DESIGN 15 TONS/DAY PRODUCTION FACILITY OF POLYOLS FROM WASTE PET BOTTLES

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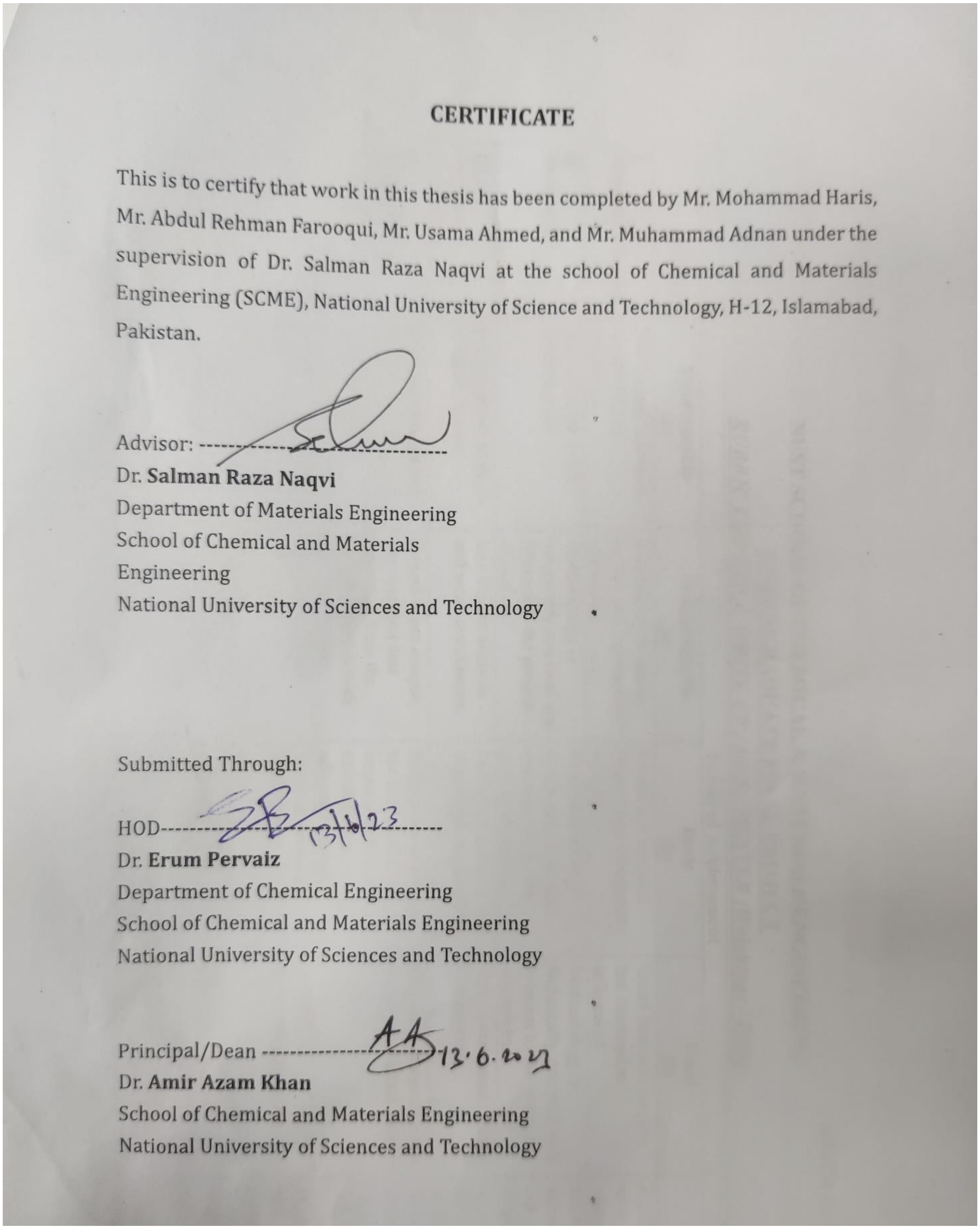

CERTIFICATE

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DEDICATION

This Work is dedicated to our Parents, Teachers and Friends who always had our back when we needed them the most.

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First, we would like to express our utmost gratitude to Almighty Allah. Without Allah's mercy, we would never been able to complete our project.

We would like to thank our parents and friends for their support in motivating and praying for us.

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ABSTRACT

As the problem of plastic waste management increases in Pakistan, the need for better and more efficient chemical recycling methods also arises. Our team worked on the utilization of waste PET (Polyethylene Terephthalate) bottles in order to obtain useful monomers to close the loop on chemical recycling of plastics. This includes the process we have used to de-polymerize the PET, "supercritical methanolysis" as well as the challenges associated with separation of useful products from the depolymerization.

The PET flakes must be reduced in size through some pre-treatment like crushing, or even dissolution is methanol/ethylene glycol. The reactant methanol must be vaporized for the reaction to occur in the supercritical phase of methanol through heating whether in the reactor itself or in a heat exchanger. The solid-vapor mixture is to be fed to a reactor where along with high RPM agitation, the mixture is allowed to react for 30 minutes under 300 ^oC temperature and 80 bar pressure. The reaction mixture now contains the desired products, ethylene glycol (EG) and dimethyl terephthalate (DMT).

In order to obtain a high purity of EG, DMT must be separated from the reactor product stream using crystallization, after which it is filtered out and dried. The rest of the mixture is sent to two distillation columns, one removing the large quantity of methanol from the mixture and the next distilling out our main product, EG at a very high purity of 99.95%.

The objective of this proposed process is to provide two valuable monomer products needed to make PET plastic which in turn can be used in the polymerization process to replace some requirement of fresh monomers needed to produce it. Furthermore, these chemicals are also valuable in other applications such as being used in making solvents, pharmaceutical products, plasticizers, dyes, and pigments etc. This in turn completes the loop on recycling plastics chemically.

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ΔH: Change in enthalpy

A: Area

^{o}C: Degree centigrade

C: constant in USD

Ce: purchased equipment cost in USD

D: Diameter

F: Molar Flow Rate

H: Height

J: Joule

L: h

Mol: Mole

P: Pressure

Q: Energy Flow rate

t: time

V: Volume

Cp: Specific Heat Capacity at Constant Pressure

T: Temperature

K: Thermal Conductivity

h: Thermal Conductivity

CHAPTER NO 1

INTRODUCTION

1.1 Overview

Polyethylene terephthalate (PET) is a plastic resin that is widely used in the manufacture of plastic bottles. In the past years due to the increase in the demand for plastic bottles their production has been greatly increased. The problem lies in the disposal of plastic waste mainly the PET bottles. According to the report from United Nation Development Program (UNDP) Pakistan produces 20 million tons of waste out of which around 5 to 10 percent is plastic waste.

Around 60 percent of this waste is deposited in the landfills or dumped into the water bodies, such as ocean, rivers, and lakes. PET waste contains harmful contaminants and bacteria that pose serious damage to the environment and human health. Even when the PET partially or fully degrades into the microplastics it produces toxins that further endanger the aquatic ecosystem.

The PET waste also gets blocked into the drainage system which results in the wastewater accumulation giving rise to diseases. The bottles also contain harmful chemicals that leach out to the water bodies and sink into the ground water. These chemicals further get absorbed by the plants and thereby enter the food chain.

Sometimes, instead of dumping the PET waste into the open lands or water bodies an alternate method is used called the Incineration in which the plastic is burnt. This burning of the plastic produces very harmful fumes that include carbon-dioxide, dioxins, and furans. Incineration also produces soot that gets settled on the plants.

To reduce plastic pollution some methods should be developed to recycle them.

1.1.1 Polyethylene Terephthalate (Pet)

It is a thermoplastic which is commonly used in the manufacture of various sorts of products including packaging material and bottles. The properties of the PET such as resistance to chemicals and moisture, transparency, and its ability to be molded into various shapes make it a very good choice to be used in packaging industry.

It is created by the reaction of Dimethyl Terephthalate (DMT) or Terephthalic acid (TPA) with ethylene glycol. The resulting polymer chain is strong and can be molded into various sorts of applications.

The chemical structure of PET can be represented as

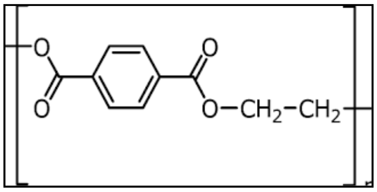


Figure 1: Structure of PET

1.1.2 Ethylene Glycol (EG)

It is a colorless, odorless, and sweet tasting liquid with a chemical formula C6H6O2.Ethylene glycol is an essential raw material in the manufacture of polyesters such as PET and is also widely used a solvent because of its miscibility is water. It has a relatively high boiling point and low freezing point that makes it an effective antifreeze agent and coolant in automobiles and HVAC systems.

Its chemical structure can be represented as follows.

Figure 2: Structure of Ethylene Glycol

It is important to note that apart from its various uses it is toxic in nature. Thus, proper storage, handling and safety measures should be adopted.

1.2 Objective

The main objective of this project is to design a process that recycles the PET waste through a depolymerization reaction and produces polyols. The specific objectives include:

Investigating depolymerization process, the mechanism and the conditions required to breakdown the PET polymer to its respective monomers.
Evaluating the method used for the depolymerization in terms of efficiency, yield of the process and the quality of the polyols produced.
Reduce the environmental impact of plastic waste by converting them to monomers so that they can be repolymerized again, reducing the need for the fresh plastic manufacture.
By accomplishing these objectives, the project aims to contribute to the development of efficient and sustainable strategies for recycling PET bottles, thereby reducing waste generation, conserving resources, and promoting a circular economy approach.

1.3 Methodology

1.3.1 Supercritical Methanolysis

In this process the PET is treated with supercritical methanol where it is maintained at high temperature and pressure above its critical point. The advantages of this method are:

This process is very efficient and offers high conversion rates (approximately 98 percent) and the yield of monomers. The reaction conditions and the properties of the supercritical methanol further facilitate the depolymerization reaction.
The reaction operates at mild conditions as compared to other methods of depolymerization reducing the energy requirement and potential degradation of monomers.

This process is selective in terms of monomers recovery. The targeted monomers are Ethylene glycol (EG) and Dimethyl terephthalate (DMT).

The use of supercritical methanol offers less environmental impact than other processes with less waste generation.

This reaction also does not require a catalyst.

REACTION:

$$PET + 2MeOH \rightarrow EG + DMT$$

Other depolymerization reactions that can be used are:

1.3.2 Glycolysis

Glycolysis is another method used for PET depolymerization. In this method, the PET is treated with diols under elevated temperature and pressure. The main reaction product is Ethylene glycol, which can be reused to produce more plastic. This catalyst that is used for this reaction is zinc acetate and titanium dioxide having a conversion rate of 95 percent.

REACTION:

$$PET + EG \rightarrow EG + DMT$$

1.3.3 Hydrolysis

This method involves the breakdown of the PET using a water stream under high pressure and temperature. The targeted products are Ethylene glycol and Terephthalic acid. The reaction requires a acidic or alkaline catalyst such as hydrochloric acid (HCL) and sodium hydroxide (NaOH).

REACTION:

$$PET + H_2O \rightarrow EG + TPA$$

The hydrolysis and glycolysis reactions are not selective in terms of monomers recovery and also the environmental impact is high.

CHAPTER NO 2

LITERATURE REVIEW

2.1 Introduction

PET (Polyethylene Terephthalate) is hard plastic with decomposition temperature of >350° C. It is widely used as packing material for fizzy drinks, textile, jars etc. PET waste is major contributor towards plastic buildup in entire world. There is no natural way that can depolymerize PET in the lands, so there is a need to develop a process to get rid of this waste PET.

2.2 Methods Description

2.2.1 Methanolysis

The process of methanolysis in PET recycling results in the production of DMT (dimethyl terephthalate) and EG (ethylene glycol), both of which are essential raw materials for PET production. While methanolysis tends to be more costly compared to glycolysis, it offers advantages in handling lower quality feedstocks. This capability reduces feedstock expenses as methanolysis is more tolerant of contamination.

2.2.1.1 Vapor Methanolysis

The utilization of superheated vapor methanol instead of liquid methanol presents an alternative for transesterification in PET recycling. Naujokas and Ryan proposed a methanolysis process that involves dissolving scrap PET waste using oligomers of DMT and EG obtained from glycolysis, followed by sparging superheated methanol vapor into the solution. By conducting the reaction at lower pressures, the methanol remains in a vapor state, facilitating the removal of resulting DMT as a vapor. This vapor methanolysis process demonstrates increased tolerance for contaminated PET compared to conventional liquid-phase methanolysis, as esters and alcohols are removed as vapors. Additionally, vapor removal of the products from the reactor promotes reaction conversion, leading to nearly complete conversion.

Typically, the reaction takes place in an agitated tank where methanol gas is introduced into the liquid solution. To facilitate mass transfer of reactants between phases in the two-phase reaction, thorough mixing between the phases is necessary. An agitated vessel with gas sparging is often employed for practical reasons. The agitation assists in dispersing the gas into small bubbles, enabling effective contact between the gas and liquid. Gamble et al. proposed a staged column reactor for depolymerization and separation of monomer components from higher boiling materials.

The influence of temperature on gas-liquid reactions, such as vapor methanolysis, is more intricate than in homogeneous reactions like liquid methanolysis. Increasing the temperature enhances the reaction rate, but it also reduces the solubility of methanol gas in the liquid, which contributes to a decrease in the reaction rate. Pressure, too, has a complex influence, as increasing pressure accelerates the reaction rate while decreasing the removal rate of the products (DMT and EG). Various effects contribute to both increasing and decreasing the reaction rate.

Kim and Han investigated the effects of several parameters, including methanol feeding rate, methanol purity, reaction pressure, reaction temperature, and catalyst amount, on DMT production yield in a vapor methanolysis reactor. They found that the DMT production yield increases with the methanol feeding rate and reaches a maximum at a reaction temperature of 250-260°C and a reaction pressure of 3-6 atm.

Vapor methanolysis is currently successfully employed in PET scrap recycling. Volatile PET monomers can be removed as vapors, eliminating the need for extensive separation processes. This approach reduces overall operation costs, as the obtained product, such as BHET and related monomers, can be used as raw materials in TPA-based or DMT-based production plants without extensive separation efforts.

2.2.1.2 Liquid Methanolysis

PET methanolysis involves the depolymerization of PET bottles using methanol at temperatures ranging from 180 to 280°C and pressures between 20 and 40 atm.

Commonly used catalysts for the transesterification reaction include zinc acetate, magnesium acetate, cobalt acetate, and lead dioxide. The high-pressure conditions ensure that methanol remains in a liquid state throughout the reaction. PET can be directly subjected to methanol or undergo glycolysis followed by methanolysis. The yield of DMT typically falls within the range of 80% to 85%. To separate and purify the products of methanolysis, distillation or crystallization methods are commonly employed.

The purified DMT obtained from the process can be recycled for PET polymerization. Methanolysis can be performed in both batch and continuous modes. In the continuous process, a sophisticated apparatus is required to introduce PET waste into the methanolysis reactor operating under high pressure.

2.2.1.3 Supercritical Methanolysis

Recently, researchers have utilized supercritical methanol, operating at temperatures of 300°C and pressures exceeding 80 atm, for PET methanolysis. The reactivity of supercritical methanol has gained attention in PET depolymerization. Supercritical fluids possess high density near their critical point, resembling a liquid, while retaining the kinetic energy of gas molecules. PET decomposition occurs significantly faster under these conditions compared to liquid methanol. The rate of PET depolymerization in supercritical methanol was found to exceed that of vapor methanol depolymerization. The importance of temperature, methanol-to-PET weight ratio, and reaction time for DMT yield and degree of depolymerization, while noting that pressure above the critical point of methanol was less influential. Supercritical methanolysis exhibits a much higher depolymerization rate compared to vapor or liquid methanolysis. However, the rigorous reaction conditions increase the process's cost and pose challenges for continuous operation.

2.2.2 Hydrolysis

Water can serve as an alternative to break polyester chains, leading to the formation of TPA and EG. The depolymerized product obtained from this process can be directly utilized in TPA-based PET synthesis plants. The hydrolysis of PET chains can occur under neutral, acidic, or basic conditions, resulting in the production of hydroxyl and carboxylic end groups. When a water molecule attacks the chain, it induces chain scission and generates a carboxylic end group.

$$\boxed{\begin{gathered}\sim C(\mathrm{O}) - \mathrm{C_6H_4} - C(\mathrm{O}) - \mathrm{O} - \mathrm{C}H_2\mathrm{CH_2} - \mathrm{O}\sim\; + \mathrm{H_2O} \rightarrow \sim C(\mathrm{O}) \\ - \mathrm{C_6H_4} - C(\mathrm{O}) - \mathrm{OH} + \mathrm{HO} - \mathrm{CH_2CH_2} - \mathrm{O}\sim\end{gathered}}$$

Figure 3: Hydrolysis Reaction

However, despite active research in recent years, hydrolysis is not yet a commercially viable option. One significant challenge hindering its commercialization is the purification of recycled TPA. Purifying TPA from the reaction mixture poses difficulties due to its low solubility and vapor pressure. Some impurities present in PET waste, which are not soluble in water-based agents, cannot be effectively separated through trans-crystallization using acetic acid/water.

2.2.2.1 Acid Hydrolysis

Patents have been filed that outline the acidic hydrolysis of PET using concentrated sulfuric acid (14.5 M) at atmospheric pressure and temperatures ranging from 25 to 100 degrees Celsius. The resulting hydrolysis product is then neutralized with sodium hydroxide, leading to the formation of the corresponding TPA sodium salt, which is soluble in water. In the final step of the process, the solution is acidified again to precipitate TPA, resulting in a purity of at least 99%. However, this method requires the separation and purification of large quantities of concentrated sulfuric acid, as well as the purification of EG containing sulfuric acid, which adds significant expenses to the process. Additionally, the reaction mixture is corrosive, and substantial volumes of liquid waste containing inorganic salts and sulfuric acid are generated. Yoshioka et al. conducted research on the effect of sulfuric acid concentration in PET acid hydrolysis and developed a process that utilizes low-concentration sulfuric acid. They observed that PET degradation significantly increased above 5 M concentration and reached near-complete degradation around 7 M concentration. After the reaction, TPA can be separated from the unreacted PET by dissolving it in ammonia (5 M).

Yoshioka et al. also investigated the hydrolysis of PET bottles using nitric acid (7-13 M) at temperatures of 70-100 degrees Celsius for 72 hours. This process resulted in the production of TPA and EG, with EG partially oxidizing to oxalic acid, which has higher value compared to EG.

2.2.2.2 Alkaline Hydrolysis

The alkaline hydrolysis of PET involves subjecting the polyester to an aqueous solution of sodium hydroxide (4-20 wt%) under pressure at temperatures ranging from 200 to 250 degrees Celsius for several hours. Through distillation, the reaction mixture is separated, which includes ethanediol (ED) and a heat-stable salt (disodium terephthalate), and the ED is recovered. The heat stability of the terephthalate salt sets this process apart from other chemical recycling methods, as the salt can be easily separated and purified at ambient pressure and low temperature. Alkaline hydrolysis can effectively handle heavily contaminated post-consumer PET with a relatively straightforward process. It requires lower capital and operating costs compared to methanolysis since it operates at lower temperatures and pressures. Pure TPA is obtained by neutralizing the reaction mixture with a strong acid.

