stream data leaving the process for simulation

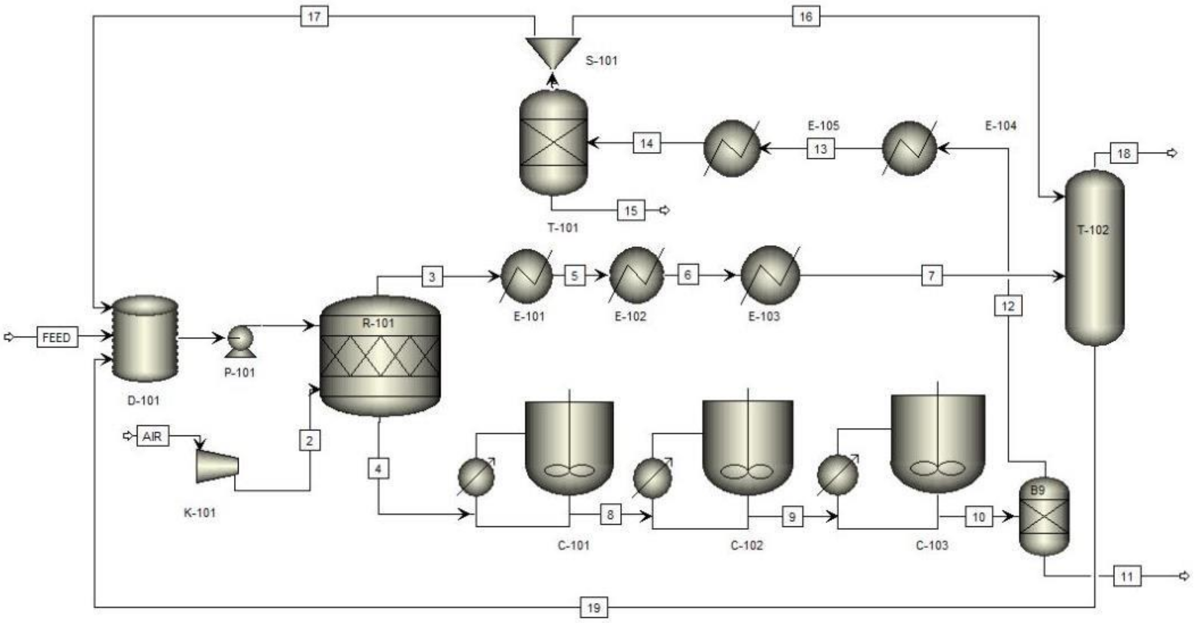


Figure 8.10: Simulated plant

8.7 Instrumentation

Instrumentation has been implemented on the reactor to monitor and control various parameters. Specifically, flow, temperature, level, and pressure are equipped with dedicated instruments. Additionally, a cascade control loop has been established to ensure proper regulation between flow and temperature.

The flow instrument measures the rate at which material enters or exits the reactor. This information is crucial for maintaining a consistent flow rate and controlling the reaction process. The temperature instrument continuously monitors the temperature inside the reactor, allowing adjustments to be made to prevent any undesired temperature fluctuations.

The level instrument provides real-time feedback on the liquid level within the reactor. It helps maintain a stable operating condition by ensuring that the liquid level remains within the desired range. Lastly, the pressure instrument monitors and controls the pressure inside the reactor to ensure safe and optimal operating conditions.

To facilitate effective control, a cascade control loop has been established between flow and temperature. This means that any deviations in the reactor's temperature are detected and used to adjust the flow rate accordingly. This cascade loop aids in maintaining the desired temperature and overall stability of the reactor.

In summary, the reactor has been equipped with instrumentation to monitor and control flow, temperature, level, and pressure. A cascade control loop has been implemented to ensure the appropriate relationship between flow and temperature, facilitating efficient and reliable reactor operation.

