DESIGN OF AN UNSATURATED POLYESTER RESIN PLANT

By

Iqra Younis

Sheeza Razzaq

Inam Ullah

Hafiz Muhammad Hasnain

School of Chemical and Materials Engineering

National University of Science and Technology

2023

DESIGN OF AN UNSATURATED POLYESTER RESIN PLANT

By

283320	**Iqra Younis**
292366	**Sheeza Razzaq**
285055	**Inam Ullah**
315997	**Hafiz Muhammad Hasnain**

A THESIS

Submitted to
National University of Science and Technology in partial fulfilment of the requirements for the degree of

Bachelors

Chemical Engineering

School of Chemical and Materials Engineering (SCME)

National University of Sciences and Technology (NUST)

June, 2023

CERTIFICATE

This is to certify that work in the thesis titled, "Design of unsaturated polyester resin plant" has been conducted by **Miss Iqra Younis, Miss Sheeza Razzaq, Mr. Inam Ullah & Mr. Hafiz Muhammad Hasnain** and completed during the fall 2022 and spring 2023 semesters, under my supervision in School of Chemical and Materials Engineering, National University of Sciences and Technology, H-12, Islamabad, Pakistan.

Advisor: Asad U. Khan 12/06/[illegible]

Dr Asad U. [illegible]
Professor
School of Chemical and [illegible]
Engineering, NUST Islamabad

Dr. Asad U. Khan
Professor
Department of Chemical Engineering
School of Chemical & Materials Engineering
National University of Sciences and Technology

Submitted Through:

HoD 12/6/23

Dr. Erum Pervaiz
Department of Chemical Engineering
School of Chemical & Materials Engineering
National University of Sciences and Technology

Principal/ Dean AK 13.6.2023
Dr. Amir Azam Khan
Department of Chemical Engineering
School of Chemical & Materials Engineering
National University of Sciences and Technology

DEDICATION

Dedicated to the loving memory of our late senior, Huzaifa Javed, and our classmate, Aleeza Ahmad.

ACKNOWLEDGEMENTS

Thanks to **Almighty Allah** for His countless blessings, He gave us the courage to finish this project successfully.

We would like to extend a heartfelt acknowledgement to our supervisor, **Dr. Asad U. Khan**, for his exceptional guidance and unwavering support throughout this project. His vast experience and profound knowledge have been instrumental in our successful completion of this endeavor.

A special thanks to all our **friends** who were always there for us in difficult times. Acknowledgements to **Hamza, Mustafa,** and **Ayesha** for their unwavering emotional support. We couldn’t have done this without them.

Finally, we attribute the achievement of this milestone to the immeasurable love and unwavering prayers of our beloved **parents** and **siblings**. Their constant support and heartfelt blessings have been a guiding force throughout our journey.

ABSTRACT

Plastic waste has become a pressing environmental concern globally, and Pakistan is no exception. With an annual generation of approximately 20 million tons of solid waste, of which 5 to 10 percent consists of plastic waste, the need for effective waste management strategies is critical. This abstract presents a solution to tackle this issue by utilizing polyethylene terephthalate (PET) waste to produce unsaturated polyester resin.

The proposed project aims to address the plastic waste crisis in Pakistan through the recycling and transformation of PET waste into high-quality unsaturated polyester resin. By diverting PET waste from landfills, incineration, and improper disposal practices, the project aims to reduce the overall volume of plastic waste.

In addition to its waste reduction benefits, the production of unsaturated polyester resin from PET waste contributes to the principles of a circular economy. This approach establishes a closed-loop system where waste materials are transformed into valuable raw materials, minimizing resource consumption and environmental impact.

Moreover, the project holds the potential for significant economic growth. The utilization of PET waste for resin production can create employment opportunities through the establishment of recycling facilities and resin production units. This contributes to the socio-economic development of local communities.