Yoshioka et al. Describe an alkali hydrolysis process using concentrated NaOH solution, from which TPA and oxalic acid can be derived from PET waste. Heating the aqueous NaOH solution converts PET into sodium terephthalate and EG. The introduction of oxygen into the solution oxidizes EG into oxalic acid and CO2. The TPA yield is nearly 100% because the sodium terephthalate is not affected by oxidation. The oxidation step enhances process economics as oxalic acid is a more valuable product than EG. Notably, the oxidation step can also remove the green color from green PET bottles. TPA impurities in PET alkaline hydrolysis can be significantly reduced by introducing an oxidation step to convert impurities into insoluble forms.

In recent years, studies have explored alkali degradation of PET in solvents other than water. Collins and Zeronian used methanolic sodium hydroxide as a solvent and observed faster degradation compared to using aqueous sodium hydroxide. Hu et al. utilized sodium hydroxide dissolved in anhydrous EG to degrade PET and obtained disodium terephthalate as a major product. TPA was easily recovered by dissolving the sodium salt in water and then acidifying it with HCl. The authors also demonstrated that potassium hydroxide dissolved in ethanol and methanol could be used for alkaline hydrolysis. Different ethers such as dioxane, tetrahydrofuran, and 1,2-dimethoxyethane, when used as cosolvents in nonaqueous alkali solutions, can accelerate the degradation of PET. The ether component aids in swelling the PET solid, while the alcoholic component assists in the attack of NaOH or KOH on the chemical structure of PET.

2.2.2.3 Neutral Hydrolysis

The hydrolytic scission of PET using water or steam can be performed under high-pressure conditions at temperatures above the melting points to yield TPA and EG at neutral pH. The rate of PET hydrolysis is significantly higher in the molten state compared to its solid form. Campanelli et al. demonstrated that complete depolymerization of PET could be achieved within 2 hours at 265 degrees Celsius with an initial reactant ratio of water to PET of 5.1. Metal salts have been found to catalyze the hydrolysis of simple esters in aqueous solutions. Campanelli et al. reported that zinc acetate and sodium acetate increase the rate of PET hydrolysis by approximately 20%. The catalytic effect of these salts, including zinc and sodium salts, is attributed to their electronic destabilization of the polymer-water interface during the hydrolysis process. Neutral hydrolysis does not result in unwanted liquid effluents containing inorganic salts, and the reaction system for neutral hydrolysis is not corrosive.

However, the challenge with neutral hydrolysis is the separation of impurities from the TPA product. Most impurities present in PET are not easily separated from TPA, requiring more intensive purification methods compared to acid or alkaline hydrolysis. Purification techniques such as filtration of the TPA solution dissolved in caprolactam or in an aqueous solution of sodium hydroxide, as well as crystallization of TPA from caprolactam, can be employed. The EG generated during the reaction can be purified through extraction or distillation processes.

2.2.3 Glycolysis

Glycolysis is a solvolysis reaction that involves the use of glycol, such as ethylene glycol (EG), and its derivatives as reactive solvents for the chemical depolymerization of PET. It is an important commercial process for PET depolymerization. In glycolysis, the ester linkages of the PET polymer are broken and replaced with hydroxyl terminals through the molecular degradation of PET by glycols in the presence of trans-esterification catalysts.

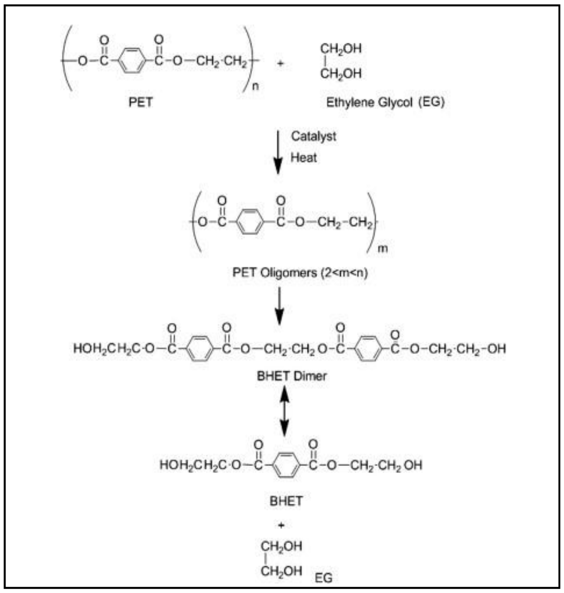


Figure 4: Glycolysis step by step reactions

The main products obtained from glycolysis using EG, diethylene glycol, propylene glycol, or dipropylene glycol are bis(2-hydroxyethyl) terephthalate (BHET) and other oligomers, known as PET glycolyates. These products have various applications, including the production of polyurethane foams, copolyesters, hydrophobic dye stuffs, unsaturated resins, and acrylic coatings. BHET can be combined with fresh BHET and used for PET production using methods based on either DMT or TPA. Glycolysis involves the following steps:

1. Initiation step: The carbonyl carbon of the ester group in the PET polymer is attacked by the free electron pair present in the glycol (e.g., EG).

2. The hydroxyl ethyl group of the glycol reacts with the carbonyl carbon of PET, resulting in the breaking of the long polymer chain into short oligomers and the subsequent formation of BHET.

2.2.3.1 Catalyzed Glycolysis

Glycolysis is a highly promising method for enhancing the rate of PET depolymerization, particularly when catalysts are employed. Although several factors, such as reaction time, temperature, PET-to-solvent ratio, and others, influence the glycolysis rate, the use of catalysts is essential for achieving efficient depolymerization. Metal-based trans-esterification catalysts are commonly employed to accelerate the reaction rate.

The conversion of PET dimers into BHET monomers is a reversible process. Metal-based catalysts facilitate the attack of glycol (e.g., EG) on PET, forming a complex with the carbonyl group and leading to the formation of BHET.

There are various glycolytic depolymerization processes that involve the use of catalysts, including:

1. Metal derivatives: Catalysts based on metals are widely utilized to promote glycolysis. These catalysts enhance the reactivity of PET and facilitate the formation of BHET.

2. Zeolites: Zeolite catalysts have shown promise in glycolytic depolymerization processes. These porous materials provide a suitable environment for the reaction to occur and enhance the efficiency of PET degradation.

3. Ionic liquids: Ionic liquids have gained attention as potential catalysts for glycolysis. These liquid salts possess unique properties that can facilitate the depolymerization process and improve the yield of desired products.

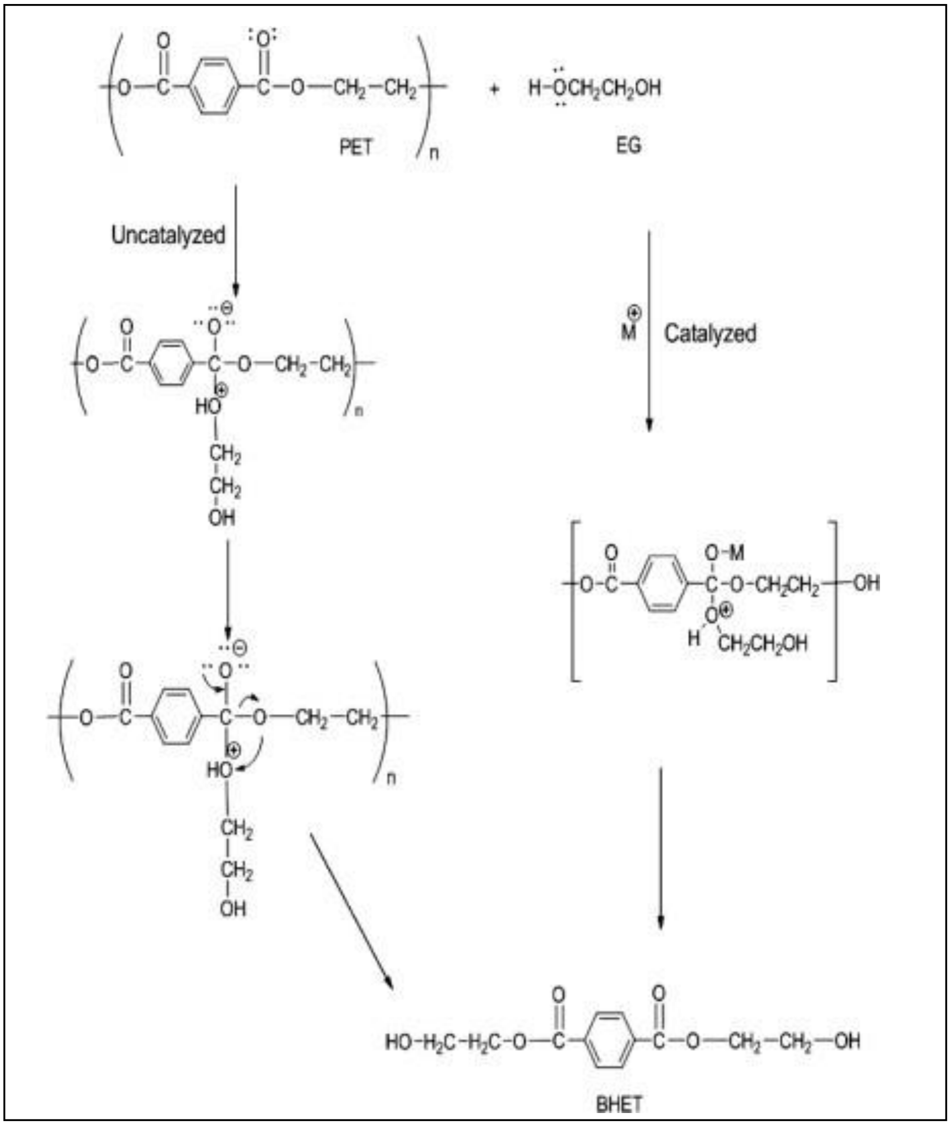


Figure 5: Glycolysis in Presence and absence of catalyst

The use of catalysts in glycolysis is crucial for achieving higher reaction rates and obtaining desirable product yields. Ongoing research aims to explore and develop more efficient catalyst systems for PET depolymerization through glycolysis.

2.2.3.2 Solvent-Assisted Glycolysis

Solvent-assisted glycolysis involves the depolymerization of PET using EG in the presence of another solvent as the reaction medium. When xylene (C8H10) is added to PET glycolysis reactions catalyzed by ZnAc, it improves the yield of BHET by providing mixability to the PET-glycol mixture. At temperatures of 170 to 225°C, EG has limited solubility in xylene but readily dissolves in PET. Additionally, the glycolyzed products are soluble in xylene. As a result, the reaction proceeds, and the glycolyzed products transfer from the PET-glycol phase to the xylene phase.

In 2015, Wang and colleagues reported the use of deep eutectic solvents as catalysts for mild and rapid glycolysis of PET. These solvents, which have low toxicity, are easily prepared, cost-effective, and exhibit good biological compatibility, share similarities with ionic liquids. The researchers synthesized several mixtures of urea-metal salts by combining urea and metal salts at various molar ratios. Under optimal conditions (EG: 20 g, PET: 5 g, catalyst (n(urea)/n(ZnCl2)): 4/1, 0.25 g) at 170°C and atmospheric pressure, they achieved 100% PET conversion and 83% selectivity of BHET in just 38 minutes. The enhanced catalytic activity was attributed to the synergetic catalysis of hydrogen bonding and coordination bonding between the eutectic solvent catalyst and EG.

Urea has also been investigated as a green, low-cost, highly active catalyst for PET degradation, demonstrating 100% conversion of PET waste. In one experiment, the PET waste:EG:urea ratio was 1:4:0.1, and the reaction was conducted under atmospheric pressure at 160°C for 2.5 hours. Despite being used up to 10 times, urea exhibited efficient catalytic performance. Researchers proposed a mechanism based on density functional theory, suggesting that the formation of hydrogen bonds between the carbonyl oxygen of urea and EG increases the O-H bond length of the hydroxyl group in EG, facilitating the loss of a hydrogen atom. This leads to increased nucleophilicity of the oxygen in EG, enabling it to attack the ester group carbon in PET more easily and promote PET glycolysis. Based on this understanding, it was inferred that catalysts capable of forming hydrogen bonds with alcohols can enhance PET degradation.

2.2.3.3 Supercritical Glycolysis

Supercritical glycolysis involves the degradation of PET by EG at temperatures and pressures above the critical point of EG (446.7°C and 8.2 MPa). The use of supercritical fluids in the reaction eliminates the need for catalysts, which can be difficult to separate from the reaction products, making the process more environmentally preferable.

In a study comparing supercritical and subcritical processes, the reaction was conducted at 450°C and 15.3 MPa, and the results were compared to those obtained from subcritical processes carried out at 350°C and 2.49 MPa, and 300°C and 1.1 MPa, respectively. The supercritical method achieved equilibrium between the dimer and BHET early in the process, and within 30 minutes, the yield of BHET reached its maximum at 93.5%. This method also suppressed the formation of by-products and provided a very high yield of BHET.

2.2.3.4 Microwave Assisted Glycolysis

The use of microwave radiation as a source of heat supply significantly reduces the reaction time of glycolysis, decreasing it from 8 hours to just 35 minutes without affecting the yield of the BHET monomer. Researchers are focused on developing more efficient catalysts to be used in combination with microwave radiation, aiming to further increase the monomer yield and reduce the overall reaction time.

In one study, Cho et al. investigated non-aqueous, microwave-irradiated glycolysis in an alkaline atmosphere to develop an economically viable treatment process with reduced reaction time. The effectiveness of the process depended on two parameters: the concentration of the alkali catalyst and the irradiation time, which had an impact on the reaction temperature.

Another study by Chaudhary et al. demonstrated that using microwaves can reduce the total reaction time of glycolysis to approximately 30 minutes.

2.3 Existing Processes

2.3.1 Eastman Kodak Process

The depolymerization process developed and patented by Eastman Kodak Co. involves an installation that includes a dissolver, a depolymerization reactor, and a rectifying column. This system is designed to break down polyester chains into shorter lengths. To begin the process, the molten polymer from the reactor and the liquid from the rectifying column are introduced into the dissolver. This helps in reducing the chain length of the polyester. Subsequently, the polyester undergoes methanolysis using superheated methanol within the reactor.

During the methanolysis step, the superheated methanol vapor passes through the reaction mixture in the reactor, effectively heating it. This results in the formation of a molten mixture comprising low molecular weight polyesters, monomers, monohydric alcohol-ended oligomers, glycols, and DMT. The methanol serves a dual role in the process. It acts as a depolymerization agent, breaking down the polyester, and also functions as a carrier gas stream, removing vapor products from the reaction mixture.

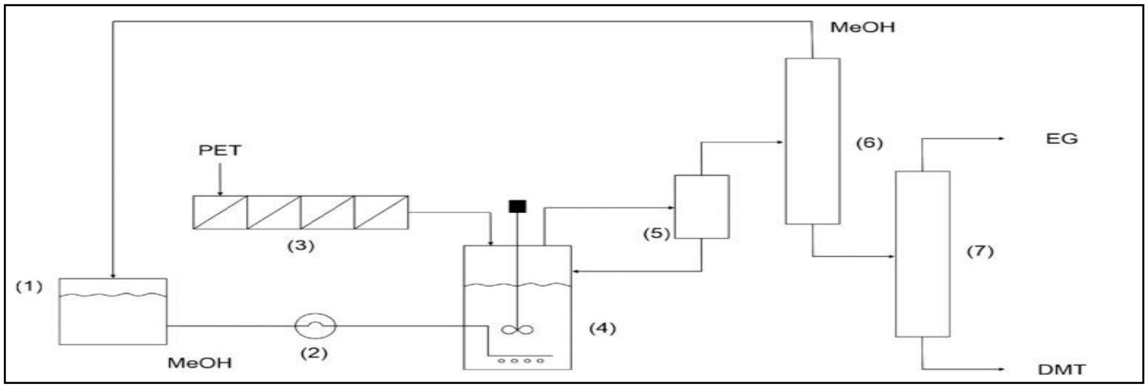


Figure 6: Eastman Kodak Process

2.3.2 Teijin Process

Teijin Ltd. employs its proprietary decomposition method to convert waste PET resin into raw materials used in the production of textiles and films. The process involves partial glycolysis and liquid methanolysis, followed by hydrolysis.

In partial glycolysis, recovered PET flakes are depolymerized using ethylene glycol (EG) containing a PET depolymerization catalyst. The depolymerization occurs at temperatures between 175 and 190 degrees Celsius under a pressure of 0.1 to 0.5 MPa. This step yields BHET (bis(hydroxyethyl) terephthalate) and its oligomers.

BHET is concentrated through distillation and then subjected to an ester interchange reaction, resulting in the formation of crude dimethyl terephthalate (DMT) and ethylene glycol (EG). The mixture is recrystallized in a methanol (MeOH) solvent. Distillation is employed to further purify the recrystallized DMT. Purified DMT is hydrolyzed with water at temperatures ranging from 230 to 250 degrees Celsius, producing terephthalic acid (TPA). Solid-liquid separation is utilized to obtain TPA cakes from the reaction mixture.

Teijin Fiber Ltd. established a plant in 2003 with a DMT production capacity of 50,000 tons per year. The DMT is used in the manufacturing of PET fibers and films.

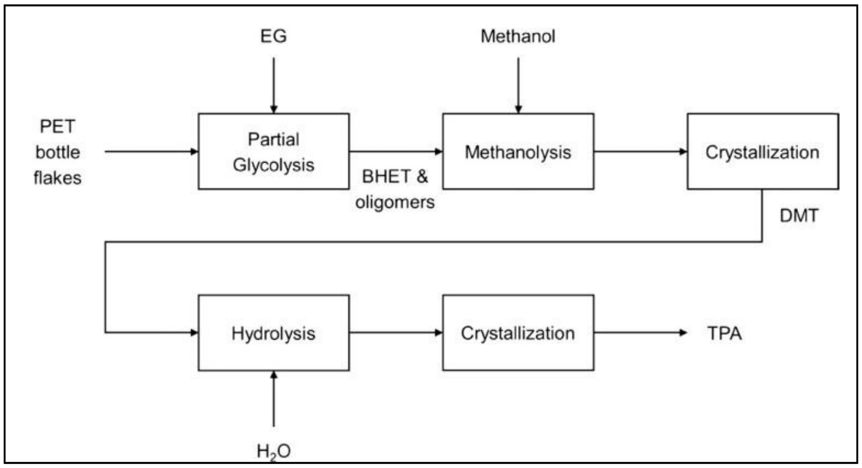


Figure 7: Teijin Process

2.3.3 Chungnum National University Process

Chungnam National University (CNU) has developed a novel recycling process for obtaining DMT (dimethyl terephthalate) and EG (ethylene glycol) from PET bottles. The process combines partial glycolysis and methanolysis to efficiently produce DMT and EG. The synergistic effect of these two processes accelerates the depolymerization process.

The proposed CNU methanolysis process consists of two steps: high-pressure semi-batch glycolysis/methanolysis and low-pressure continuous methanolysis. In the high-pressure step, the polyester chain is shortened through random scission, resulting in the production of oligomers and DMT. The high reaction pressure enhances the methanolysis rate by maintaining a highly dissolved concentration of methanol. However, the reaction is influenced by equilibrium effects. To address this, the equilibrium is shifted by continuously removing the vapor mixture of DMT, EG, and ethanol.