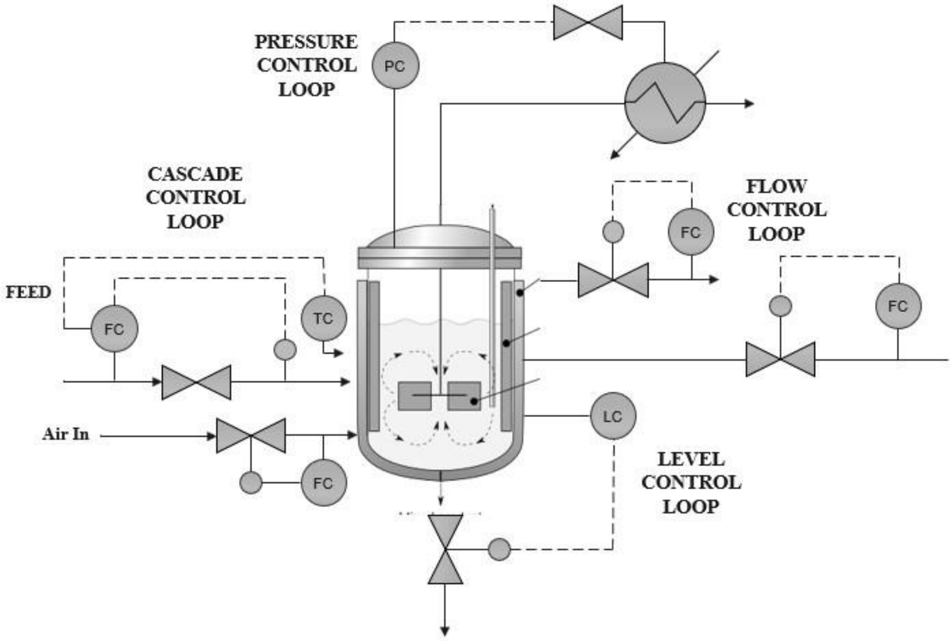


Figure 8.11: Control Loop applied on Reactor

CHAPTER 9

HAZOP STUDY

9.1 Hazard and Operability Study (HAZOP):

A HAZOP survey is one of the most common and widely accepted methods of systematic qualitative hazard analysis. It is used for both new or existing facilities and can be applied to a whole plant, a production unit, or a piece of equipment It uses as its database the usual sort of plant and process information and relies on the judgment of engineering and safety experts in the areas with which they are most familiar. The result is, therefore, reliable in terms of engineering and operational expectations, but it is not quantitative and may not consider the consequences of complex sequences of human errors. The objectives of a HAZOP study can be summarized as follows:

- To identify (areas of the design that may possess a significant hazard potential.
- To identify and study features of the design that influence the probability of a hazardous incident occurring.
- To familiarize the study team with the design information available.

- To ensure that a systematic study is made of the areas of significant hazard potential.
- To identify pertinent design information not currently available to the team.
- To provide a mechanism for feedback to the client of the study team detailed comments.

9.2 Steps of the HAZOP Study:

Specify the purpose, objective, and scope of the study. The purpose may be the analysis of a yet to be built plant or a review of the risk of nonexisting unit. Given the purpose and the circumstances of the study, the objectives listed above can he made more specific. The scope of the study is the boundaries of the physical unit, and the range of events and variables considered. For example, at one time HAZOPs were mainly focused on fire and explosion endpoints, while now the scope usually includes toxic release, offensive odor, and environmental endpoints. The initial establishment of purpose, objectives, and scope is very important and should be precisely set down so that it will be clear, now and in the future, what was and was not included in the study. These decisions need to be made by an appropriate level of responsible management.

Select the HAZOP study team. The team leader should be skilled in HAZOP and in interpersonal techniques to facilitate successful group interaction. As many other experts should be included in the team to cover all aspects of design, operation, process chemistry, and safety. The team leader should instruct the team in the HAZOP procedure and should emphasize that the end objective of a HAZOP survey is hazard identification; solutions to problems are a separate effort. [10]

9.3 How the study was carried out

1) Collect data. Theodore16 has listed the following materials that are usually needed.
    - Process description.
    - Process flow sheets.
    - Data on the chemical, physical and toxicological properties of all raw materials, intermediates, and products.
    - Piping and instrument diagrams (P&IDs).
    - Equipment, piping, and instrument specifications.
    - Process control logic diagrams.
    - Layout drawings.
    - Operating procedures.

- Maintenance procedures.
- Emergency response procedures.
- Safety and training manuals.