Furthermore, the production of high-quality unsaturated polyester resin from PET waste opens avenues for export opportunities. Unsaturated polyester resin finds applications in various industries such as construction, automotive, marine, and aerospace. By tapping into international markets with a sustainable product, Pakistan can enhance its export capabilities, boosting economic growth and foreign exchange earnings.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

CHAPTER 1

INTRODUCTION

Unsaturated polyester resins (UPRs) are a versatile class of thermosetting polymers that find extensive use in a wide range of applications. They are commonly employed in industries such as automotive, construction, marine, electrical, and consumer goods. The production of UPRs involves the polycondensation reaction of unsaturated dicarboxylic acids or anhydrides with diols. This reaction leads to the formation of a linear polyester backbone containing unsaturated double bonds. The presence of unsaturation in the polyester backbone enables UPRs to undergo crosslinking when combined with a reactive monomer, typically a vinyl-type monomer like styrene. This process results in the formation of covalent bonds between the polyester chains and the monomer, leading to the creation of a three-dimensional network structure. The resulting network imparts excellent mechanical properties, chemical resistance, and dimensional stability to UPRs. A notable advantage of UPRs is their ability to be molded into complex shapes using various techniques such as hand lay-up, spray-up, filament winding, and compression molding. This versatility, combined with their relatively low cost, makes UPRs a popular choice for industries requiring lightweight, durable, and cost-effective materials. UPRs can be customized to meet specific application requirements by adjusting the composition of the polyester backbone and the selection and proportion of monomers. Further enhancement of mechanical and thermal properties can be achieved by incorporating various additives. However, UPRs do have some limitations. They are susceptible to degradation when exposed to UV radiation, which can result in color fading, loss of gloss, and reduced mechanical properties. Additionally, UPRs may exhibit shrinkage during the curing process, leading to dimensional instability and internal stresses in the final product. To overcome these limitations, modified versions of UPRs have been developed. For instance, UV-stabilized resins are formulated to resist UV degradation, while low-shrinkage formulations minimize dimensional changes during curing. These modifications improve the performance of UPRs in specific applications.

1.1 Unsaturated Polyester Resin

A thermosetting polymer made from the reaction between a dicarboxylic acid and a diol that, when crosslinked, form a three-dimensional network, offering good mechanical properties, corrosion resistance, and low weight.

1.1.1 Chemical Properties

- UP Unsaturated polyester resins (UPRs) exhibit several chemical properties that contribute to their widespread use in various applications. Here are some important chemical properties of UPRs:
- Crosslinking: UPRs undergo crosslinking when combined with a reactive monomer, typically styrene, and initiated by a free-radical initiator. This crosslinking process results in the formation of a three-dimensional network structure, providing UPRs with their excellent mechanical properties, chemical resistance, and dimensional stability.
- Chemical Resistance: UPRs generally possess good resistance to a wide range of chemicals, including acids, alkalis, and solvents. The specific chemical resistance can vary depending on the formulation of the UPR and the nature of the chemical exposure. Isophthalic resins and vinyl ester resins, for example, offer enhanced chemical resistance compared to orthophthalic resins.
- Water Absorption: UPRs have a certain degree of water absorption, which can affect their properties over time. Moisture absorption can cause dimensional changes, reduced mechanical properties, and increased susceptibility to degradation. However, the water absorption of UPRs can be reduced by incorporating additives or using modified formulations.
- UV Stability: UPRs are susceptible to degradation when exposed to ultraviolet (UV) radiation from sunlight. Prolonged exposure to UV

radiation can lead to color fading, loss of gloss, and reduced mechanical properties. UV stabilizers and additives can be incorporated into UPR formulations to enhance their UV resistance.

- Flammability: Pure UPRs are generally combustible materials. However, the flammability of UPRs can be reduced by incorporating flame retardant additives or using halogenated polyester resins, which exhibit improved fire resistance and self-extinguishing properties.
- Thermal Stability: UPRs typically exhibit good thermal stability up to moderate temperatures. However, prolonged exposure to high temperatures can result in degradation and loss of mechanical properties. The thermal stability of UPRs can be enhanced by incorporating heat stabilizers or using modified formulations.
- It is important to note that the specific chemical properties of UPRs can vary depending on the specific formulation, additives, and processing conditions used. Manufacturers often tailor UPR formulations to meet the desired chemical resistance, UV stability, flammability, and thermal stability required for different applications.