In the low-pressure methanolysis reactor, superheated methanol vapor is introduced at the bottom, where the methanolysis reaction takes place, and its products are removed as a vapor mixture. The low-pressure methanolysis reactor is integrated with a rectifier, where methanol is recovered at the top and recycled back to the low-pressure methanolysis reactor. The bottom products, consisting of DMT, EG, and methanol, are further purified through processes such as crystallization or distillation to obtain high-purity DMT and EG.

This vapor methanolysis approach enables the recycling of low-grade polyester bottles into high-purity DMT. The combination of glycolysis and methanolysis in a hybrid process significantly enhances the depolymerization rate compared to conventional methods. The recycling of vapor from the rectifier to the methanolysis reactor, along with the introduction of fresh methanol to the rectifier, leads to substantial energy savings and reduces conversion costs. Integrating the methanolysis reactor with the rectifier facilitates easy adjustment of operating pressure and composition of the bottom product, resulting in reduced separation workload.

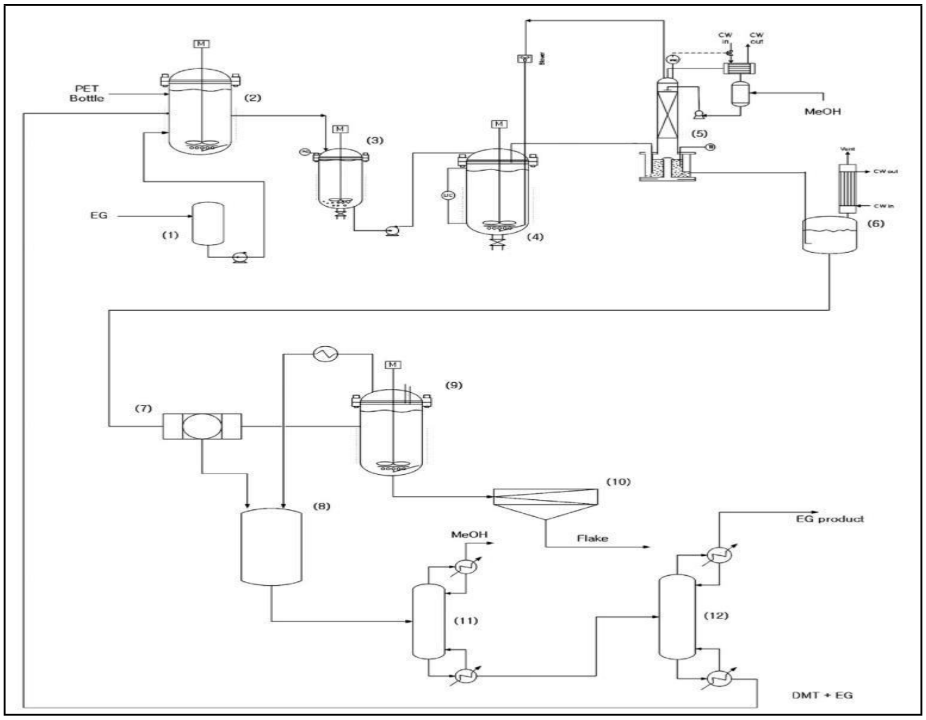


Figure 8: CNU Process

2.3.4 Mitsubishi Process

Mitsubishi Heavy Industries, Ltd. (MHI) of Japan has developed an innovative chemical recycling process utilizing supercritical methanol to depolymerize postconsumer PET bottles and obtain monomers suitable for the production of PET resin. The pilot plant process involves several key steps, including shredding the PET bottles, depolymerization of the shredded material using supercritical methanol, separation and purification of DMT (dimethyl terephthalate) and EG (ethylene glycol) obtained from the depolymerization, and hydrolysis of DMT into TPA (terephthalic acid).

In this process, postconsumer PET bottles are initially transformed into flakes through shredding. These flakes are then subjected to depolymerization using supercritical methanol, resulting in the production of a mixture containing DMT, EG, and methanol. The subsequent step involves separating and purifying the components primarily through distillation. The EG is purified by isolating it from the mixture of EG and excess methanol in an EG/methanol purification process. The purified DMT monomer is further converted into highly purified terephthalic acid (PTA) through hydrolysis.

The converted PTA and purified EG can then be utilized in existing PET resin production plants for polymerization. These sequential steps establish an efficient cyclical recycling system, allowing for the transformation of postconsumer PET bottles into pure monomers that can be used as feedstocks in PET resin production.

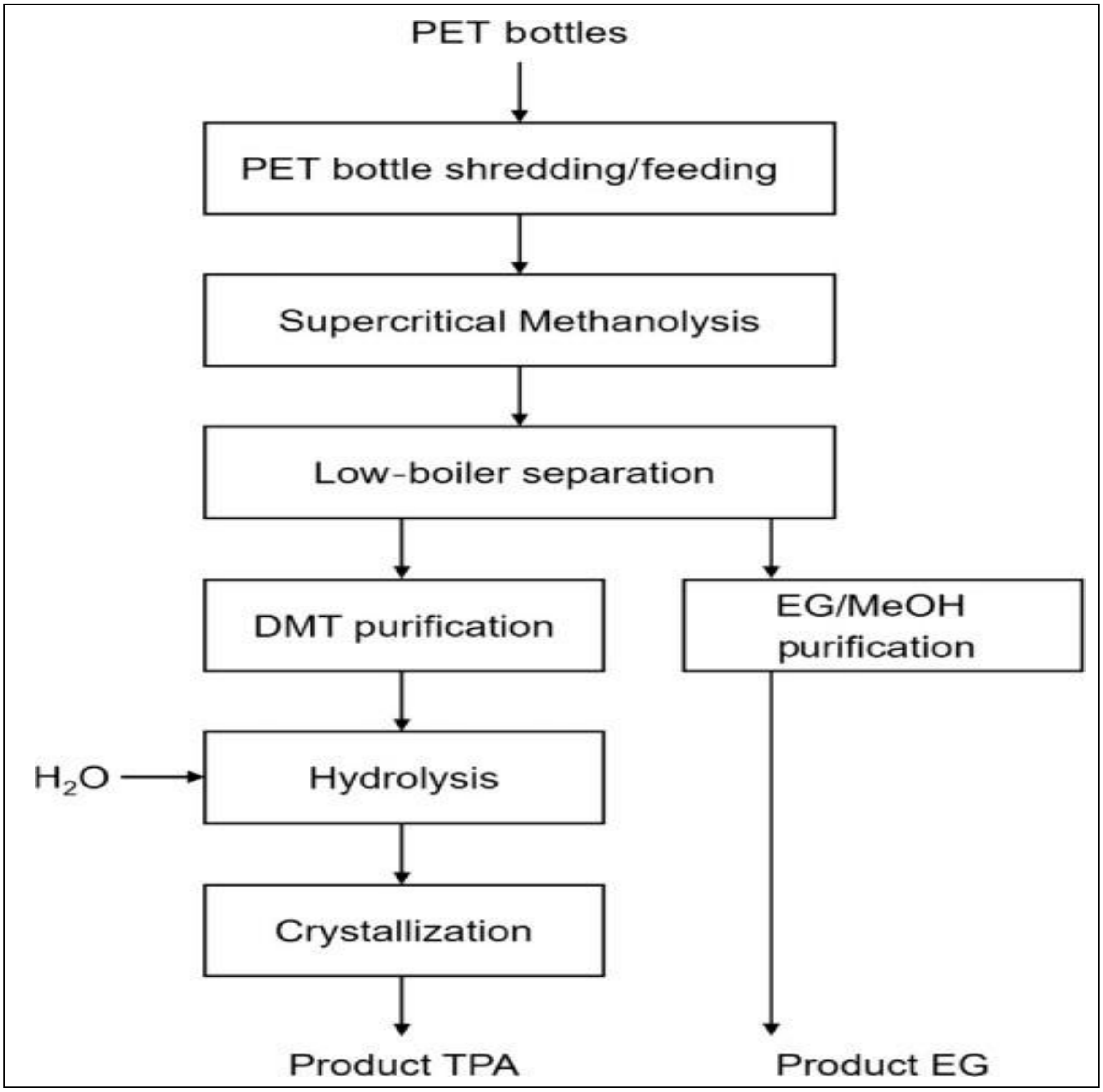


Figure 9: Mitsubishi Process

CHAPTER NO 3

PROCESS DESCRIPTION

3.1 Process

The process is mainly divided into two parts.

1. The depolymerization of PET to produce the monomers i.e., DMT and EG
2. Purification of DMT and EG

This first step is to crush the PET bottles using a cone crusher. The size of the bottles is reduced to approximately 300μm. This crushed PET is mixed with liquid methanol using a mixer and the output stream is sent to a series of pumps. The first pump will increase the pressure of the upcoming stream to 4bar, and the second pump will increase the pressure to about 80 bar.

Next step is to increase the temperature of the feed to 300°C using a spiral type of heat exchanger. The purpose of increasing the temperature and pressure was to meet the reaction conditions that occur in the presence of the supercritical methanol at elevated temperatures and pressure. In supercritical state the fluid has both the properties of liquid and gas which makes them hard to distinguish, that's why the PET and methanol mixture will have a greater density as in liquid and have a greater kinetic energy when in gas state. Moreover, the rate of reaction under these conditions will be very high.

After the temperature and pressure are increased, the stream is sent to a reactor (CSTR). The reaction, which follows third order mechanism, is given below.

$PET + MeOH \rightarrow DMT + EG$

Now the second part of the process begins. We need to purify the monomers. The DMT and EG form azeotropes which are very hard to separate. For this we are using a crystallizer which will crystallize the DMT, and the mixture is sent to the filter where the solid DMT is removed which is then sent to the vacuum filter to remove any vapors associated. These vapors and the liquid stream from the filter are then mixed and sent to the separator columns.

The first column is the Methanol Separator which will recover the maximum amount of methanol from overhead. This recycled methanol is sent back to the process to be reused. The bottom product of the column contains Ethylene Glycol and some traces of unreacted PET, EG and methanol.

The bottom product is then sent to the separator column two that will recover maximum amount of the Ethylene glycol which is the desired product of our process.

3.2 Equipment

3.2.1 Cone Crusher

A cone crusher is a mechanical device used to reduce the size of rocks and ores in various industries. It is designed to crush materials by squeezing them between an eccentrically rotating mantle and a concave, or bowl liner. The cone crusher operates through a motor that drives the eccentric sleeve to rotate, causing the mantle to move in a circular motion. As the mantle approaches the concave, the rocks or ores are compressed and crushed into smaller pieces.

One of the key components of a cone crusher is the crushing chamber, which is formed by the mantle and the concave. The geometry of the chamber plays a crucial role in determining the crusher's performance. A larger chamber allows for a higher throughput and better particle size distribution, while a smaller chamber produces finer crushed material.

To control the size of the output material, cone crushers are equipped with an adjustable gap setting mechanism. By changing the distance between the mantle and the concave, the operator can regulate the size of the final product. This feature makes cone crushers suitable for a wide range of applications, from producing aggregates for construction to processing ores in mining operations.

Cone crushers come in different designs and configurations, including the popular Symons cone crusher, which is known for its robust construction and high efficiency.

Other variations include the compound cone crusher and the hydraulic cone crusher, each offering unique advantages depending on the specific application.

In terms of maintenance, cone crushers require regular inspection and servicing to ensure optimal performance. This includes checking the wear of the mantle and concave, as well as monitoring the lubrication system to prevent excessive wear and overheating. Additionally, cone crushers often feature a tramp release system to protect the crusher from damage caused by uncrushable materials.

Overall, cone crushers are reliable and efficient machines used in the crushing process. They play a vital role in various industries by reducing the size of rocks and ores, enabling further processing, and maximizing the value of the extracted materials.

3.2.2 Film Type Crystallizer

In industrial processes, a film-type crystallizer is used to facilitate the controlled crystallization of substances from solutions or melts.

The crystallizer of the film type works by depositing a thin film of the melt or solution on a heated surface. This allows for controlled cooling or evaporation to cause crystallization. The thin film increases the ratio of surface area to volume, facilitating effective heat and mass transfer, which is necessary for the formation of crystals with distinct shapes.

A heated surface, like a rotating drum or a plate, on which the solution or melt is spread is one of the most important parts of a film-type crystallizer. The surface temperature is maintained by the heat source, and mechanisms like scraper blades or wipers assist in maintaining a uniform and thin film. Crystals form on the surface because of the controlled cooling or evaporation process, which can then be harvested or processed further as required.

Film crystallizers are used in a variety of industries, including food processing, pharmaceuticals, and chemical manufacturing. They are advantageous due to their efficient heat and mass transfer, controllable crystal size, and high crystal purity. Film-type crystallizers are useful in applications that require precise control over the crystallization processes to obtain crystals with particular properties for further use or purification.

3.2.3 Indirect Steam Dryer

An indirect steam dryer is a highly efficient and versatile drying system that utilizes steam as a heat source to remove moisture from various materials. It is designed to achieve optimal drying results while minimizing energy consumption and maintaining product quality.

Unlike direct steam dryers, which involve direct contact between the material being dried and the steam, indirect steam dryers employ an intermediate heat transfer medium to transfer heat to the material. This indirect heating method offers several advantages, including enhanced safety and the ability to handle heat-sensitive materials.

The indirect steam dryer consists of a rotating drum or cylinder, which serves as the drying chamber. The wet material is fed into the dryer at one end and gradually moves through the length of the cylinder due to the rotation. As the material travels, it is exposed to a continuous flow of steam that circulates through the cylinder's outer jacket or through internal heat transfer surfaces.

The steam, supplied from an external source, flows through the jacket or heat transfer surfaces, transferring its thermal energy to the intermediate medium (often thermal oil or water). This heat transfer medium then delivers the heat to the material in the drying chamber, resulting in the evaporation of moisture.

The indirect steam dryer is equipped with various mechanisms to optimize the drying process. These may include specially designed flights or baffles within the drying chamber to ensure thorough mixing and even distribution of the material, maximizing heat transfer efficiency.

The vapor generated from the drying process is typically collected and condensed to recover the valuable products or capture any volatile substances released. The condensed water can be treated and reused, contributing to the overall sustainability of the drying system.

Indirect steam dryers find applications in a wide range of industries, including food processing, pharmaceuticals, chemicals, and agriculture. They are particularly effective in drying heat-sensitive materials such as powders, granules, fibers, and pastes, where maintaining product integrity is crucial.

In summary, an indirect steam dryer is a sophisticated drying system that utilizes steam as a heat source indirectly through an intermediate medium. It offers enhanced safety, efficient drying, and the ability to handle delicate materials, making it a valuable solution for numerous industrial drying applications.

3.3 Process Flow Diagram:

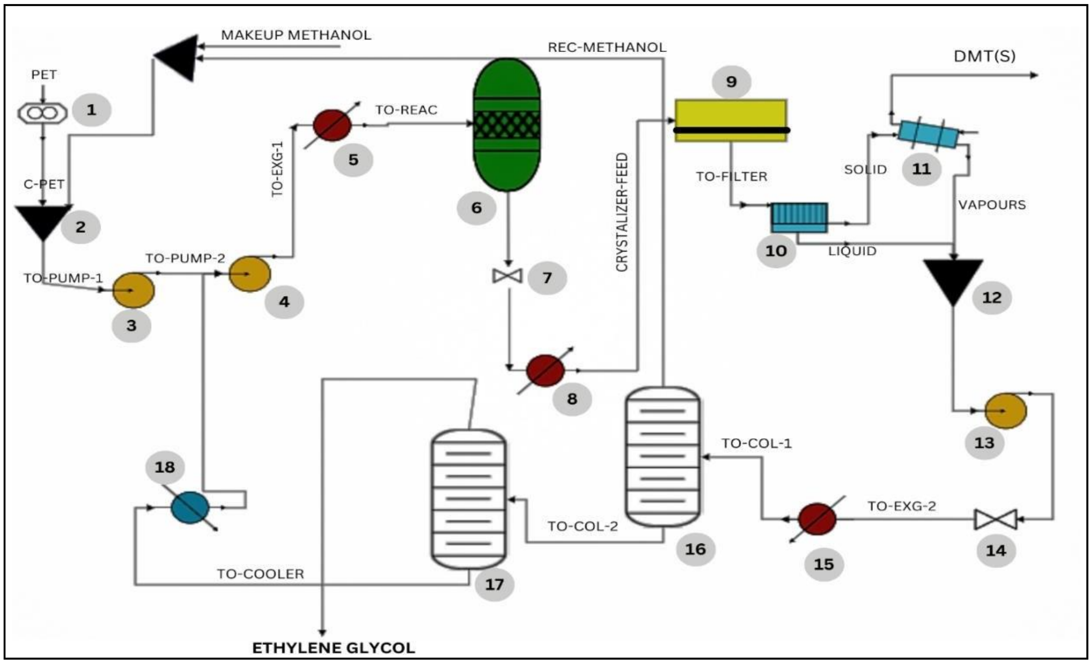


Figure 10: Process Flow Diagram

CHAPTER NO 4

MATERIAL BALANCE

The material balance was carried out by applying the law of conservation of mass to each of the important components present within the proposed design.

Input = Output + Accumulation ± Generation/Consumption

From law of conservation of mass, we get:

Mass flow rate of component in = Mass flow rate of component out
From here on, the results of material balance for each component
are shown in tabular form.