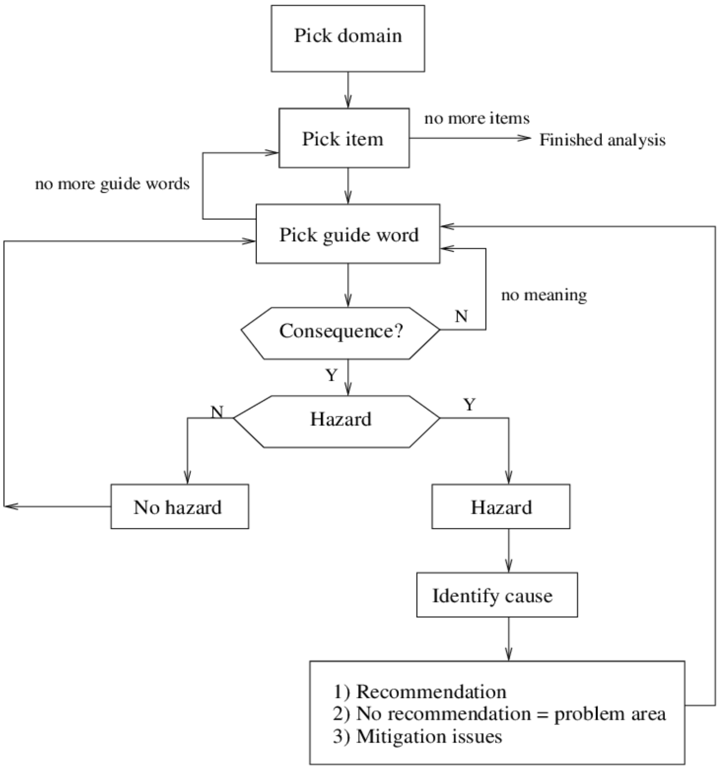
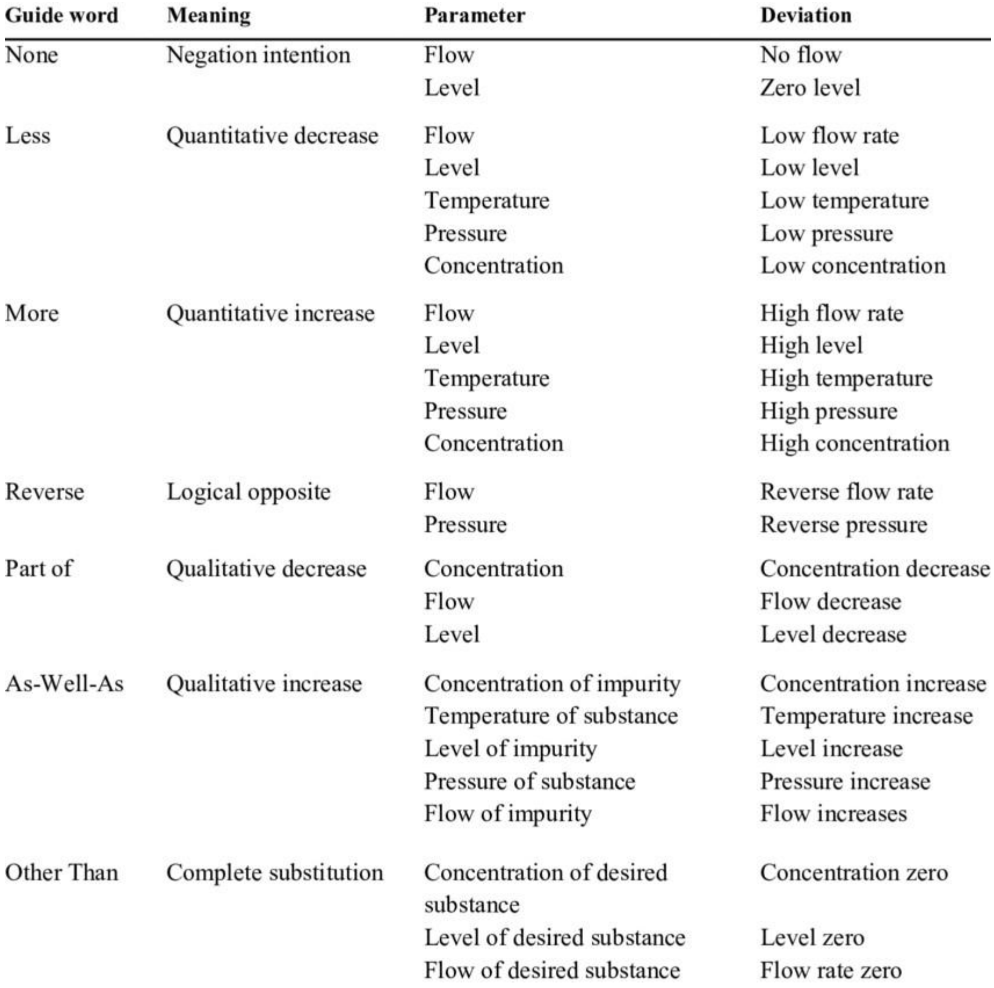