1.1.2 General Uses

- UP resins find wide application due to their excellent mechanical properties, corrosion resistance, and lightweight nature.
- They are commonly used for clear casting, coatings, buttons, body fillers, work surfaces, polyester concrete, and Gel Coats for composite materials.
- The building and sanitary ware industry heavily relies on reinforced UP resins for structural parts, cladding panels, sheeting, roofing tiles, pipes, and bathroom furniture.
- In the transport sector, UP resins are extensively used in airplanes, trucks, buses, and coaches for bumper beams, body panels, sunroof frames, dashboard carriers, seat structures, and battery supports. They offer weight reduction, corrosion resistance, and potential cost savings in painting.

- Rail cars, rolling stock, shipping containers, and luxury boat hulls are also manufactured using UP resin composites.
- UP resins find applications in the caravan panel market and are widely used in storage vessels due to their chemical resistance properties.

  In summary, UP resins are highly versatile materials that find application across multiple industries, benefiting from their favorable mechanical properties, resistance to corrosion, and lightweight characteristics.

1.1.3 Types of Unsaturated Polyester Resins

There are different types of unsaturated polyester resins (UPRs) available, each with its specific characteristics and applications. Here are some commonly used types of UPRs:

- **Orthophthalic Polyester Resins:** Orthophthalic resins are the most widely used UPRs. They offer good mechanical properties, chemical resistance, and cost-effectiveness. They find applications in general-purpose composites, automotive parts, construction materials, and consumer goods.
- **Isophthalic Polyester Resins:** Isophthalic resins exhibit improved chemical resistance and enhanced resistance to water and humidity compared to orthophthalic resins. They are commonly used in applications that require better resistance to corrosion, such as tanks, pipes, and chemical storage systems.
- **Dicyclopentadiene (DCPD) Modified Polyester Resins**: DCPD modified resins offer enhanced toughness, impact resistance, and heat resistance compared to traditional UPRs. They are used in demanding applications where high mechanical strength and dimensional stability are required, such as automotive body panels, wind turbine blades, and electrical components.
- **Vinyl Ester Resins**: Vinyl ester resins are hybrid materials that combine the properties of UPRs and epoxy resins. They exhibit excellent chemical resistance, mechanical strength, and fatigue resistance. Vinyl ester resins are

commonly used in applications that require high chemical resistance, such as chemical storage tanks, corrosion-resistant pipes, and marine components.

- **Halogenated Polyester Resins**: Halogenated polyester resins contain halogen elements such as chlorine or bromine. They offer improved fire resistance and self-extinguishing properties, making them suitable for applications that require fire retardancy, such as electrical enclosures and transportation interiors.
- **Bio-based Polyester Resins**: Bio-based UPRs are derived from renewable resources such as vegetable oils or bio-based diols. They offer environmental benefits by reducing reliance on fossil fuels. Bio-based UPRs find applications in various industries where sustainability and eco-friendliness are emphasized.

These are just a few examples of the types of UPRs available in the market. The choice of UPR type depends on the specific requirements of the application, such as mechanical properties, chemical resistance, fire resistance, and cost considerations. Manufacturers often offer a range of UPR formulations to cater to different application needs.

1.2 Industry Overview

The unsaturated polyester resin (UPR) industry is a vital sector in the chemical and materials industry. UPRs are thermosetting polymers formed by the reaction of unsaturated polyols and organic acids or anhydrides. They are widely used for their excellent properties and versatility in various applications.

1.2.1 Applications

1.2.1.1 Construction Industry

In the construction industry, unsaturated polyester resins are extensively used for manufacturing corrosion-resistant pipes, tanks, and structural components. These resins offer excellent chemical resistance, making them suitable for handling harsh environments and corrosive substances. Their durability and low maintenance requirements make them ideal for long-lasting infrastructure solutions. Moreover, unsaturated polyester resin-based composites are used in architectural applications, providing lightweight and aesthetically pleasing materials for facades, cladding, and decorative elements.

1.2.1.2 Automotives Industry

The automotive sector benefits significantly from the use of unsaturated polyester resins. These resins are employed in the production of lightweight parts, such as body panels, interior components, and structural reinforcements. By replacing traditional materials with composites incorporating unsaturated polyester resins, manufacturers can achieve weight reduction, leading to improved fuel efficiency, reduced emissions, and enhanced overall vehicle performance. Additionally, the corrosion resistance and design flexibility of these resins contribute to the durability and aesthetics of automotive components.