4.1 Mixer-1

Mass flow rate entering in Mixer = Mass flow rate leaving the Mixer

Table 1: Mixer1 Material balance

Units	In		Out
kg/hr	**CPET**	**METHANOL**	**MIXFEED**
METHANOL	0	3026.10	3026.10
PET	1812.01	0	1812.01
DMT	0	0	0
EG	0	0	0
DMT(S)	0	0	0
Total	**1812.01**	**3026.10**	**4838.11**

4.2 Mixer-2

From law of conservation of mass, we get:

Mass flow rate of component in = Mass flow rate of component out

Table 2: Mixer2 Material balance

Units	In		Out
kg/hr	**MIX-FEED**	**REC-1**	**TO-PUMP**
METHANOL	3026.10	6.67E-08	3026.10
PET	1812.01	1.18	1813.19
DMT	0	246.22	246.22
EG	0	4.70	4.70
DMT(S)	0	0	0
Total	**4838.11**	**252.09**	**5090.20**

4.3 Reactor

Mass flow rate entering in Reactor = Mass flow rate leaving the Reactor

Table 3: Reactor Material balance

Units	In	Out
kg/hr	**REA-FEED**	**REAC-OUT**
METHANOL	3026.10	2441.13
PET	1813.19	58.93
DMT	246.22	2018.92
EG	4.70	571.32
DMT(S)	0	0

Total	**5090.20**	**5090.30**

4.4 Crystallizer

Mass flow rate entering in Crystallizer = Mass flow rate leaving the Crystallizer

Table 4: Crystallizer Material balance

Units	In	Out
kg/hr	**CRY-FEED**	**TO-FILTR**
METHANOL	2441.13	2441.13
PET	58.93	58.93
DMT	2018.91	209.97
EG	571.32	571.32
DMT(S)	0	1808.95
Total	**5090.30**	**5090.30**

4.5 Dryer

Mass flow rate entering in Dryer = Mass flow rate leaving the Dryer

Table 5: Dryer Material balance

Units	In	Out
kg/hr	**SOLID**	**DRY-PRO**
METHANOL	24.41	0
PET	57.75	57.75
DMT	2.09	0
EG	5.71	0
DMT(S)	1772.77	1772.77
Total	**1862.75**	**1830.52**

4.6 Mixer-3

Mass flow rate entering in Mixer = Mass flow rate leaving the Mixer

Table 6: Mixer3 Material balance

Units	In		Out
kg/hr	**LIQUID**	**VAPOUR**	**TO-COL-1**
METHANOL	2416.72	24.41	2441.13
PET	1.18	0	1.18
DMT	207.87	2.10	209.97
EG	565.60	5.71	571.32
DMT(S)	36.18	0	36.18
Total	**3227.55**	**32.22**	**3259.77**

4.7 Distillation Column1

Table 7: REC-COL-1 Material balance

Units	In	Out	
kg/hr	**TO-COL-1**	**METH-REC**	**TO-COL-2**
METHANOL	2441.13	2440.89	0.24
PET	1.18	0	1.18
DMT	209.97	trace	246.15
EG	571.32	trace	571.32
DMT(S)	36.18	0	0
Total	**3259.77**	**2440.89**	**818.88**

4.8 Distillation Column2

Mass flow rate entering in Column2 = Mass flow rate leaving the Column2

Table 8: REC-COL-2 Material balance

Units	In	Out	
kg/hr	**TO-COL-2**	**RECYCLE**	**ETH-GLY**
METHANOL	0.24	0	0.24
PET	1.18	1.18	0
DMT	246.15	246.15	0
EG	571.32	1.31	570.00
DMT(S)	0	0	0
Total	**818.88**	**248.64**	**570.25**

CHAPTER NO 5

ENERGY BALANCE

After completing the material balances, we then performed energy balance on the appropriate equipment. As energy can neither be created nor destroyed but it can be converted to other forms of energy so all the energy going into the system will be converted to heat or performed work. Energy balance applied on the equipment's are:

5.1 Pump

Pumps are used to increase the pressure of liquids. Following equation was used to calculate the duty of the pump:

$$Q_{p1} = \dot{m}\left(\Delta Z + \frac{\Delta P}{\rho g} + \Delta\frac{v^2}{2g}\right) + Q_{losses}$$

Ignoring elevations, changes in velocity and losses, and incorporatingefficiency of pump, the equation is reduced to:

$$\eta Q_{p1} = \dot{m}\left(\frac{\Delta P}{\rho}\right)$$

Table 9: Pump Duty

PUMP	Efficiency	0.75
	In	**Out**
	TO-PUMP	**REA-FEED**
Molar flow (kmol/hr)	105.23	105.23
Mass flow (kg/hr)	5090.20	5090.20
Density	863.16	

Temperature	334.80	337.30
Pressure	1	80
Work Input (KW)	**17.2546899**	

5.2 Reactor

Following reaction takes place in the reactor:

PET + 2METHANOL → EG + DMT

Table 10: Reactor Duty

Reactor	In	Out
	REA-FEED	**REAC-PRO**
Molar flow (kmol/hr)	105.23	96.10
Mass flow (kg/hr)	5090.20	5090.30
Liquid phase/vapor phase	106.50	90.98
Solid phase	50.34	53.07
Avg Cp	101.47	90.85
Temperature (K)	337.31	573
Sensible heat	686606.64	2619268.78

Heat of vaporization methanol (kJ/Kmol)	36000	
Delta H vaporization	5.33E+06	
Delta h using heat of reaction, to get reactor cooling water duty	3.40E+06	
Heat of reaction (kJ/kmol PET)	-1.04E+06	
REACTOR DUTY	-4.12E+06	6.00E+06

5.3 Crystallizer

In Crystallizer the liquid dimethyl terephthalate is crystallized into solid form.

Table 11: Crystallizer Energy balance

Crystallizer	In	Out
	CRY-FEED	**TO-FILTR**
Molar flow (kmol/hr)	96.10	96.10
Mass flow (kg/hr)	5090.20	5090.20
Liquid phase/vapor phase	47.98	91.00
Solid phase	192.49	250.30

Avg Cp	48.44	82.61
Temperature (K)	591.33	297.85
Sensible Heat	-1847988.6	
Heat of crystallization	-686770	
Total	-8.25E+06	

5.4 Distillation Columns

The energy balance for a distillation column is based on the law of conservation of energy, which states that energy cannot be created or destroyed, only transformed. The energy balance equation for a distillation column is as follows:

$$\mathbf{Q = H_{feed} + H_{reboiler} - H_{condenser} - H_{bottoms}}$$

Table 12: Distillation Column1 Energy balance

REC-COL1	In	Out	
	TO-COL1	**METH-REC**	**TO-COL2**
Molar flow (kmol/hr)	86.6682203	76.18254455	10.48567571
Mass flow (kg/hr)	3259.77313	2440.888727	818.8843993
Temperature (C)	29.6053659	64.20060972	240.8943326

Temperature (K)	302.605366	337.2006097	513.8943326
Cp (kJ/kmolK)	99.0115042	107.3028836	220.1052292
Latent Heat (kJ/kmol)	38781.2		45610.8
Enthalpy	254048.111	524814.7352	555972.5703
Boiling Point (C)		64.7	
Reflux Ratio	1		
Vapor Rate from column (kmol/hr)		152.3650891	
Heat Load on Boiler (kJ/hr)		**5.69E+06**	
Heat Load on Condenser (kJ/hr)		**4.87E+06**	

Table 13: Distillation Column2 Energy balance

REC-COL2	In	Out	
	To-COL2	**RECYCLE**	**ETH-GLY**
Molar flow (kmol/hr)	10.49	1.29	9.19
Mass flow (kg/hr)	818.88	248.64	570.25
Temperature (C)	240.86	347.45	192.75

Temperature (K)	513.86	620.45	465.75
Cp (kJ/kmolK)	213.50	335.97	192.85
Latent Heat (kJ/kmol)	38781.20		45610.80
Enthalpy	539231.32	151152.88	341645.23
Boiling Point (C)		197	
Reflux Ratio	0.17		
Vapor Rate from column (kmol/hr)		18.38	
Heat Load on Boiler (kJ/hr)		**1.29E+06**	
Heat Load on Condenser (kJ/hr)		**1.34E+06**	

5.5 Cooler

The energy balance for coolers is based on the conservation of energy. In other words, the total energy of a system remains constant. In the case of a cooler, the system is the air inside the cooler and the coolant. The coolant is typically water or a glycol-water mixture. The coolant flows through the cooler and absorbs heat from the air inside the cooler. The heat is then carried away from the cooler and dissipated to the environment.

The energy balance equation for a cooler can be expressed as:

Heat Input = Heat Output + Heat Losses

Energy balance for Cooler is given as:

Table 14: Distillation Column Energy balance

Cooler	In	Out
	RECYCLE	**REC-1**
Molar flow (kmol/hr)	1.29	1.29
Mass flow (kg/hr)	248.64	248.64
Cp (kJ/kmolK)	386.41	208.56
Enthalpy	173848.43	6751.36
Temperature	347.45	25
Pressure	4	1
Heat duty (kJ/hr)	**-167097.07**	

CHAPTER NO 6

EQUIPMENT DESIGN

6.1 De-polymerization Reactor

The De-polymerization reactor is a continuous stirred tank – type reactor (CSTR) in which the vapor-solid mixture is agitated at a high RPM and provided with sufficient residence time for the desired reaction to occur with the conversion required. This reactor has been selected due to the high-level agitation required for the solid particles to remain suspended in the vapor and continue reacting with it. The reaction taking place in the reactor is given below:

$$(C_{10}H_8O_4)_n + 2n\,(CH_3OH) \;------\rightarrow n(C_{10}H_{10}O_4) + n(C_2H_6O_2)$$

Where, 1 mole of PET reacts with 2 moles of methanol to give 1 mole of DMT and 1 mole of ethylene glycol (our desired product).

Table 15: Reaction Parameters

PARAMETER	VALUE	UNITS
Temperature	300	C
Pressure	80	bar
Conversion	0.97	
Residence time	30	min
Activation energy	131.8	kJ/mol

This is a reaction of the general form:

$$A + 2B \;------\rightarrow C + D$$

Which can be assumed to have the following rate equation:

$$-r_A = kC_A C_B{}^2$$

In the design calculations for the reactor, we need the volume required as well as the dimensions for the reactor, to calculate the volume, we need to plug in the boundary conditions of the reactor into the integrated rate equation for the reactor given below, to first get the value of the rate constant (k):

$$\frac{1}{C_B{}^2} \ln\left(\frac{C_A}{C_{A_0}}\right) = -kt$$

The value of k obtained was: **0.009 mol^6/kmol^{2}s**

$$V = \frac{F_{ao} X_a}{-r_a}$$

The results are given in this table:

Table 16: Reaction calculation results

PARAMETER	VALUE	UNITS
F_{A0}	0.003	kmol/s
C_{A0}	0.066	kmol/m^3
C_{B0}	2.407	kmol/m^3
C_A	0.002	kmol/m^3
C_B	2.343	kmol/m^3
t	1800.000	S
k	0.009	m^6/kmol^{2}s
V	15.538	m3
L/D	3.000	
D	1.875	m
L	5.626	m

6.2 Heat Exchanger

For the reaction to take place at the required temperature and pressure conditions, pumping and heating is required, the feed mixture is heated in a shell and tube heat exchanger (after pumping to raise the pressure to 80 bar) to increase the feed temperature to 300 °C.. Kern's method will be used to get an initial idea about that magnitude of calculated values in the design, followed using Aspen Exchanger Design and Raring (ASPEN EDR) software for accurate determination of ideal geometry and size.

Fluid allocation

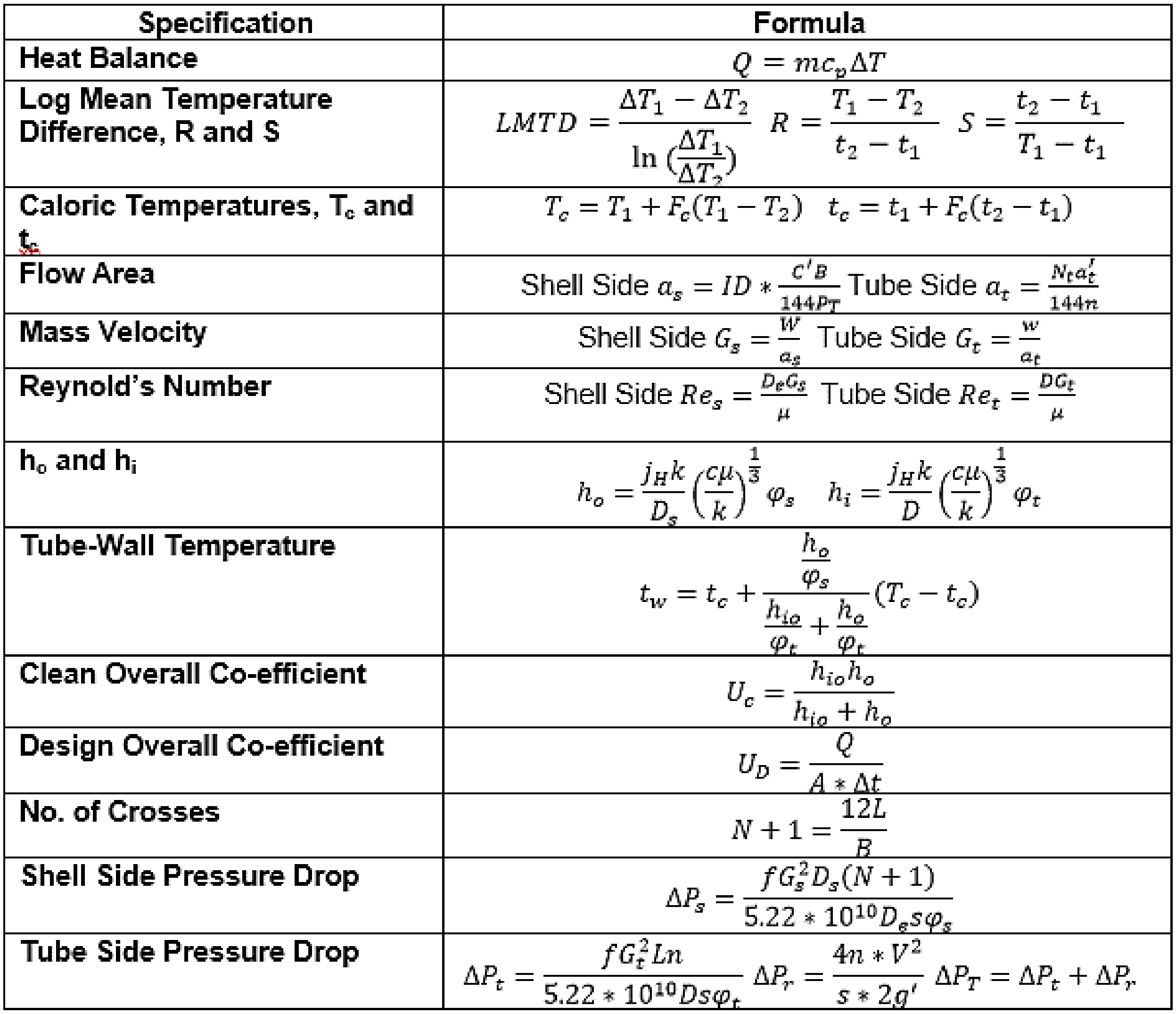
- The tube side consists of the cold fluid which is the reactor feed mixture containing PET, Ethylene Glycol, Dimethyl Terephthalate and Methanol.
- The shell side consists of the hot fluid, steam at 95 bar pressure.

Table 17: Fluid Allocation and parameters

Cold Fluid - Tube Side		**Hot Fluid - Shell Side**	
Parameters	Value	Parameters	Value
Inlet Temperature (°C)	64.3	Inlet T (°C)	324.26
Outlet T (°C)	300.1	Outlet T (°C)	210.59
Mass flowrate (kg/hr)	12832	Mass Flowrate (kg/hr)	18015
Avg. Cp (kJ/kg °C)	2.178	Cp (kJ/kg°C) vapor	8.865
Avg. density (kg/m^3)	899.71	Density (kg/m^3) vapor	639.445
Avg. viscosity (Cp)	0.251	Viscosity (Cp) vapor	0.10155
Thermal conductivity (W/m °C)	0.1323	Thermal Conductivity (W/m °C)	0.5797

Kern’s Method

Kern’s method equations:



Specification	Formula
Heat Balance	$Q = mc_p\Delta T$
Log Mean Temperature Difference, R and S	$LMTD = \frac{\Delta T_1 - \Delta T_2}{\ln\left(\frac{\Delta T_1}{\Delta T_2}\right)}$ $R = \frac{T_1 - T_2}{t_2 - t_1}$ $S = \frac{t_2 - t_1}{T_1 - t_1}$
Caloric Temperatures, T_c and t_c	$T_c = T_1 + F_c(T_1 - T_2)$ $t_c = t_1 + F_c(t_2 - t_1)$
Flow Area	Shell Side $a_s = ID * \frac{C'B}{144P_T}$ Tube Side $a_t = \frac{N_t a_t'}{144n}$
Mass Velocity	Shell Side $G_s = \frac{W}{a_s}$ Tube Side $G_t = \frac{w}{a_t}$
Reynold’s Number	Shell Side $Re_s = \frac{D_e G_s}{\mu}$ Tube Side $Re_t = \frac{DG_t}{\mu}$
h_o and h_i	$h_o = \frac{j_H k}{D_s}\left(\frac{c\mu}{k}\right)^{\frac{1}{3}}\varphi_s$ $h_i = \frac{j_H k}{D}\left(\frac{c\mu}{k}\right)^{\frac{1}{3}}\varphi_t$
Tube-Wall Temperature	$t_w = t_c + \frac{\frac{h_o}{\varphi_s}}{\frac{h_{io}}{\varphi_t} + \frac{h_o}{\varphi_t}}(T_c - t_c)$
Clean Overall Co-efficient	$U_c = \frac{h_{io}h_o}{h_{io} + h_o}$
Design Overall Co-efficient	$U_D = \frac{Q}{A * \Delta t}$
No. of Crosses	$N + 1 = \frac{12L}{B}$
Shell Side Pressure Drop	$\Delta P_s = \frac{fG_s^2 D_s(N+1)}{5.22 * 10^{10} D_e s\varphi_s}$
Tube Side Pressure Drop	$\Delta P_t = \frac{fG_t^2 Ln}{5.22 * 10^{10} Ds\varphi_t}$ $\Delta P_r = \frac{4n * V^2}{s * 2g'}$ $\Delta P_T = \Delta P_t + \Delta P_r$

Figure 11: Kern’s method equations summarized.

Using the equations given in the table above, we determined the value of the following parameters: Heat duty, LMTD, Reynolds and Prandtl number, Film coefficient, Clean and Design coefficients, Area, and Pressure drop.

These calculated values have been summarized in the table given below:

Table 18: Kern's method parameters

Parameters	**Tube Side**	**Shell Side**
Duty (kW)	4602.2	
LMTD (^oC)	67.66	
Reynold number	12826	76782
Prandtl number	4.36	-
h (film coefficient)	1910	11576
U_c ($W/m^2\,^oC$)	1530	
U_d ($W/m^2\,^oC$)	990	
R_d ($m^2\,^oC$ /W)	0.0001	
Area (m^2)	54.9	
Pressure Drop (kPa)	31.23	37.82

Geometry and Sizing

After the calculation of these parameters, Aspen EDR was used to finalize the design by allowing selection of appropriate geometry and sizes for different dimensions required for heat exchanger design. This was done by modifying and improving upon the design by using the Aspen EDR software based on the operational warnings it gives while running the exchanger. This includes warnings about temperature cross, fouling parameter issues, number of passes for shell and tube side etc. After some trial and error, the final sizing and geometry is given in the table below.

Table 19: Tube side sizing parameters

Tube Side	
Number	180
Length (m)	5.156
OD (m)	0.01905
ID (m)	0.01483
Pitch	Triangular
Passes	4
Material	Carbon Steel

Table 20: Shell side sizing parameters

Shell Side	
OD (m)	0.46
ID (m)	0.39
Passes	1
Baffle Spacing (m)	0.15
Material	Carbon Steel

6.3 Ethylene Glycol Separator

The most critical equipment in this whole process besides the de-polymerization reactor is the second distillation column which separates out the ethylene glycol which is the main product of the process. Rigorous design of this distillation column is needed as a highly pure product; 99.95% ethylene glycol, is required for it to be sold as a valuable product.

The design method used for this purpose is the Erbar-Maddox method of distillation column design using the Antoine equations. The Erbar-Maddox correlation allows us to relate the ideal stages for a given separation requirement to the min. and max. reflux ratios.

The light key and heavy key components are decided based on their boiling points to be Ethylene glycol and Dimethyl terephthalate.