Figure 9.1: Method of Hazop Study

Table 37*:* Hazard analysis



Guide word	Meaning	Parameter	Deviation
None	Negation intention	Flow	No flow
		Level	Zero level
Less	Quantitative decrease	Flow	Low flow rate
		Level	Low level
		Temperature	Low temperature
		Pressure	Low pressure
		Concentration	Low concentration
More	Quantitative increase	Flow	High flow rate
		Level	High level
		Temperature	High temperature
		Pressure	High pressure
		Concentration	High concentration
Reverse	Logical opposite	Flow	Reverse flow rate
		Pressure	Reverse pressure
Part of	Qualitative decrease	Concentration	Concentration decrease
		Flow	Flow decrease
		Level	Level decrease
As-Well-As	Qualitative increase	Concentration of impurity	Concentration increase
		Temperature of substance	Temperature increase
		Level of impurity	Level increase
		Pressure of substance	Pressure increase
		Flow of impurity	Flow increases
Other Than	Complete substitution	Concentration of desired substance	Concentration zero
		Level of desired substance	Level zero
		Flow of desired substance	Flow rate zero

Conduct the study. Using the information collected, the unit is divided into study "nodes" and the sequence diagrammed in Figure, is followed for each node. Nodes are points in the process where process parameters (pressure, temperature change between nodes because of the operation of various pieces of equipment' such as distillation columns, heat exchanges, or pumps. Various forms and work sheets have been developed to help organize the node process parameters and control logic information.

When the nodes are identified and the parameters are identified, each node is studied by applying the specialized guide words to each parameter. These guide words and their meanings are key elements of the HAZOP procedure. [10]

Table 38: H*AZOP Analysis on Reactor*

PARAMETER	GUIDE WORDS	CAUSES	CONSEQUENCES	ACTION REQUIRED
FLOW	NO	Pump failure. manual valve closed.	Potential pipe failure. potential slip hazard.	Install flow meters.
	LOW	Line blockage.	Prolonged treatment process	Consider relocating tank isolation valves from the piping to directly on the tank.
	REVERSE	Backflow due to high back pressure.	Loss of cooling. contamination.	Install check valve.
TEMPERATURE	LOW	Low water supply temperature. heat exchanger fouling.	Possible runaway on heating.	Install heat exchangers.
	HIGH	High water supply temperature.	Cooling system capacity limited, temperature increases.	Install cooling water high temperature alarms, injection of cooling water.

PRESSURE	MORE	Uncontrolled reaction occurs. operating fault, faulty pressure sensors.	Reactor material could weaken causing leak or explosion.	Install high pressure alarms. add valve controls onto product and reactant lines.
	LESS	Not enough reactant coming in the reactor, pump failure.	Can cause backflow. An uncontrolled amount of oxygen or paraxylene could	Emergency shutdown. maintenance procedure.
		reaction is less than anticipated.	go into the reactor and react without supervision.	
VOLUME	LESS THAN	Build up of material inside the reactor would cause the available volume to decrease.	Reaction kinetics would be affected, and the reaction would be unpredictable.	Routinely check for build-up in the reactor and clean the reactor.