1.2.1.3 Marine Industry

In the marine industry, unsaturated polyester resins are crucial for boat building and other marine applications. Their excellent water resistance, resistance to UV degradation, and high strength make them ideal for manufacturing boat hulls, decks, and various structural components. Unsaturated polyester resin-based composites offer enhanced performance, including improved impact resistance, reduced weight, and increased durability compared to traditional materials like wood or metal. These resins enable the construction of lightweight, fuel-efficient, and long-lasting marine vessels.

1.2.1.4 Electrical Industry

The electrical industry relies on unsaturated polyester resins for electrical insulation purposes. These resins possess excellent dielectric properties, providing insulation and protection to electrical components and wiring systems. Their thermal stability and flame-retardant characteristics make them suitable for various electrical applications, including transformers, switchgear, circuit boards, and insulating coatings. Furthermore, the development of low-smoke and low-toxicity formulations enhances their safety features, particularly in critical applications.

1.2.2 Market Demand

The demand for unsaturated polyester resins has been steadily increasing due to their unique properties and wide application range. Factors driving market demand include rapid urbanization, infrastructure development, growing automotive production, and increasing demand for lightweight and durable materials. The market demand for unsaturated polyester resins is also influenced by emerging technologies and sustainability trends, with a focus on eco-friendly and bio-based resin formulations.

1.2.2.1 Rapid Urbanization and Infrastructure Development

The ongoing process of rapid urbanization and infrastructure development worldwide drives the demand for UPRs. As cities expand and infrastructure projects multiply, there is a need for durable, corrosion-resistant, and cost-effective materials. UPR-based composites offer these qualities, making them ideal for a wide range of construction applications such as pipes, tanks, panels, and structural components.

1.2.2.2 Growing Automotive Production

The automotive industry is a major consumer of UPRs. With the increasing demand for vehicles globally, there is a growing need for lightweight materials that contribute to fuel efficiency and reduce emissions. UPR-based composites enable manufacturers to produce lighter parts without compromising strength and performance. These composites find applications in exterior panels, interior components, and structural reinforcements, driving the demand for UPRs in the automotive sector.

1.2.2.3 Lightweight and Durable Materials

The demand for lightweight and durable materials is pervasive across industries. UPR-based composites offer an excellent combination of strength, stiffness, and low weight, making them suitable for a wide range of applications. Industries such as aerospace, marine, consumer goods, and electrical embrace UPR-based composites to achieve weight reduction, improved performance, and enhanced durability.

1.2.2.4 Growth Prospects

The unsaturated polyester resin industry is expected to witness significant growth in the coming years. The increasing adoption of composites as a substitute for traditional materials in various industries is a major driver for the growth. Composites offer benefits such as high strength-to-weight ratio, corrosion resistance, design flexibility, and improved durability. Furthermore, the demand for eco-friendly and sustainable materials is creating opportunities for bio-based unsaturated polyester resins derived from renewable sources. The development of advanced manufacturing processes and technologies, such as additive manufacturing (3D printing) using resin-based materials, is also expected to contribute to the industry's growth.