First, the inlet and outlet streams must be defined based on required separation:

Inlet Stream of Ethylene Glycol separator				
Component	**Mass flow (kg/hr)**	**Molecular Weight**	**Moles**	**Mole Fraction**
Methanol	1.25	32.00	0.04	0.00
DMT	246.28	194.00	1.27	0.12
EG	571.77	62.00	9.22	0.88
TOTAL	819.30	TOTAL	10.53	1

Table 21: Inlet stream values

Table 22: Outlet tops stream values

Ethylene Glycol Product				
Component	**Mass (Kg/hr)**	**mw**	**Moles**	**Mol.frac**
Methanol	1.25	32.00	0.04	0.0042

EG	567.06	62.00	9.15	0.995
DMT	0.08	194.00	4.13E-04	4.47E-05
TOTAL	568.39	TOTAL	9.19	1

Table 23: Outlet bottoms stream values

Recycle				
Component	Mass (Kg/hr)	mw	Moles	Mol.frac
EG	4.71	62.00	0.08	0.06
DMT	246.12	194.00	1.27	0.94
TOTAL	250.83	TOTAL	1.34	1

Dew and bubble point calculations

Antoine equation constants for the volatile components in the mixture (PET is not volatile):

Table 24: Antoine constant values

ANTOINE EQUATION CONSTANTS			
Component	A	B	C
Methanol	8.07247	1574.99	238.86
EG	7.76432	1851.88	181.744
DMT	8.04387	2819.15	258.023

Now that the initial information for all streams as well as the Antoine constants are known, dew and bubble point calculations must be conducted to find the top and bottom temperatures of the column, the operating pressures for the top and bottom were obtained through simulation; 1 bar in the condenser and 4 bar in the reboiler.

Table 25: Relative volatilities in feed

Feed							
Component	A	B	C	LogPo	Po (mmHg)	Po (Pa)	Relative Volatilities
Methanol	8.07247	1574.99	238.86	4.78966	61611.4	8214153	248.978
EG	7.76432	1851.88	181.744	3.38276	2414.12	321855	9.75569
DMT	8.04387	2819.15	258.023	2.3935	247.458	32991.5	1

Feed temperature = 240.9 ^{o}C

Table 26: Relative volatilities in tops

$$\log\,(P_o) = A - \frac{B}{C+T}$$

Component	A	B	C	LogPo	Po (mmHg)	Po (Pa)	Relative Volatilities
Methanol	8.07247	1574.99	238.86	4.44427	27814.5	3708288	416.986
EG	7.76432	1851.88	181.744	2.85192	711.089	94803.8	10.6604
DMT	8.04387	2819.15	258.023	1.82415	66.7038	8893.09	1

$$\sum x_i = \sum \frac{y_i}{K_i}$$

Table 27: Dew point calculation in tops

T (Top) (^oC)	195.2
ki	yi/ki
37.0829	0.00012
0.94804	1.05028
0.08893	0.0005
Sum	1.05089

The value of dew point is calculated as the temperature at which the summation yi/Ki term approaches unity. The temperature value obtained from this hit and trial is 195.2 ^oC.

Table 28: Relative volatilities in bottoms

Component	A	B	C	LogPo	Po (mmHg)	Po (Pa)	Relative Volatilities
Methanol	8.07247	1574.99	238.86	5.36187	230077	3.1E+07	103.497
EG	7.76432	1851.88	181.744	4.22975	16972.5	2262808	7.63484
DMT	8.04387	2819.15	258.023	3.34695	2223.03	296379	1

Table 29: Bubble point calculation in bottoms

$$\sum y_i = \sum K_i x_i$$

T (Bottom) (C)	342.189
ki	Ki(xi)
-	-
5.65702	0.31935
0.74095	0.69912
Sum	1.01847

The value of bubble point is calculated as the temperature at which the summation Kixi term approaches unity. The temperature value obtained from this hit and trial is 342.2 °C.

Calculating minimum number of stages using the Fenske Equation

Table 30: Mean relative volatilities.

Component	A	B	C	LogPo	Po (mmHg)	Po (Pa)	Relative Volatilities
Methanol	8.07247	1574.99	238.86	4.90307	79996.69	10665319	207.74
EG	7.81568	1851.88	181.744	3.54083	3474.04	463166	9.022
DMT	8.16254	2819.15	258.023	2.58554	385.07	51339	1

$$N = \frac{log\left[\left(\frac{x_d}{1-x_d}\right)\left(\frac{1-x_b}{x_b}\right)\right]}{\log\left(\alpha_{avg}\right)}$$

Minimum number of stages = 5.83; Approximately 6 stages

Calculating minimum reflux ratio

For this process we need to use the mean relative volatilities of the system to calculate Θ and Rm (minimum reflux ratio).

$$\sum \frac{\alpha_i x_{i,f}}{\alpha_i - \theta} = 1 - q = 0, where\ q = 1\ for\ boiling\ feed$$

Table 31: Calculating theta.

Theta		**1.122**	
Component	**Relative Volatilities**	**Mole Fraction**	$\frac{\alpha_i x_{i,f}}{\alpha_i - \theta}$
Methanol	207.7416747	0.003711269	0.003731422
EG	9.021660163	0.875735488	1.000117449

DMT	1	0.120553242	-0.988141331
		Sum	0.01570754

Value of theta obtained = 1.122, summation must equal zero according to equation.

$$\sum \frac{\alpha_i x_{i,d}}{\alpha_i - \theta} = R_m + 1$$

Table 32: Calculating minimum reflux ratio.

Theta		**1.122**	
Component	**Relative Volatilities**	**Mole Fraction**	$\frac{\alpha_i x_{i,d}}{\alpha_i - \theta}$
Methanol	207.7416747	0.00425469	0.004277798
EG	9.021660163	0.99570058	1.137121354
DMT	1	4.4725E-05	-0.000366598
		Sum	1.141032555

Value of Minimum Reflux ratio obtained = 1.122, value of the summation is the minimum reflux ratio obtained for a given value of theta.

Now theoretical number of stages are calculated using the Erbar-Maddox correlation graphs (figure 6.2):

Table 33: Calculating theoretical number of stages.

Rm+1=1.141		
Rm	0.141032555	Trial and error
Actual Reflux Ratio	0.3	
Theoretical Number of Stages		
Rm/Rm+1	0.123600816	
R/R+1	0.230769231	

Nm/N (from graph)	0.432		
N	13.88888889	Approx…	14

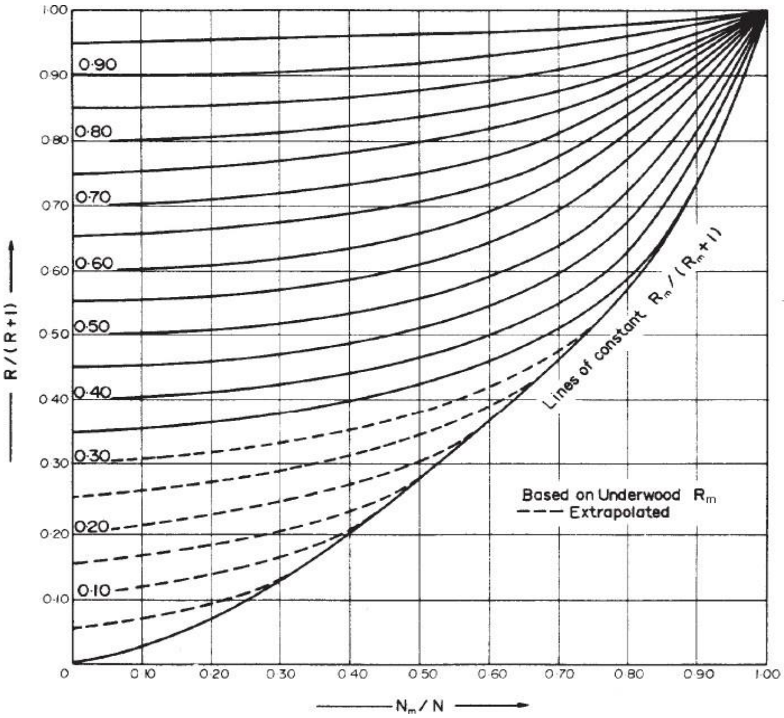


Figure 12: Nm/N (theoretical number of stages).

The theoretical number of stages are found to be 14.

Calculating actual number of stages using O'Connell's relation

The O'Connell's relation uses the average viscosity values of the components in the column to calculate the efficiency of the column and then use it to find the actual number of plates.

O'Connell's relation:

$$E_0 = 51 - 32.5 \log(\mu_{avg}\alpha_{avg})$$

Table 33: Calculating actual number of stages.

Feed

Component	**Mole fraction**	**Viscosity (CP)**	**Avg Viscosity**
Methanol	0.003711269	0.01785571	6.62674E-05
EG	0.875735488	0.010906	0.00955077
DMT	0.120553242	0.01489248	0.001795336
TOTAL	1	-	0.011412374
Eo	83.08847036	83.09%	
Actual Number of Stages	15.64597343	Approx…	16

The column efficiency was found to be 83% and the actual number of stages is 16.

Calculating the feed point location using the Kirk-Bride equation

The Kirk Bride equation uses many variables to calculate the feed point stage of the column, to ensure proper separation to components within the column, it is also used to make sure that feed and feed enters the column at a similar pressure condition to the stage it is entered on. The equation is given below:

$$\log\left(\frac{N_r}{N_s}\right) = 0.206\log\left[\left(\frac{B}{D}\right)\left(\frac{x_{f,HK}}{x_{f,LK}}\right)\left(\frac{x_{b,lK}}{x_{b,HK}}\right)^2\right]$$

Where, Nr = Number of stages in reboiler and Ns = Number of stages in stripper.

Table 34: Determination of feed point location.

Feed Point Location (Kirk Bride equation)	
log (Nr/Ns)	0.928346026
Nr/Ns	8.479027143
Nr + Ns	15
Nr	13
Ns	2
Feed Stage	13

Calculating the diameter of the distillation column

We use the velocities of vapor, as well as other values to calculate the diameter of the column using the following equation:

$$D_C = \sqrt{\frac{4V_w}{\mu\rho_v u_v}}$$

Where, V_w is the maximum vapor rate.

The velocity of vapor in the column u_v can be found from the following equation:

$$u_v = (-0.171 l_t^{2} + 0.27 l_t - 0.047)\left[\frac{(\rho_L - \rho_v)}{\rho_v}\right]^{1/2}$$

Where, l_t is the plate spacing.

This calculation, along with other parameters required for the design of the distillation column are presented on the table in the next page

Table 35: Calculation of column diameter.

Reflux Components	**Mass Flow rate (Kg/hr)**	
TOTAL	170.516496	
Liquid Flow rate (Lw)	0.047	kg/s
Vapor Flow rate (Vw)	0.205	kg/s
Density of Vapor	1.60753	kg/m^3
Density of Liquid	952.805	kg/m^3
Tray Spacing	0.3	m
%Flooding at max flow rate	85	

Uv	0.45	m/s
Net Area Required	0.28	m^2
Column Diameter (Dc)	0.599224103	m
Total Downcomer area	12%	
Downcomer Area	0.033845893	m^2
Column Cross Section Area	0.315895005	m^2
Initial Column Height	4.8	m
Actual Column Height	5.28	m
L/D	8.811394563	

CHAPTER NO 7

SIMULATION

7.1 Simulation Main Flowsheet

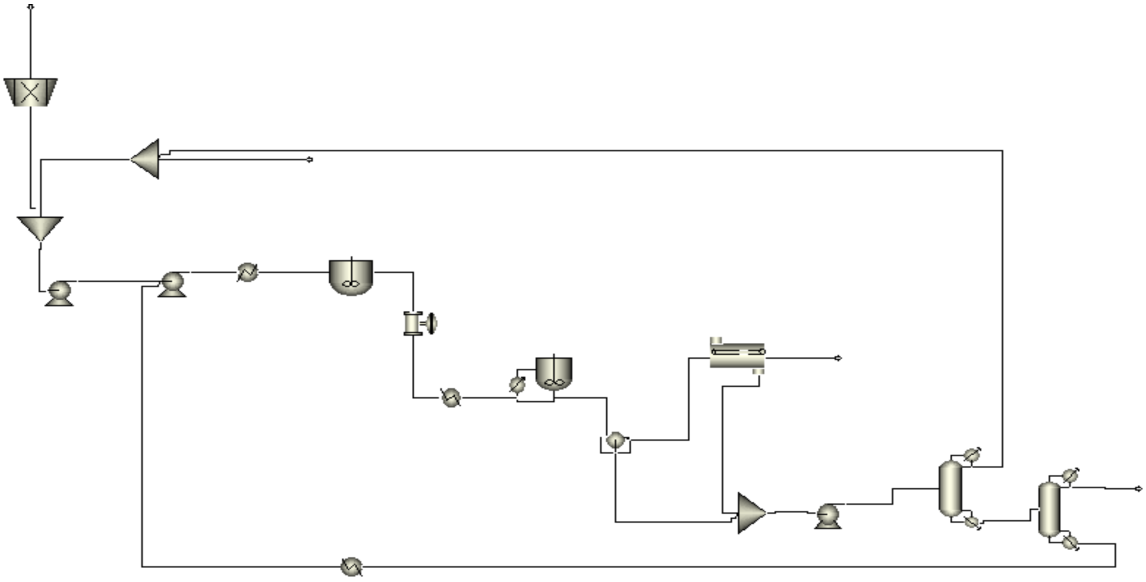
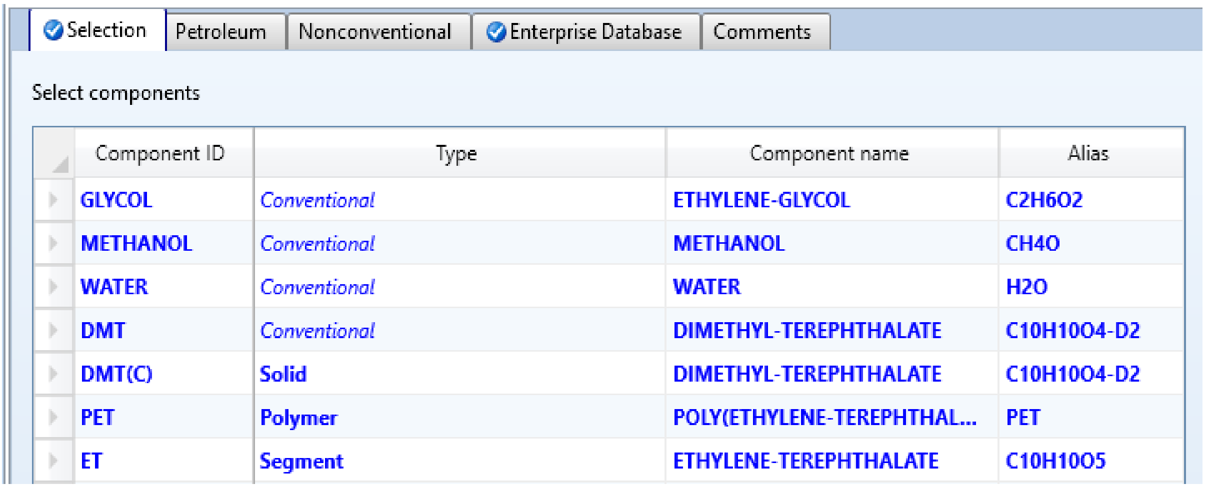


Figure 13: Simulation Flowsheet

7.2 Components List



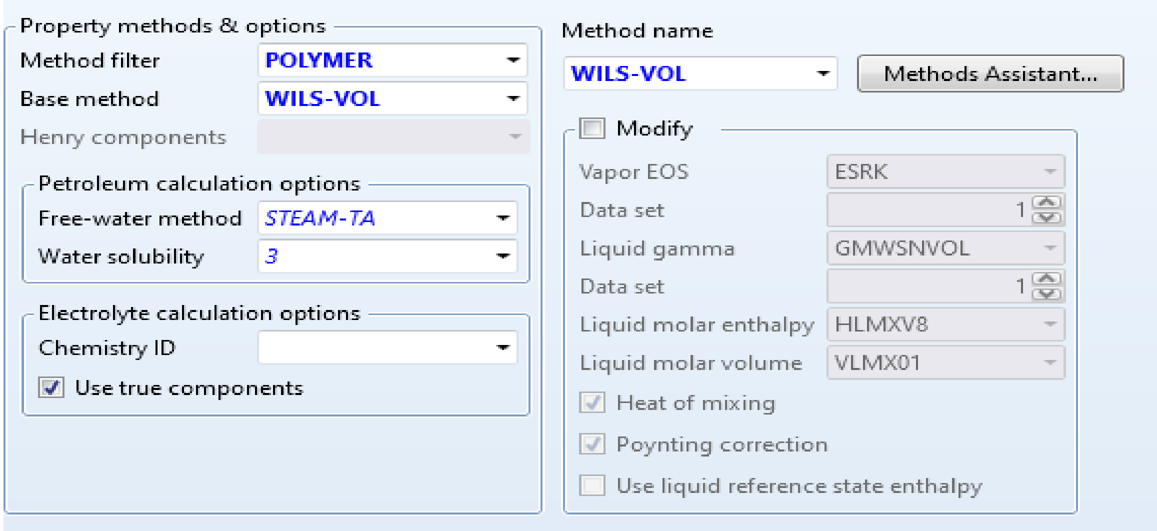
Select components

Component ID	Type	Component name	Alias
GLYCOL	Conventional	ETHYLENE-GLYCOL	C2H6O2
METHANOL	Conventional	METHANOL	CH4O
WATER	Conventional	WATER	H2O
DMT	Conventional	DIMETHYL-TEREPHTHALATE	C10H10O4-D2
DMT(C)	Solid	DIMETHYL-TEREPHTHALATE	C10H10O4-D2
PET	Polymer	POLY(ETHYLENE-TEREPHTHAL...	PET
ET	Segment	ETHYLENE-TEREPHTHALATE	C10H10O5

Figure 14: Components List

7.3 Fluid Package

Wilson-Vol property package with method filter of Polymer is used. Wilson-Vol helps in calculation of enthalpy, fugacity coefficient, activity coefficient and VLE data of non-ideal systems. Wilson-Vol is used for optimization of process in Aspen Plus.