Table 39: HAZOP Analysis on HP Absorber

PARAMETER	GUIDE WORDS	CAUSES	CONSEQUENCES	ACTION REQUIRED
LEVEL	HIGH	Output blockage. Inflow greater than outflow. Pressure surge	Product not according to desired specifications.	Install level sensors on the absorbers.
	LOW	Leak, Outflow greater than inflow. Unlet flow stops.	Limited mass transfer.	Install low level alarms. Make bypass. check maintenance procedure and schedule.
TEMPERATURE	MORE	Ambient conditions. temperature control malfunctioning.	Higher temperature in expulsion some of the components start to vaporize.	Install temperature sensors. install high temperature alarms.
	LESS	Too much cooling power. reducing pressure.	Product is not according to the desired specifications.	Install temperature indicators. install low temperature alarms.

PRESSURE	MORE	Pressure control malfunctioning. less/no flow of the mixture.	The absorber might explode.	Install pressure relief valve with automatic feed from temperature control system. install high pressure alarm.
	LESS	The absorber is over cooled. leakage.	Pressure in the system drops. product is not according to the desired specifications.	Install low pressure alarms.
COMPOSITION	CHANGE	Process control upsets. incorrect feedstock specifications.	Desired product is not achieved.	Test quality of feed regularly.

Table 40: HAZOP analysis on crystallizer

PARAMETER	GUIDE WORDS	CAUSES	CONSEQUENCES	ACTION REQUIRED
TEMPERATURE	HIGH	Sensor failure and not calibrated. Inadequate mixing and agitation.	Risk of overheating. Reduced equipment life.	Inspection and calibrating sensors continuously applying preventive maintenance in sensor.
	LOW	Blockages our restrictions in the heating system. Inadequate Insulation or Heat loss.	Delayed Crystallization. Reduced Productivity.	Low Temperature Alarm. Temperature control system.

PRESSURE	MORE	Control valve or regulator malfunction. Process overloading or excessive feed rate.	Risk of overpressure. Equipment Failure.	Install pressure relief valve.
	LESS	Leaks or air ingress in the system.	Loss of agitation thus incomplete mixing.	Install low pressure alarms.
COMPOSITION	CHANGE	Process control is upset. Incorrect feedstock specifications.	Product contamination. Quality issues, Reduced yield.	Composition control system, Impurity monitoring.
LEVEL	HIGH	Blocked or restricted discharge. Inadequate level monitoring.	Overfilling and equipment damage. Inconsistent product quality and yield.	Implement regular inspect and maintenance discharge pathwa
	LOW	Control system malfunction. Insufficient feed flow rate.	Reduced production capacity and product quality issues	Ensure adequate feed flow rate through system optimization.
CRYSTALLIZATION RATE	SLOW	Inadequate ation. supersatur	Undesired crystal size distribution.	Optimize process conditio achieve c supersaturation.

Table 41: HAZOP analysis on pump

PARAMETER	GUIDE WORDS	CAUSES	CONSEQUENCES	ACTION REQUIRED
Pressure	NO	Pump failure, power outage, shaft failure, faulty pressure sensor	Upset in downstream feed to reactor	Maintenance procedures

	MORE	Faulty pressure sensor, Operation error	Explosion, deterioration of bearings.	Install high pressure alarms
	LESS	Pump failure, power outage, shaft failure, faulty pressure sensor	Upset in downstream feed to reactor	Maintenance procedures
Flow	NO	Blocked pipelines, pump failure	Upset in downstream feed to reactor	Proper monitoring of pumps and installation of alarms on valve
	LESS	Low rotational speed of shaft, improper suction at the inlet, partial opening of downstream valve	Upset in downstream feed to reactor	Check and increase speed of shaft rotation, install control system to change valve opening according to flow
	MORE	Too high shaft power	More energy consumption	Check and decrease the speed of shaft
				rotation, check operating procedures

Table 43: HAZOP Analysis on Compressor

PARAMETER	GUIDE WORDS	CAUSE S	CONSEQUENCES	ACTION REQUIRED
TEMPERATURE	HIGH	Inadequate lubrication or c cooling parts.	Increased friction,l wear, and potentia failure.	Implement proper lubrication and cooling mechanisms.
	LOW	Control system malfunction	Inaccurate temperature control and instability.	Implement redundant temperature control systems.