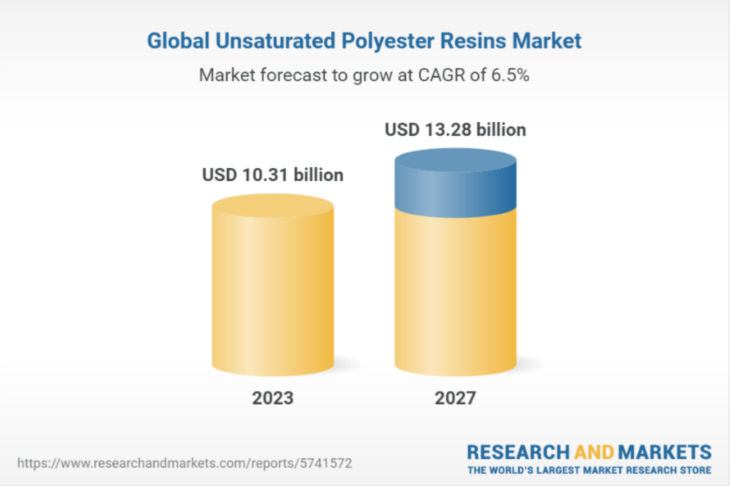


Figure 1 : Growth of Global Unsaturated Polyester Resins Market

CHAPTER 2

POLYMERS AND UNSATURATED POLYESTER RESINS

2.1 Introduction

This chapter provides an in-depth understanding of polymers and their relevance to the production of unsaturated polyester resins. It begins with a comprehensive overview of polymers, their structure, and properties. Subsequently, the focus shifts to unsaturated polyester resins, highlighting their synthesis, characteristics, and applications. This chapter aims to establish a strong foundation of knowledge concerning the polymers utilized in the production of unsaturated polyester resins.

2.2 Polymers

Polymers are large molecules composed of repeating subunits called monomers. These monomers are chemically bonded together through various reactions, forming long chains or networks. Polymers possess diverse properties that make them suitable for a wide range of applications. They can be classified into different categories based on their structure, such as linear, branched, crosslinked, or network polymers. The properties of polymers, including mechanical, thermal, and chemical properties, greatly depend on their molecular structure, composition, and processing techniques.

2.2.1 Types of Polymers

Polymers can be classified into various types based on their composition, molecular structure, and processing characteristics. Some of the commonly encountered polymer types include:

2.2.1.1 Thermoplastics

Thermoplastics are polymers that can be melted and re-molded multiple times without undergoing any significant chemical change. They have linear or branched structures and are held together by intermolecular forces. When heated, thermoplastics soften and become viscous, allowing them to be shaped into different forms. Common examples of thermoplastics include polyethylene, polypropylene, polystyrene, and polyvinyl chloride (PVC). These polymers find applications in packaging, automotive components, household goods, and many other industries.

2.2.1.2 Thermosets

Polymers Unlike thermoplastics, thermosetting polymers undergo irreversible chemical changes upon heating and curing. They form a three-dimensional network structure due to the presence of covalent crosslinks. Once cured, thermosetting polymers become rigid and cannot be re-melted or reshaped. Examples of thermosetting polymers include unsaturated polyester resins, epoxy resins, phenolic resins, and polyurethane. These polymers are widely used in composites, adhesives, coatings, and electrical insulation applications.

2.2.1.3 Elastomers

Elastomers are polymers with the ability to undergo large deformations and return to their original shape after the applied stress is removed. They possess a highly crosslinked structure that allows them to stretch and retract. Elastomers exhibit excellent elasticity and resilience, making them suitable for applications requiring flexibility and shock absorption. Natural rubber and synthetic rubbers, such as polyisoprene and polybutadiene, are common elastomers used in the production of tires, seals, gaskets, and various rubber products.

2.2.1.4 Biodegradable Polymers

In recent years, there has been a growing interest in developing environmentally friendly polymers that can undergo degradation by natural processes. Biodegradable polymers can be derived from renewable resources or synthesized through eco-friendly processes. These polymers offer potential solutions for reducing plastic waste and minimizing environmental impact. Examples of biodegradable polymers include polylactic acid (PLA), polyhydroxyalkanoates (PHA), and polybutylene succinate (PBS). They find applications in packaging, agriculture, biomedical devices, and other sectors.

2.2.2 Polymerization Reactions

Polymerization reactions play a vital role in the synthesis of polymers. They involve the combination of monomers to form larger chains or networks. Polymerization can occur through different mechanisms, such as addition polymerization and condensation polymerization. In addition polymerization, monomers add together without the formation of any by-products. On the other hand, condensation polymerization involves the elimination of small molecules, such as water or alcohol, as by-products during the polymerization process. The choice of polymerization mechanism depends on the specific monomers and desired properties of the resulting polymer. Let's explore some common polymerization reactions:

2.2.2.1 Addition Polymerization

Addition polymerization, also known as chain-growth polymerization, involves the successive addition of monomers to a growing polymer chain. This reaction occurs through the activation of a reactive site, such as a carbon-carbon double bond (alkene) or a carbon-nitrogen double bond (nitrile). The reactive site undergoes a free-radical, cationic, or anionic initiation, leading to the formation of a propagating chain. As more monomers are added, the polymer chain grows until the reaction is terminated. Termination can occur by the combination of two growing chains or by the addition of a chain-terminating agent.