Property methods & options

Method filter: POLYMER

Base method: WILS-VOL

Henry components:

Petroleum calculation options

Free-water method: STEAM-TA

Water solubility: 3

Electrolyte calculation options

Chemistry ID:

☑ Use true components

Method name: WILS-VOL

☐ Modify

Vapor EOS: ESRK

Data set: 1

Liquid gamma: GMWSNVOL

Data set: 1

Liquid molar enthalpy: HLMXV8

Liquid molar volume: VLMX01

☑ Heat of mixing

☑ Poynting correction

☐ Use liquid reference state enthalpy

Figure 15: Fluid Package

7.4 Crusher

Type = Cone Crusher

Inlet Particle Size = 2 cm

D_{50} = 300 µm

Mechanical Efficiency = 33 %

Power Required = 44 kW

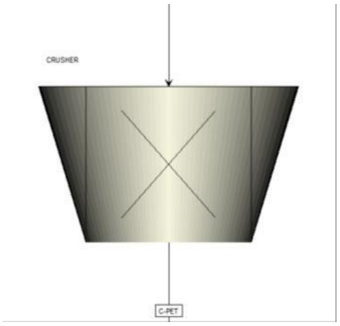


Figure 16: Crusher

7.5 Pump 1

Inlet Pressure = 1 bar

Outlet Pressure = 4 bar

Efficiency = 75 %

Power Requirement = 1.2 kW

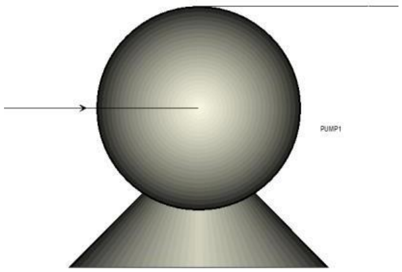


Figure 17: Pump 1

7.6 Pump 2

Inlet Pressure = 4 bar

Outlet Pressure = 80 bar

Efficiency = 75 %

Power Requirement = 16 kW

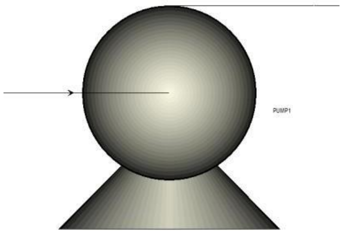


Figure 18: Pump 2

7.7 Reactor

Continuous Stirred Tank Reactor is used for depolymerization of PET into its monomers DMT and Ethylene Glycol. In CSTR,

Pressure = 80 bar

Temperature = 300° C

Residence time = 30 min

Rate constant (k) = 0.008991 l^2/mol^2s

Reactor Volume = 15.538 m^3

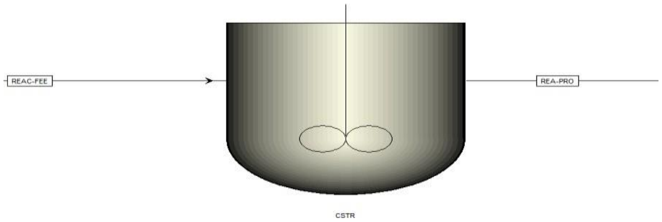
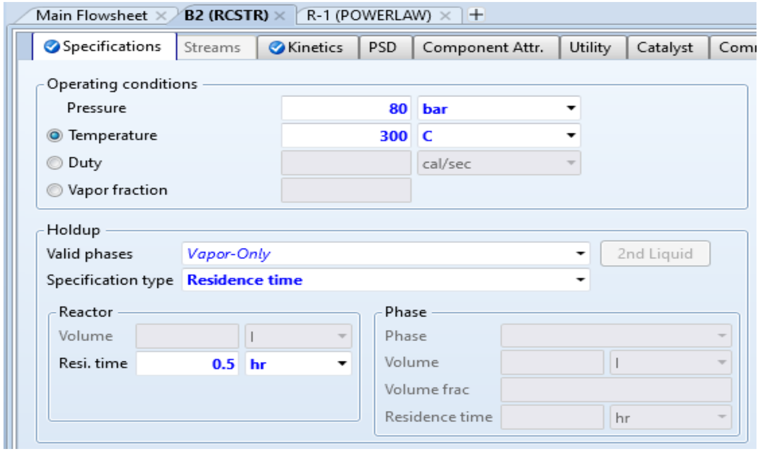


Figure 19: CSTR



Operating conditions

Pressure 80 bar

● Temperature 300 C

○ Duty cal/sec

○ Vapor fraction

Holdup

Valid phases Vapor-Only

Specification type Residence time

Reactor

Volume l

Resi. time 0.5 hr

Phase

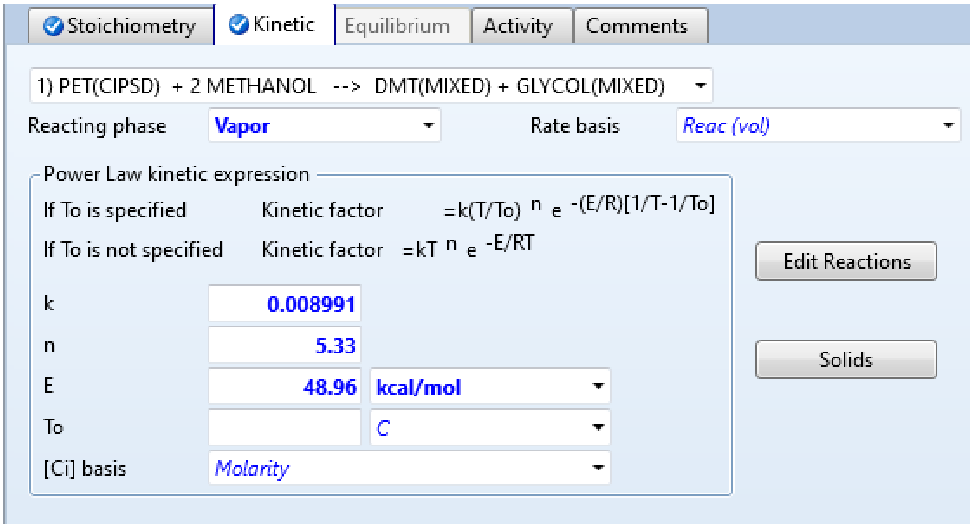
Phase

Volume l

Volume frac

Residence time hr

Figure 20: CSTR Environment



1) PET(CIPSD) + 2 METHANOL --> DMT(MIXED) + GLYCOL(MIXED)

Reacting phase: Vapor

Rate basis: Reac (vol)

Power Law kinetic expression

If To is specified: Kinetic factor $=k(T/To)^{n} e^{-(E/R)[1/T-1/To]}$

If To is not specified: Kinetic factor $=kT^{n} e^{-E/RT}$

k: 0.008991

n: 5.33

E: 48.96 kcal/mol

To: C

[Ci] basis: Molarity

Figure 21: Reaction Kinetics

7.8 Crystallizer

Operating Temperature = 24.85° C

Operating Pressure = 1 bar

Phase = Liquid

Solubility data of Dimethyl Terephthalate and Methanol is used to simulate crystallizer. The Concentration vs Temperature data is fed in the Solubility environment of crystallizer.

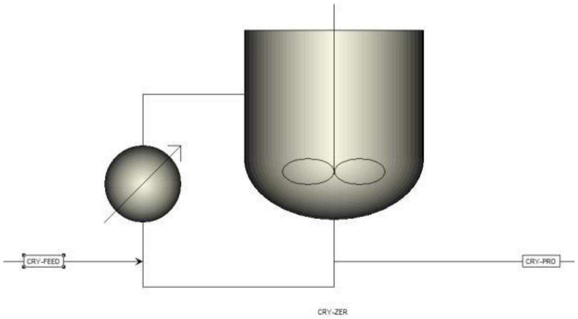
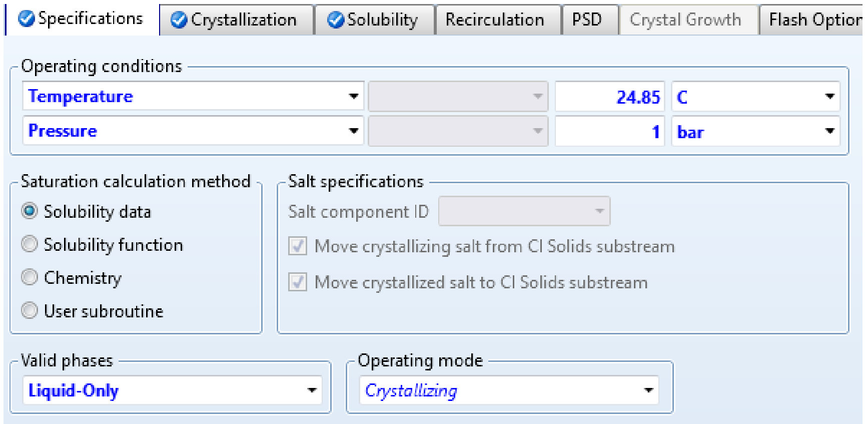


Figure 22: Crystallizer



Specifications | Crystallization | Solubility | Recirculation | PSD | Crystal Growth | Flash Option

Operating conditions

Temperature		24.85	C
Pressure		1	bar

Saturation calculation method

● Solubility data

○ Solubility function

○ Chemistry

○ User subroutine

Salt specifications

Salt component ID

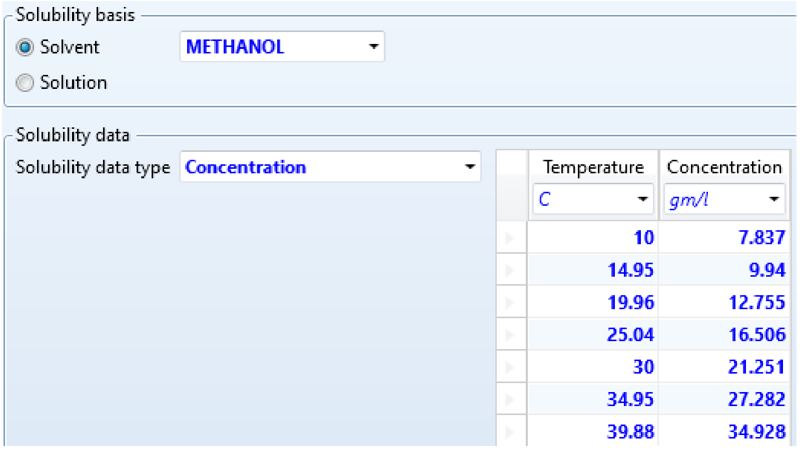
☑ Move crystallizing salt from CI Solids substream

☑ Move crystallized salt to CI Solids substream

Valid phases: Liquid-Only

Operating mode: Crystallizing

Figure 23: Crystallizer Environment



Solubility basis

● Solvent: METHANOL

○ Solution

Solubility data

Solubility data type: Concentration

Temperature	Concentration
C	gm/l
10	7.837
14.95	9.94
19.96	12.755
25.04	16.506
30	21.251
34.95	27.282
39.88	34.928

Figure 24: Solubility Data

7.9 Dryer

Type = Indirect Heating Tube Dryer

Operating Pressure = 1 bar

Operating Temperature = 160° C

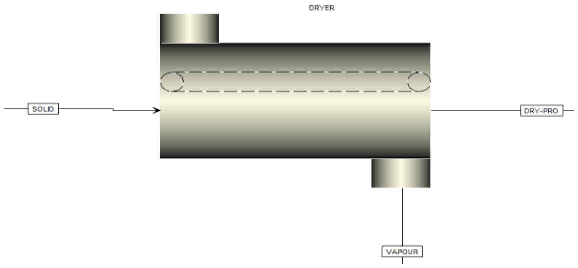


Figure 25: Dryer

7.10 Methanol Column

No of Stages = 12

Feed Stage = 6

Column Pressure = 1 bar

Reflux Ratio = 2.85

Methanol Recovery = 98.3 %

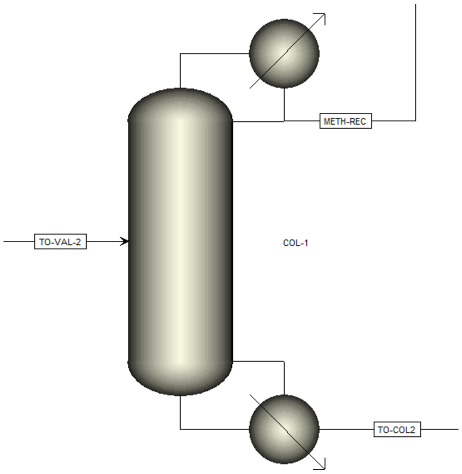
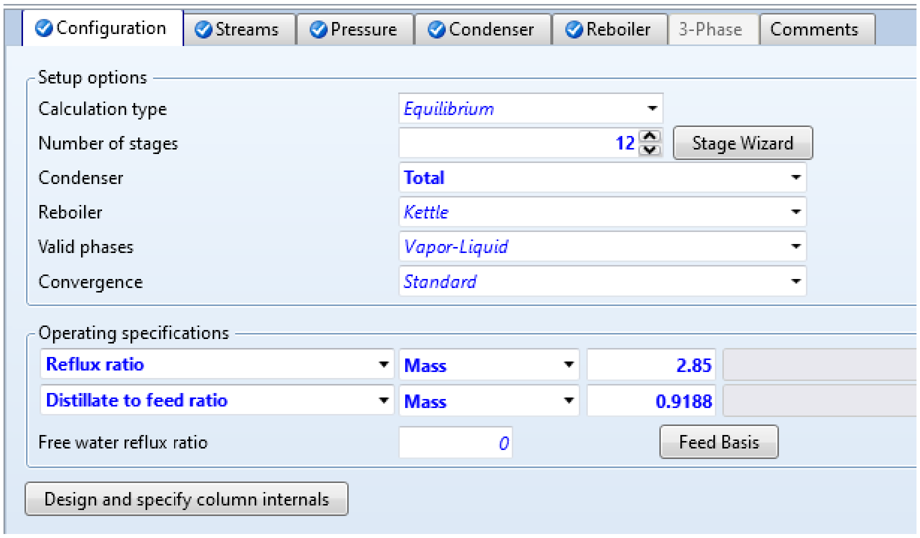


Figure 26: Methanol Column



Setup options

Calculation type: Equilibrium

Number of stages: 12

Condenser: Total

Reboiler: Kettle

Valid phases: Vapor-Liquid

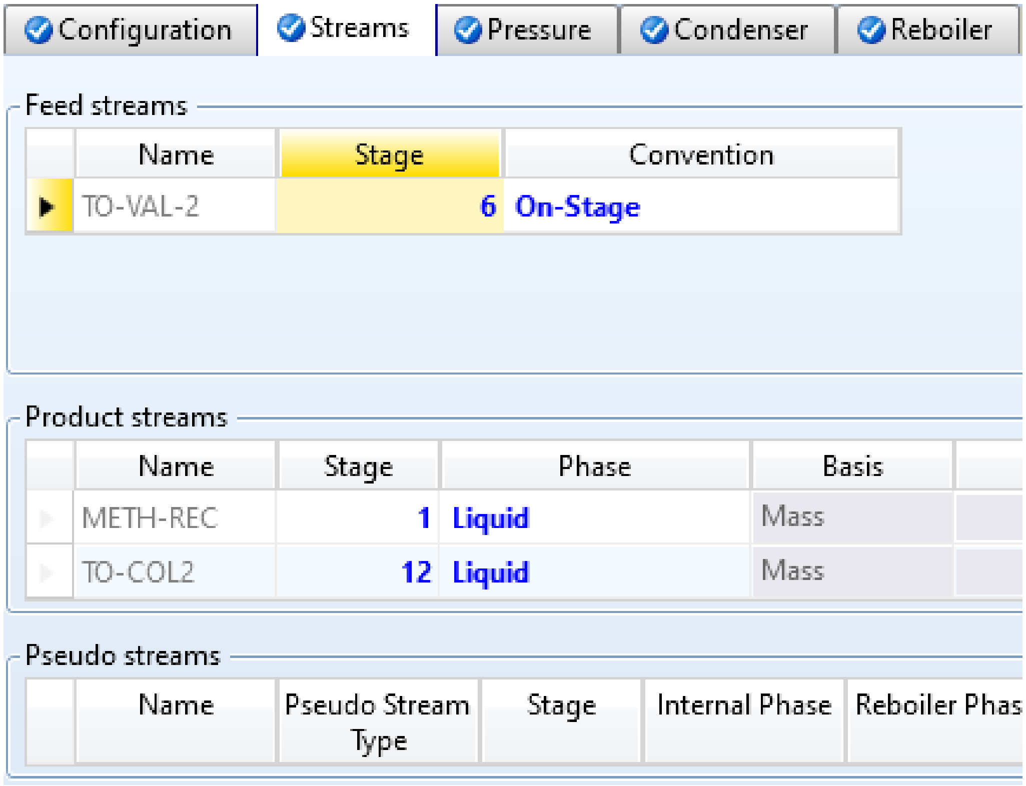
Convergence: Standard

Operating specifications

Reflux ratio	Mass	2.85
Distillate to feed ratio	Mass	0.9188

Free water reflux ratio: 0

Figure 27: Methanol Column Specs



Feed streams

Name	Stage	Convention
TO-VAL-2	6	On-Stage

Product streams

Name	Stage	Phase	Basis
METH-REC	1	Liquid	Mass
TO-COL2	12	Liquid	Mass

Pseudo streams

Name	Pseudo Stream Type	Stage	Internal Phase	Reboiler Phas

Figure 28: Feed Stage

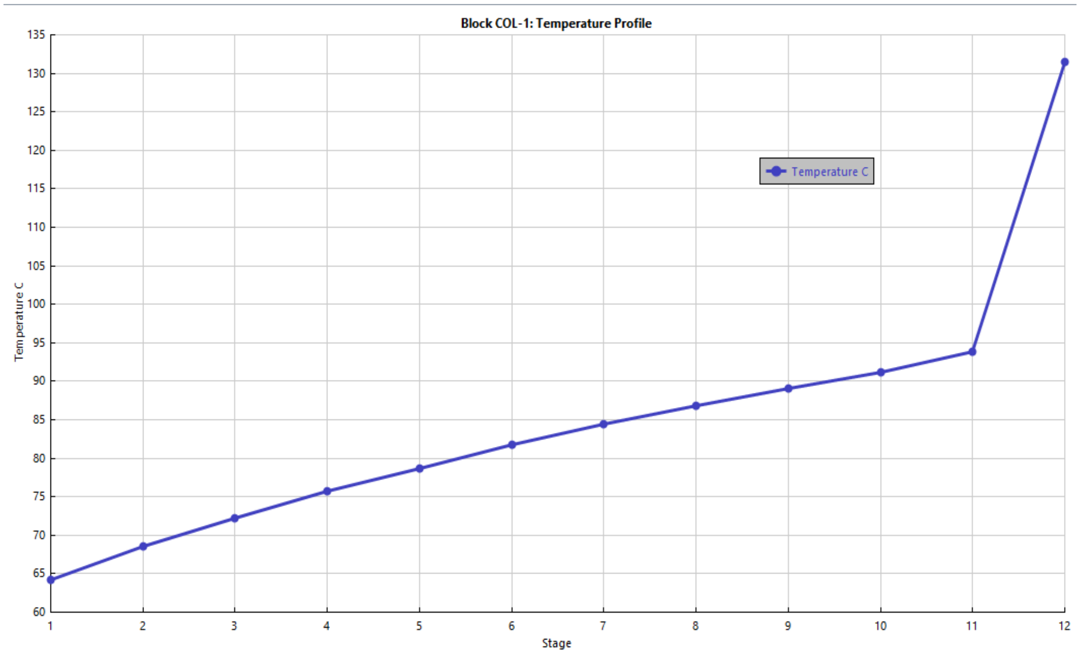


Figure 29: Temperature Profile across Stages

7.11 Ethylene Glycol Column

No of Stages = 16

Feed Stage = 13

Column Pressure = 1 bar

Reflux Ratio = 1

Ethylene Glycol Recovery = 99.8 %

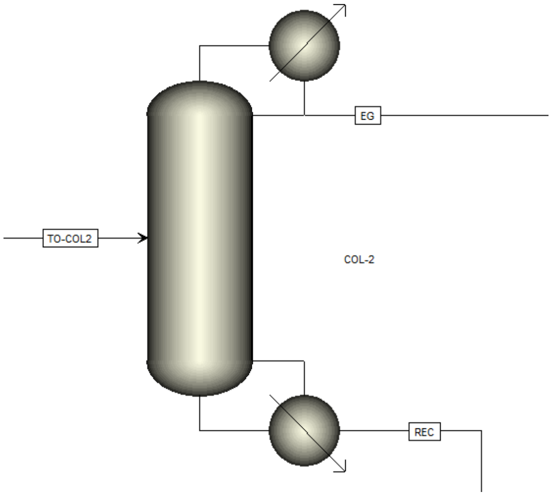
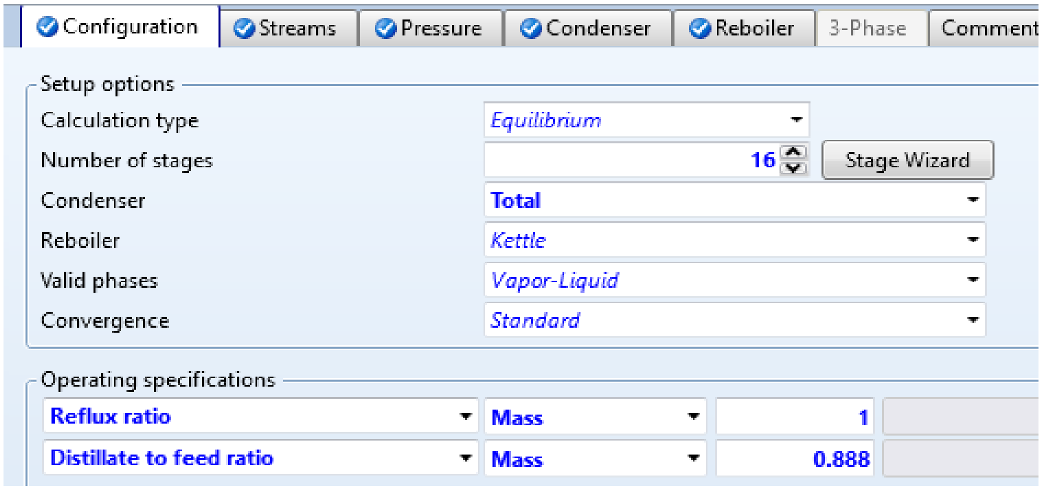