PRESSURE	MORE	Process l. overloa ge ys. Blocked dischar pathwa	Excessive stres on equipment and potential failure. Pressure build- up, equipment e, damag and reduced efficiency	Optimize process desig operational li Implement regular inspe and cleanin discharge pat
	LESS	ent ssure. Insuffici feed pre	Reduced production capaci y and performance.	Ensure ade feed pre through s optimization.
FLOW	NONE	Compressor Failure.	The air is not compressed.	Low flow pressure alarm. Interlock to shutdown airflow.
	MORE	Failure of compressor controls.	High rate of reaction. High reactor temperature.	Install high temperature Alarms.
	REVERSE	Compressor Failure, High pressure at reactor.	Air backflow in the compressor.	Add a check valve to prevent backflow.

Table 42: HAZOP analysis on condensers

PARAMETER	GUIDE WORDS	CAUSES	CONSEQUENCES	ACTION REQUIRED
DUTY	LESS	Low flow rate of coolant. Process stream overheats/is not cooled enough. Heat transfer efficiency of the heat exchanger is too low due to factors like fouling.	Process stream overheats/is not cooled enough.	Proper checking up on heat exchanger condition before commencing operation. Increase the flow rate of coolant stream. Design oversized heat exchanger to reduce fouling effect

TEMPERATURE	LESS	Coolant flowrate too high	Desired Outlet temperature is not achieved.	Proper checking up on heat exchanger condition before commencing operation. Decrease flow rate of coolant.
	MORE	Process stream inlet temperature above set point.	Product unable to cooled to desired temperature. Equipment damage/failure.	Check the temperature of the inlet stream to the heat exchanger constantly.
PRESSURE	NONE	Compressor Failure.	The air is not compressed.	Low flow pressure alarm. Interlock to shutdown airflow.
	MORE	Failure of compressor controls.	High rate of reaction. High reactor temperature.	Install high temperature Alarms.
	REVERSE	Compressor Failure, High pressure at reactor.	Air backflow in the compressor.	Add a check valve to prevent backflow.

FLOW	LESS	Valve Malfunction The pipe is partially blocked or ruptured.	Lower heat transfer. Process stream not cooled to desired temperature.	Constant checking of the pipeline and their condition to check leakages and take corrective measures.
	MORE	High inlet Process stream flowrate.	Failure of inlet valve to close.	Control valves must be constantly tested and decrease the inlet flow rate of the process stream.

CONCLUSION

In conclusion, this thesis has explored the production of crude terephthalic acid (CTA) from the oxidation of paraxylene using the AMOCO process. Through an in-depth analysis of the various steps involved in the production of CTA, the relevant material and energy requirements, and the costs involved. The process uses advantaged technologies that offer several key benefits compared to the conventional processes, as discussed in the literature review.

Firstly, the AMOCO process provides a highly efficient and cost-effective route to produce CTA. The use of a single-step oxidation process significantly reduces the overall production costs by minimizing the number of process steps, energy consumption, and raw material requirements. This streamlined approach results in increased productivity and improved economics for CTA manufacturers. The use of a dehumidifier before the compressor reduces the load of the plant, and results in less electricity requirements.

Secondly, the AMOCO process ensures high product quality and purity. The reactor design is optimized to produce maximum yield. The optimized reaction conditions and carefully controlled parameters in the AMOCO process enable the production of CTA with minimal impurities such as 4-CBA. This high purity is crucial as it directly impacts the quality of downstream products, such as polyester fibers and polyethylene terephthalate (PET) resin, which require pure CTA for their production.

Furthermore, the AMOCO process offers environmental advantages. By minimizing the number of process steps and energy consumption, this process reduces greenhouse gas emissions and overall environmental impact. Additionally, the efficient use of raw materials and the integration of waste management strategies contribute to a more sustainable production process. By safely separating and disposing of all wastes formed, this process ensures that it is eco-friendly.

Moreover, the AMOCO process exhibits excellent scalability and versatility. It can be easily implemented in both large-scale industrial plants and smaller facilities, making it suitable for various production capacities. The process also accommodates different feedstock qualities, allowing for flexibility in the choice of paraxylene sources.

In summary, the AMOCO process stands out as a highly advantageous method to produce crude terephthalic acid from paraxylene oxidation. Its cost-effectiveness, high product yield, environmental safety control, and scalability make it a preferred choice for manufacturing. The findings of this thesis underscore the significance of the AMOCO process in the chemical industry and provide valuable insights for further research and development in this field.

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