Addition polymerization reactions are often initiated by heat, light, or a catalyst. Examples of addition polymerization include the polymerization of ethylene to produce polyethylene, the polymerization of styrene to produce polystyrene, and the polymerization of methyl methacrylate to produce polymethyl methacrylate (PMMA). Addition polymers generally have a high molecular weight and can be either amorphous or semi-crystalline, depending on the specific monomers and processing conditions.

2.2.2.2 Condensation Polymerization

Condensation polymerization involves the reaction between two different monomers, usually with the elimination of a small molecule, such as water or alcohol, as a by-product. This reaction occurs between functional groups in the monomers, such as carboxyl groups and hydroxyl groups, to form a covalent bond and release the by-product. The reaction proceeds through multiple steps, including initiation, propagation, and termination.

Condensation polymerization is commonly used to produce polyesters, polyamides, and polyurethanes. For example, the condensation of terephthalic acid with ethylene glycol leads to the formation of polyethylene terephthalate (PET), a widely used polyester. The properties of condensation polymers can be influenced by factors such as the molecular weight, degree of polymerization, and the presence of functional groups. They often exhibit high thermal stability and can have a more complex and heterogeneous structure compared to addition polymers.

2.2.3 Structure-Property Relationships in Polymers

The structure of polymers greatly influences their properties. The arrangement of monomer units, molecular weight, branching, crosslinking, and crystallinity all contribute to the overall performance of polymers. For example, the presence of branching or crosslinking in polymers can enhance their mechanical strength and thermal stability. Molecular weight affects the melt flow behavior, viscosity, and processing characteristics of polymers. The crystallinity of a polymer can influence its optical, thermal, and mechanical properties. Understanding the structure-property relationships is crucial for tailoring polymers with desired characteristics.

2.3 Unsaturated Polyester Resins

Unsaturated polyester resins (UPRs) are a class of thermosetting polymers widely used in various industries, including automotive, construction, marine, and electrical. UPRs are produced through the reaction between unsaturated dibasic acids or anhydrides and glycols. The reaction forms a linear or branched polyester backbone with unsaturated double bonds. UPRs are commonly modified with reactive diluents, such as styrene, to reduce viscosity and enhance processability.

2.3.1 Synthesis of Unsaturated Polyester Resins

The synthesis of UPRs involves several steps, including esterification, polycondensation, and final resinification. Initially, the unsaturated dibasic acid or anhydride reacts with glycols, such as ethylene glycol or propylene glycol, to form polyester oligomers. This esterification step is typically carried out under controlled temperature and pressure conditions. Subsequently, the oligomers are subjected to a polycondensation reaction, which increases the molecular weight and viscosity of the resin. Finally, resinification occurs by adding a suitable catalyst to promote crosslinking and curing of the UPRs.

2.3.2 Properties and Applications of Unsaturated Polyester Resins

UPRs exhibit a combination of desirable properties, making them suitable for a wide range of applications. Some key properties of UPRs include:

- **Mechanical Strength**

UPRs offer excellent mechanical properties, including high tensile strength, flexural strength, and impact resistance. These properties make them ideal for structural applications, such as in composite materials.

- **Chemical Resistance**

UPRs exhibit good resistance to various chemicals, including acids, alkalis, and solvents. This property enables their use in corrosive environments or applications requiring chemical resistance, such as chemical storage tanks or pipes.

- **Dimensional Stability**

UPRs have low shrinkage and excellent dimensional stability, ensuring that molded parts maintain their shape and size over time. This property is particularly important in applications where precise dimensions are crucial.

- **Adhesion**

UPRs exhibit good adhesion to a wide range of substrates, including metals, plastics, and composites. This property allows for strong bonding in applications such as coatings, laminates, and adhesive formulations.

- **Thermal Stability**

UPRs possess moderate to high thermal stability, enabling their use in applications that require resistance to elevated temperatures. However, they may undergo thermal degradation at very high temperatures.