Figure 30: Ethylene Glycol Column



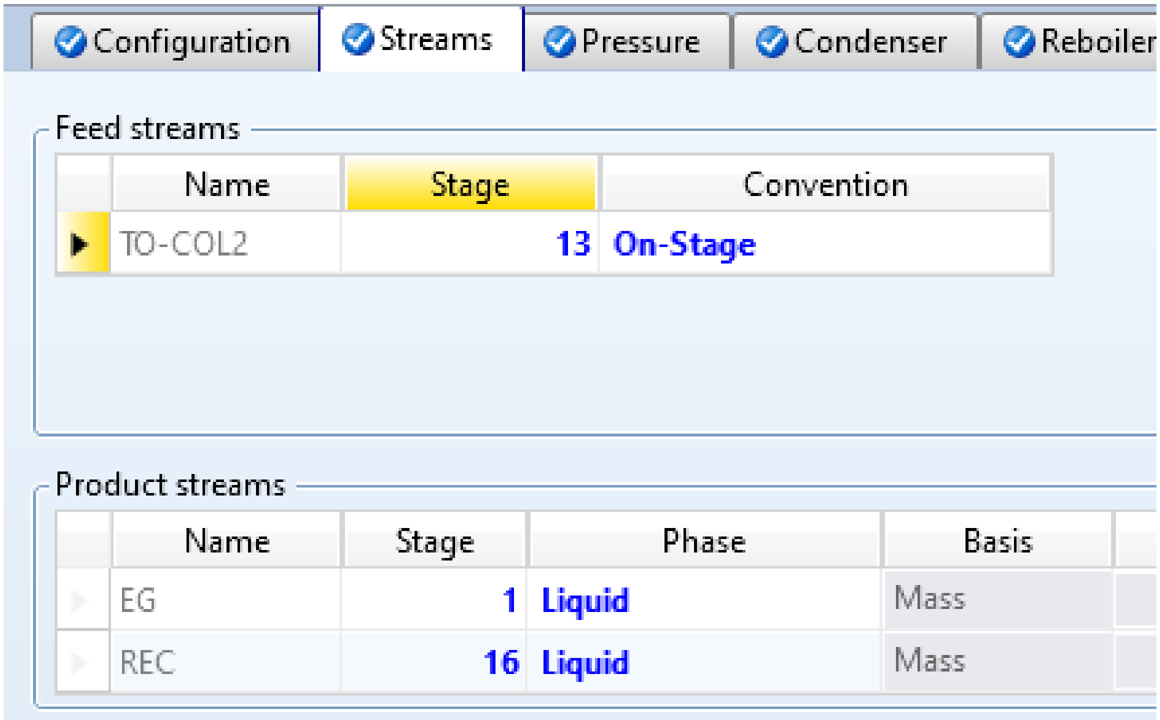
Setup options

Calculation type	Equilibrium
Number of stages	16
Condenser	Total
Reboiler	Kettle
Valid phases	Vapor-Liquid
Convergence	Standard

Operating specifications

Reflux ratio	Mass	1
Distillate to feed ratio	Mass	0.888

Figure 31: Ethylene Glycol Column Specs



Feed streams

Name	Stage	Convention
TO-COL2	13	On-Stage

Product streams

Name	Stage	Phase	Basis
EG	1	Liquid	Mass
REC	16	Liquid	Mass

Figure 32: Feed Point

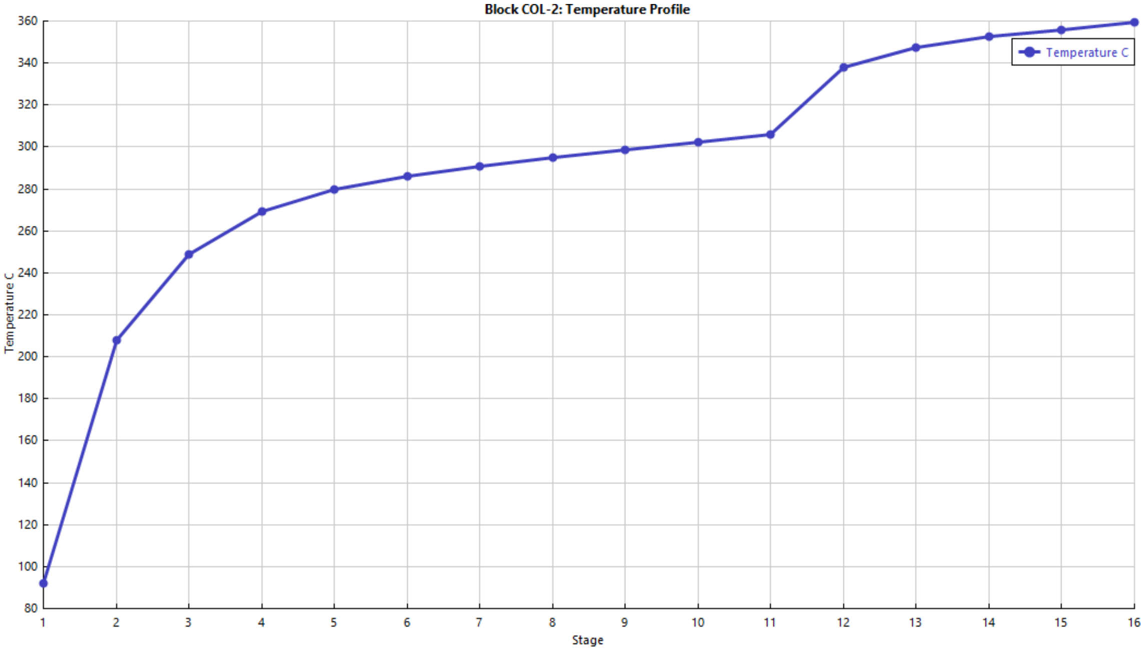


Figure 33: Temperature Profile across Stages

CHAPTER NO 8

INSTRUMENTATION

8.1 Piping & Instrumentation Diagram

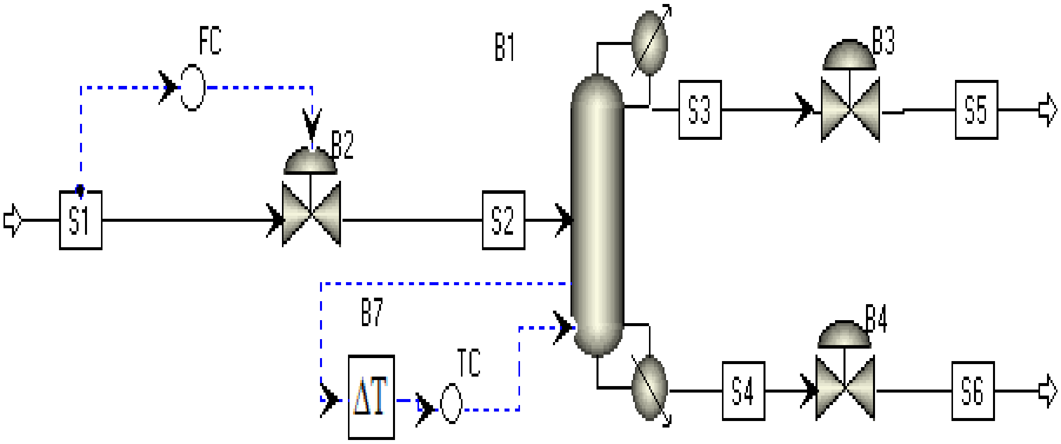


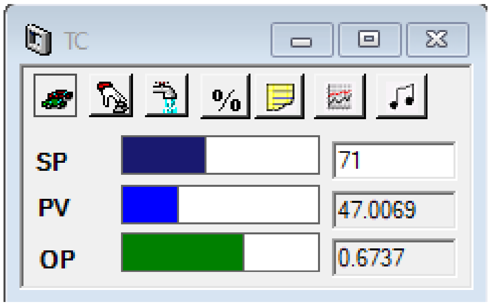
Figure 34: P&ID of Methanol Column

8.2 Temperature Control

Set Point = 71° C

Integration Time = 1.18 min

Proportional Gain = 2.1147

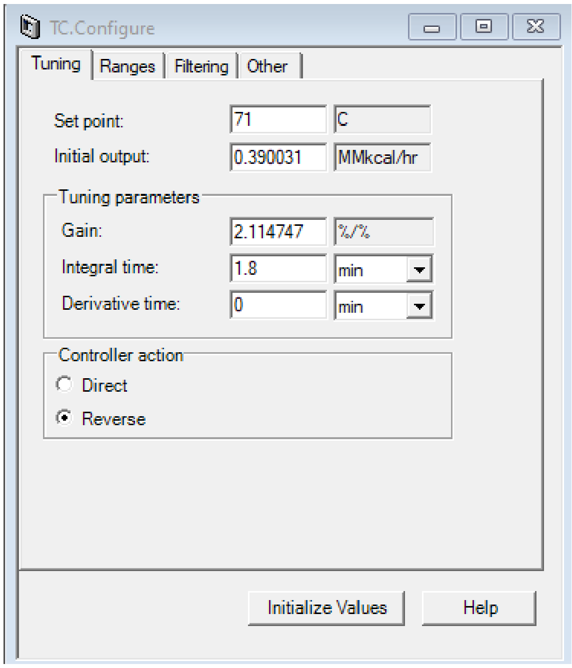


SP 71

PV 47.0069

OP 0.6737

Figure 35: Temperature Control of Methanol Column



Set point: 71 C

Initial output: 0.390031 MMkcal/hr

Tuning parameters

Gain: 2.114747 %/%

Integral time: 1.8 min

Derivative time: 0 min

Controller action

○ Direct

● Reverse

Figure 36: Tuned Values

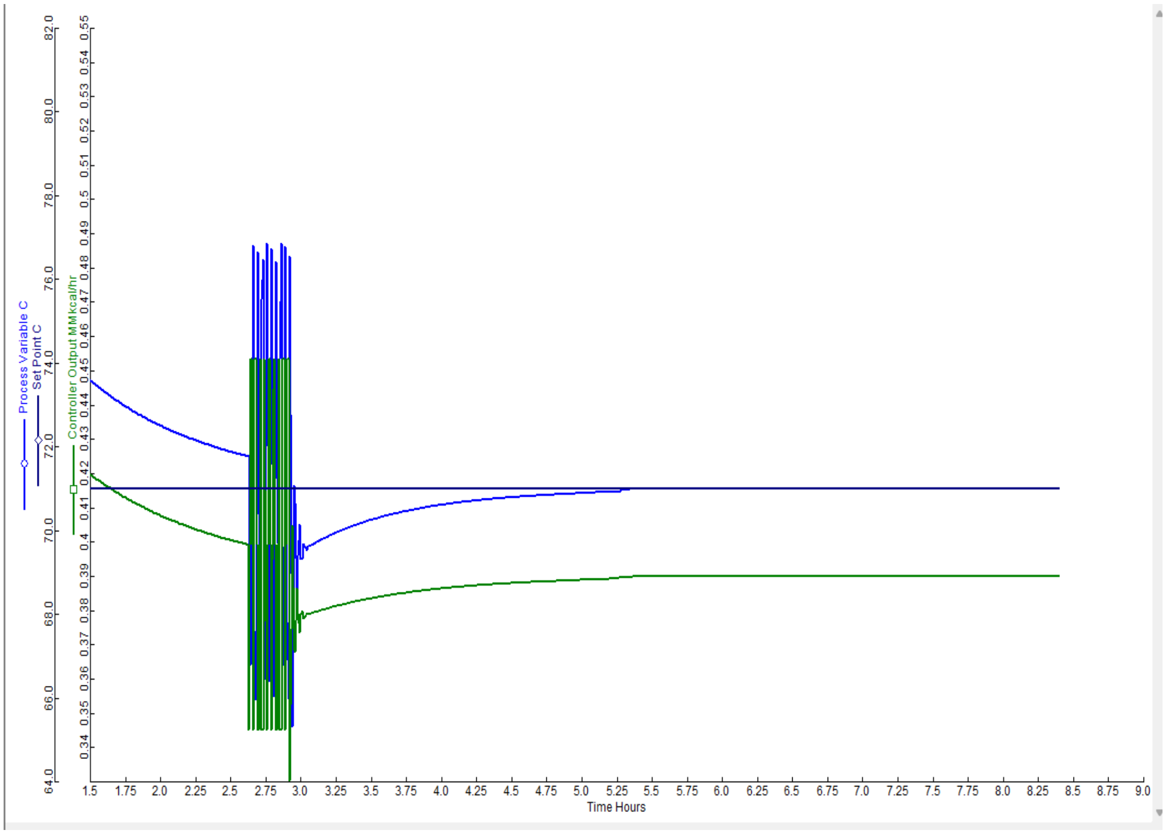


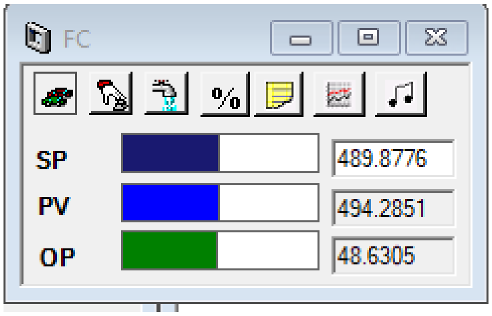
Figure 37: Temperature Control Graph

8.3 Flow Control

Set Point =490 kg hr^{-1}

Integration Time = 20 min

Proportional Gain = 1

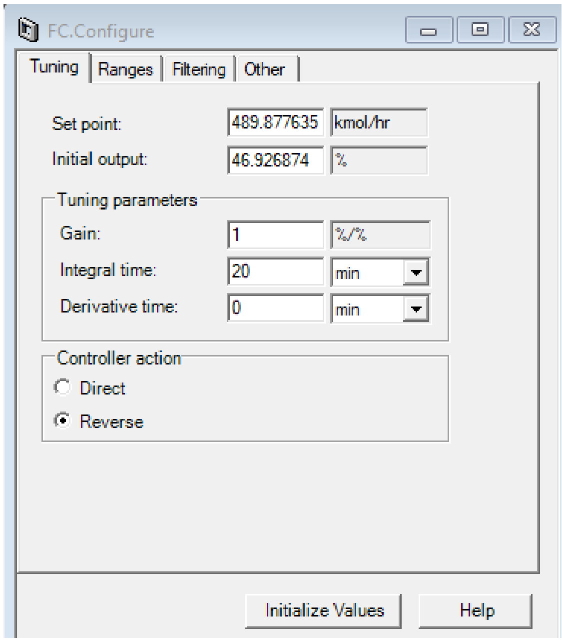


SP 489.8776

PV 494.2851

OP 48.6305

Figure 38: Flow Control of Methanol Column



Set point: 489.877635 kmol/hr

Initial output: 46.926874 %

Tuning parameters

Gain: 1 %/%

Integral time: 20 min

Derivative time: 0 min

Controller action

○ Direct

● Reverse

Figure 39: Tuned Values

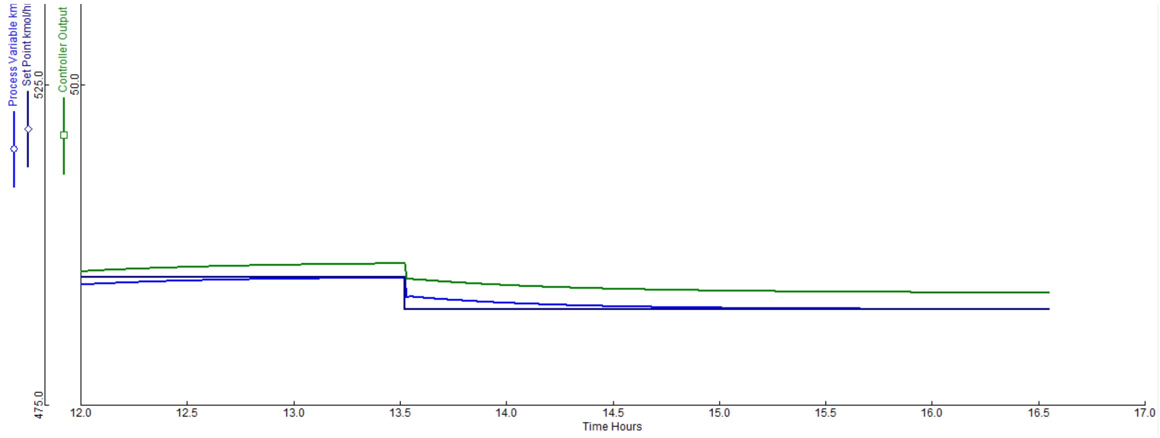


Figure 40: Flow Control Graph

8.4 Pressure Control

Set Point = 4 Bar

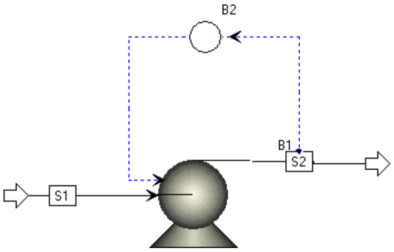


Figure 41: Pressure Control on Pump 1

CHAPTER NO 9

ECONOMIC ANALYSIS

9.1 Cost Analysis

Cost analysis is a major part of a project as it gives us an insight into the financial feasibility of the proposed project. As a viable project is the one that produces the maximum amount of project at minimum cost , so it is necessary to economically validate the project .The cost analysis of the proposed depolymerization of PET to polyols will help us asses that industrial scale implementation of the project. Our cost analysis will evaluate the revenue generated from the sales of the product.

We have used the Coulson and Richardson method for our project economic analysis assuming that the plant is operational 350 days a year.

9.1.1 Factorial Method Sample Calculation

Ethylene Glycol Separator:

Height = 5.3ft

Diameter = 0.6 m

Type of plates = Bubble cap

Number of Bubble cap trays =16

Material of construction = Stainless steel

Using values from graph 8.1 (a) and 8.1(b), COST OF EQUIPMENT = $43,200

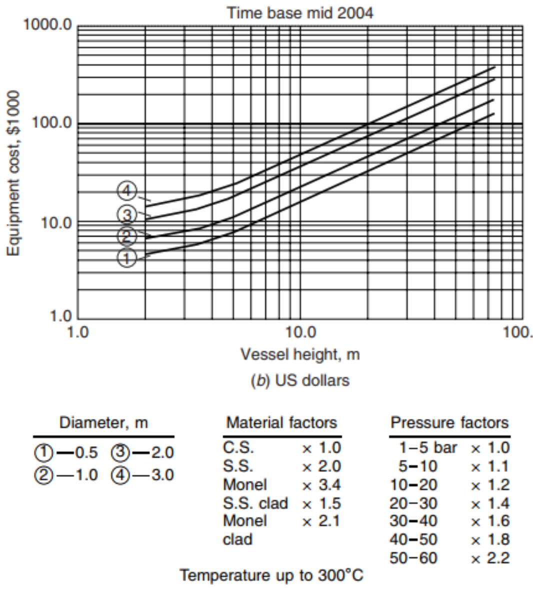


Figure 6.5*a*, *b*. Vertical pressure vessels. Time base mid-2004.
Purchased cost = (bare cost from figure) × Material factor × Pressure factor

Figure 42: Cost of vessel based on vessel height in USD.

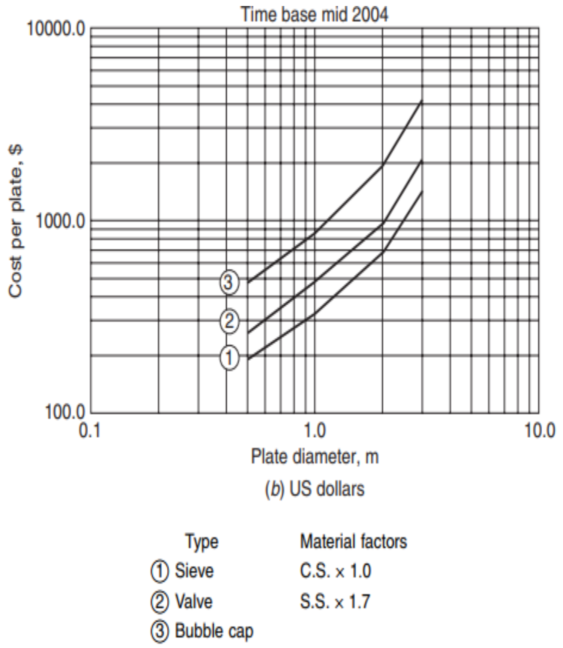


Figure 6.7*a*, *b*. Column plates. Time base mid-2004 (for column costs see Figure 6.4)
Installed cost = (cost from figure) × Material factor

Figure 43: Cost of plates in distillation column in USD

9.1.2 Purchase Cost of Equipment

Table 36: Purchase Cost of Equipment in USD

Equipment	**Equipment Cost**
Feed Pre-Heater	46655
Methanol Separator	64586
Ethylene Glycol Separator	48894
Reactor (CSTR)	10000
Crystallizer	51256
Dryer	43581
Filter	54000
Pre-crystallizer Cooler	45235
Recycle Cooler	14940
Pumps	30000
Crusher	25000
Purchased Cost of Equipment (POC)	$ 434,147.00

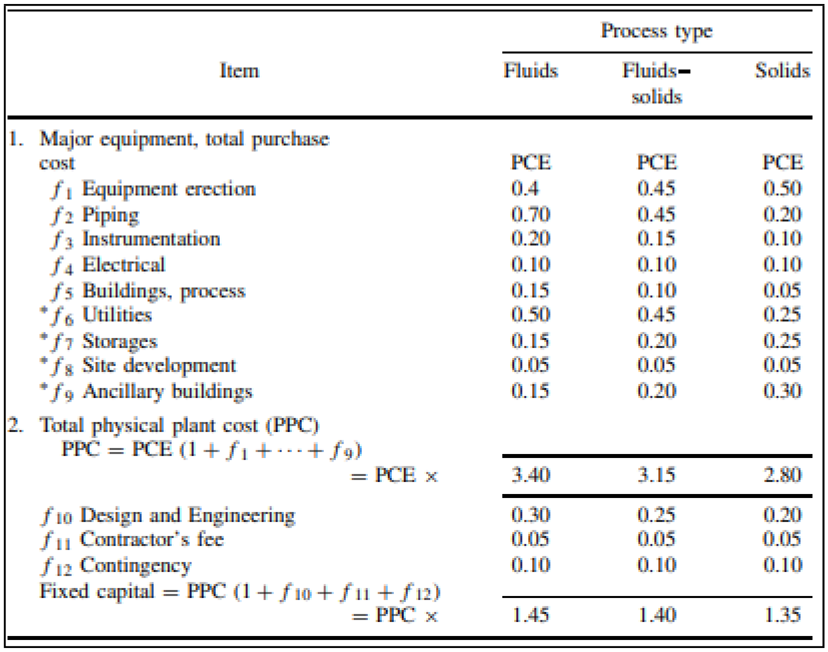
9.1.3 Total Investment Required

PHYSICAL PLANT COST

After calculating the Purchased Cost of Equipment (PCE) we find out the Physical Plant Cost (PPC) using the factors given in the table 8.1.3

$$PPC = PCE(1 + F1 + F2 + \cdots + F9)$$

$$PPC = 434147(3.4) = \mathbf{\$147,6099}$$



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

Figure 44: Factors for physical plant cost (PPC)

FIXED CAPITAL (FC)

Next step is to find out the fixed capital investment required for the plant using factors from F10 to F12 given in the table 8.1.3

$$FC = PPC(1 + f10 + f11 + f12)$$

$$FC = 1476099(1.45) = \$\mathbf{2140343}$$

WORKING CAPITAL

Working capital (WC) is taken 15% of the fixed capital (FC)

$$working\ capital = 0.15(2140343)$$

$$working\ capital = \$\mathbf{321051}$$

Now, the total investment required is the sum of fixed capital and working cost.

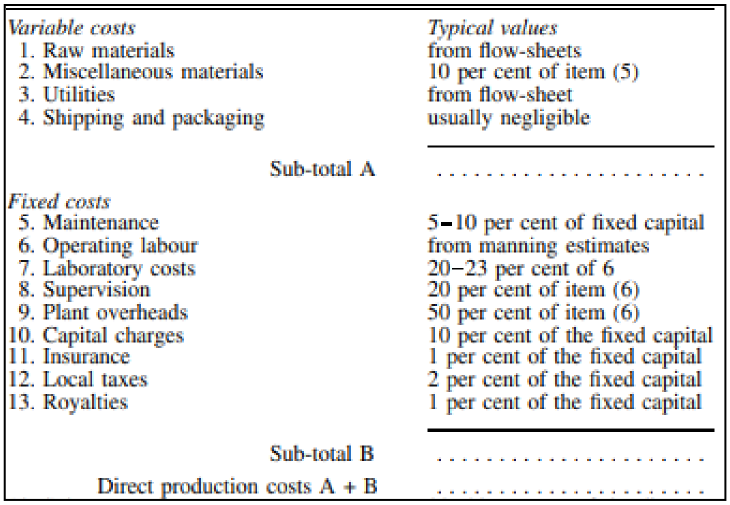
$$Total\ investment\ required = 2140343 + 321051$$

$$Total\ investment\ required = \$\mathbf{2461394}$$

9.1.4 Operation Cost

The operation cost includes two things.

1. **FIXED COST**, the cost that does not vary with the production rate which includes:
    - Maintenance cost
    - Operating labor
    - Laboratory cost
    - Supervision
    - Plant overhead
    - Capital charges.
2. **VARIABLE COST,** the cost that can vary with the production rate which includes:
    - Raw material
    - Miscellaneous operating materials



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	. . . .

- Utilities

Figure 45: Variable and Fixed costs factors

Table 37: Fixed cost

FIXED COST	
Maintenance (3% of FC)	$ 64,210.34
Operating Labor	$ 30,000.00
Plant Overheads (40% of OL)	$ 12,000.00
Laboratory (20% of OL)	$ 6,000.00
Capital Charges (2% of FC)	$ 42,806.89
Insurance (1% of FC)	$ 21,403.45
Local Taxes (1% of FC)	$ 21,403.45
Total	**$ 197,824.13**

9.1.5 Revenue and Payback Period

Revenue is calculated by multiplying the production in tons per year with the per unit price of the polyol (Ethylene Glycol) and the Dimethyl terephthalate (DMT).

$$Revenue\ generated\ (EG) = (5205)(575) = \$2{,}999{,}875$$

$$Revenue\ generated(DMT) = (14773)(2000) = \$29{,}546{,}000$$

To find out the payback period of the production facility of depolymerization of PET bottles we need to adjust the inflation by calculating the Net Present Worth by the formula given below.

$$Net\ Present\ Worth\ = \frac{Estimated\ cash\ flow\ in\ year\ k}{(1+r)^k}$$

Table 38: Revenue generated per product in USD.

Revenue			
Product	**Production (tons/yr.)**	**Price ($/ton)**	**Revenue Generated**
Ethylene Glycol	5205	$575	$2,992,875.00
Dimethyl Terephthalate	14773	$2,000.00	$29,546,000.00

Total Revenue/yr. **=$32,538,875**

Total Profit /yr.**=$896,575**

Total Profit/day**=$2,538**

Similarly, Net cash flow and the Net present worth are calculated for different values of k.

Table 39: Present worth of investment over 10 years in USD.

NET PRESENT WORTH				
No. of Years (k)	**Cash Inflow**	**Cash Outflow**	**Net Cash Flow**	**Net Present Worth (10%, k)**
0	0	$1,981,898.45	$1,981,898.45	$1,981,898.45
1	$32,538,875.00	$1,642,299.35	$896,575.65	$815,068.77
2	$32,538,875.00	$31,642,299.35	$896,575.65	$740,971.61
3	$32,538,875.00	$31,642,299.35	$896,575.65	$673,610.56
4	$32,538,875.00	$31,642,299.35	$896,575.65	$612,373.23

5	$32,538,875.00	$31,642,299.35	$896,575.65	$556,702.94
6	$32,538,875.00	$31,642,299.35	$896,575.65	$506,093.58
7	$32,538,875.00	$31,642,299.35	$896,575.65	$460,085.07
8	$32,538,875.00	$31,642,299.35	$896,575.65	$418,259.16
9	$32,538,875.00	$31,642,299.35	$896,575.65	$380,235.60
10	$32,538,875.00	$31,642,299.35	$896,575.65	$345,668.73

The next step is to find ot the Cumulative Present Worth that will give us the PAYBACK PERIOD.

Table 40 Payback Period of investment in years

CHAPTER NO 10

HAZOP ANALYSIS

A Hazard and Operability study of the proposed is fundamental to its technical feasibility from a safety point of view. Conventionally, such analyses usuallyinvolve using specific guidewords to assess the cause, effects, and preventative measures for the process. Examples of said guidewords may be “high temperature”, “low pressure” or something else of the sorts. These guidewords vary with the equipment under study within a system. Each component within a system must be considered for a thorough risk assessment. The guidewords are essentially deviations that may potentially be encountered within the equipment and help to imagine several possible scenarios. HAZOP involves.

1. Brainstorming and identifying potential deviations and guidewords applicable to the system.
2. Conducting a qualitative risk assessment to determine the severity of each deviation.
3. Employing a "bottom-up" approach that relies on the experience and predictive abilities of the observer.

10.1 Keywords

In the HAZOP study, various terms and concepts are utilized:

1. **Nodes:** These refer to pipe sections or vessels where process chemicals are present.
2. **Super nodes:** Multiple nodes considered together as one for more efficient analysis.
3. **Hazard:** A potential source of harm.
4. **Harm:** Actual injury or damage to equipment, personnel, or the environment.
5. **Risk:** The probability of harm occurring and the associated level of damage.

10.2 Methodology

The methodology for conducting a HAZOP study involves the following steps:

1. Identify all major nodes and super nodes within the system.
2. Justify why each node has been selected for the HAZOP study.
3. Choose a key process parameter for each node.
4. Apply relevant guidewords to the chosen parameter, identifying potential deviations in the process and documenting them.
5. Determine the potential causes for the identified deviations and add them to the analysis table.
6. For each brainstormed deviation, identify the consequences it would lead to and document them.
7. Repeat steps 3 through 6 for the remaining nodes until all chosen nodes have been thoroughly studied.

Following this systematic methodology ensures a comprehensive evaluation of the system, enabling the identification of potential hazards and the implementation of appropriate preventive measures.

10.3 Pump

Table 41: Hazop Analysis for Pump

Parameter	Guide Word	Causes	Consequences	Actions Required
Flow	**NO**	Closed Outlet Valve, blocked pipelines, pump failure	Lines over pressure and pumps overheating,	Proper monitoring of pump sand installation of alarms on valve

	More	Too high shaft power, Blockage in valve outlet, Fail open valve.	Overheating of the pump, Vibration which causes destruction of the internal pump(cavitation)	Check and decrease the speed of shaft rotation, Fail closes the valve at the time of delivery
	Less	Failure at the outlet valve/pump, low rotational speed of shaft, improper suction at the inlet, partial opening of downstream valve	Pressure buildup in pipelines, pump overheating	Check and increase speed of shaft rotation, install control system to change valve opening according to flow
	Reverse	Valves not closed when needed	Due to gravity, the fluid can flow from higher level vessel into lower-level vessel with product contamination	Install Check valves, Operational procedures to open and closed valve before and after the product transfer

Pressure	**NO**	Suction valve closed, pump failure, power outage, shaft failure, faulty pressure sensor	Production is stopped, pump vibration is stopped	Check the type of liquids that can be used, Make sure that NPSHA > NPSHR, Check for loss in filters
	MORE	Blockage in valve	Explosion,	Check and drain the

		outlet, Operating fault, Faulty pressure sensor, Vaporizing liquid	production is stopped, deterioration of bearings, increased leakage	pipes and system, Replace the gasket and check the damage
	LESS	Suction valve is closed, Air leakage in suction line, operating fault, faulty pressure sensor	Cavitation, Vibration causes destruction of the internal pump (wheel bearing)	Make sure that NPSHA > NPSHR, Check for loss in filters, Check and drain the pipe and system.
Temperature	**MORE**	Cooling system failure, leakage in cooling, rubbing of rotating components, shaft connected incorrectly, increased pressure in the pump	Risk of explosion in pump, bearings can be damaged, cavitation as vaporizing liquid increases, Destruction of the internal pump (wheels)	Cool different parts of the pump with water, check the level of required liquid, check pressure in the pump, check cooling system, Open and clean the pump

10.4 Distillation Column

Table 42: Hazop Analysis for Distillation Column

Process Variable	Guide Word	Deviation	Causes	Consequences	Actions
Pressure	**LESS**	Less than required pressure in column	More than desired feed preheating 2.Increase in inlet steam pressure. 3.Outlet pipe or valve blockage	1. Increase in bottoms flow rate 2. Desired separation is not achieved 3. Rupture or breakage of the vessel	1. Apply pressure safety valve PSV 2. Apply high pressure alarm on stripper 3. Check steam source to regulate steam pressure
	MORE	More than required pressure in column	Decrease in steam pressure 2. 2. Breakage in vessel wall Heat loss to surroundings	Increase in moisture entrainment in overhead. Decrease in bottoms flowrate	Apply low pressure alarm. Apply pressure control loop on steam. Check for breakage in vessel wall. Use Insulation.
	No	No flow in column	Pipe blockage Control valve failure	Column dries out. No operation Upset in	Install low level alarms. Check

Flow			Pump failure	downstream process	maintenance procedure and schedule. Make a bypass. Emergency plant shut down
	MORE	More flow in column	Control valve fully opened. Increase in pumping capacity. Control valve failure	Flooding in column Product quality changes Temperature of column falls Rise in bottom	Install high level alarms. Install Control Check maintenance procedure and schedule
Level	**HIGH**	High level	Blockage in outlet Less pressure drops across the column. Low vapor flow	Over pressure Reflux drum Condensed liquid flow back to distillation column	Install high level alarm. Check maintenance procedure and schedule
	LOW	Low level	Partially clogged pipe Leakage in pipe	Level decrease in column Improper separation	Install low level alarm. Check maintenance procedure and schedule

Temp	**High**	High temp of column	More than desired feed preheating 2. Increase in steam temperature or flowrate	Increase in stripper operating temperature. Increase in moisture entrainment in overhead. 3.Decrease in bottoms flowrate	1. Apply temperature control loops to regulate feed preheating 2. Make bypass line for bottoms to avoid overheating of feed 3. Adjust reflux flowrate.
	Low	Low temp of column	Less than desired feed preheating Increase in feed flow rate. Heat loss to surrounding.	1.Decrease in column temperature 2.Desired separation of crude oil is not achieved	1.Adjust the quantity of steam to increase the feed flow rate. 2. Install low temperature alarm

10.5 Heat Exchanger

Table 43: Hazop Analysis for Heat Exchanger

Process Variable	Guide Word	Deviation	Causes	Consequences	Actions
FLOW	**LESS**	Less flow of oil in heat Exchanger	1. Line Blockage 2. Valve failure	1. No heat transfer between fluids 2. Higher temperature of crude oil	1. Install flow alarms. 2. Temperature sensors at outlet and implementation of control for flow rates of streams
	MORE	More than optimal oil flow to heat exchanger	1. Failure of inlet oil valve to close	1. Less than required temperature of exiting crude oil stream achieved since same amount of heating oil is being used to heat a bigger process stream. 2. High pressure	1. Install temperature alarms. 2. Install crude oil flow meter. 3. High Pressure alarms for safety considerations.

				on shell side.	
	Reverse	Back flow due to high back pressure	1. Blockage in shell or tubes outlet	1. Pressure Off set	1. Install automatic sensors and control devices. 2. use check valves.
Pressure	**High**	High Pressure	1. Product line blockage 2. Higher temperature leading to high Pressure	1. Improper flow/heat exchanger 2. shell or tubes might leak or blast	1. Install a high-pressure alarm. 2. Install PSV's
	Low	Low Pressure	1. Leakage in the shell 2. Leakage in tubes	1. Improper Heat Exchange	1.Install low-pressure indicator. 2. Check for leakages

Temperature	**High**	High temperature	high heating fluid supply temperature	Required outlet temp is not achieved	3. Install high flow temperature and flow alarm
	Low	Low temperature	high heating fluid supply temperature	Improper heat exchange	4. Install controllers

CONCLUSION

The proposed process not only reduces the requirement of fresh PET usage for making PET plastic-based items like bottles, but it also allows us to overcome the restriction of only high-quality PET being recyclable, since this process works on low-grade PET just as well as high grade PET, with a near 97% conversion rate. This in-turn allows us to achieve our objective of completing (or closing) the loop on chemical recycling of waste PET bottles.

This process is also going to be cost effective despite the demanding operating since the payback period on the investment made within three years of plant operation. Pakistan will have to import a lower amount of ethylene glycol and terephthalic acid (or its variants).

The EG and DMT produced can also be used for a variety of other purposes besides acting as monomers for PET polymerization. This includes application in the polymer, medical and automobile industries.

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