2.3.3 Curing of Unsaturated Polyester Resins

The curing process of UPRs involves the crosslinking of the polyester chains through a reaction known as "styrene copolymerization." Styrene, a low-viscosity liquid monomer, is commonly added to UPR formulations as a diluent and reactive solvent. During curing, the styrene monomers diffuse into the resin and participate in the crosslinking reactions.

The crosslinking reaction is initiated by a free radical initiator, such as an organic peroxide, which decomposes upon heating. The initiator generates free radicals that react with the unsaturated double bonds present in the polyester chains and styrene monomers, leading to the formation of covalent bonds and the formation of a three-dimensional network structure.

The curing process is typically carried out at elevated temperatures, ranging from 60°C to 180°C, depending on the specific UPR formulation and application. The time required for complete curing can vary from minutes to several hours, depending on the catalyst system and the desired properties of the final product.

During the curing process, the UPR formulation undergoes a transition from a low-viscosity liquid to a solid, crosslinked material. This transformation is accompanied by an exothermic reaction, releasing heat. The heat generated during curing is important to achieve the desired crosslinking density and mechanical properties of the cured UPR.

2.3.4 Modification of Unsaturated Polyester Resins

To enhance the properties and performance of UPRs, various modifications can be made to the base resin. These modifications include:

2.3.4.1 Reinforcements

UPRs can be reinforced with fillers or reinforcing agents, such as fiberglass, carbon fibers, or mineral fillers, to improve their mechanical strength, stiffness, and impact resistance. The addition of reinforcements also helps to control shrinkage and dimensional stability.

2.3.4.2 Additives

Various additives can be incorporated into UPR formulations to achieve specific properties. Examples include UV stabilizers for improved weatherability, flame retardants for enhanced fire resistance, and pigments for coloration. Additives can also be used to improve processing characteristics, such as viscosity modifiers or thickeners.

2.3.4.3 Crosslinking Promoters

Co-agents or crosslinking promoters, such as cobalt compounds or organic amines, can be added to UPR formulations to enhance the curing process. These additives assist in initiating and accelerating the crosslinking reactions, reducing curing time and improving the overall properties of the cured UPR.

2.3.4.4 Reactive Diluents

In addition to styrene, other reactive diluents can be used in UPR formulations to control viscosity, improve handling, and enhance mechanical properties. Examples of reactive diluents include vinyl toluene, diallyl phthalate, and methyl methacrylate. These diluents participate in the crosslinking reactions and become part of the final cured UPR network.

The modification of UPRs allows for tailoring their properties to meet specific application requirements, expanding their potential applications and performance capabilities.

2.4 Conclusion

This chapter has provided a comprehensive overview of polymers and their significance in the production of unsaturated polyester resins. The understanding of polymerization reactions, structure-property relationships, and the synthesis of UPRs lays the foundation for further exploration and optimization of unsaturated polyester resin production. The subsequent chapters will delve into the experimental methods, characterization techniques, and optimization strategies in detail, aiming to enhance the performance and broaden the application range of unsaturated polyester resins.

CHAPTER 3

PROCESS DESCRIPTION

3.1 Introduction

This chapter provides a detailed description of the production process of unsaturated polyester resins (UPRs). The UPR manufacturing process involves several sequential steps, starting from the selection and preparation of raw materials to the final product formulation. Understanding the process is crucial for optimizing the production efficiency, quality control, and troubleshooting potential issues. This chapter aims to outline the key steps involved in the production of UPRs, including raw material handling, esterification, polymerization, and post-processing.

3.2 Raw Material Handling

The production of UPRs begins with the careful selection and handling of raw materials. The primary components of UPRs include unsaturated dibasic acids or anhydrides, polyols, and crosslinking agents. Other additives such as accelerators, inhibitors, and fillers are also incorporated into the formulation. The raw materials must be stored in appropriate conditions to maintain their quality and prevent contamination. Handling procedures should adhere to safety guidelines to minimize potential hazards and ensure consistent material characteristics.

3.3 Process

3.3.1 Glycolysis of PET

- Recycled PET is introduced along with Diethylene glycol into a batch reactor equipped with a heating jacket.
- The mixture is heated using mineral oil as a heat transfer medium.

- The endothermic chemical reaction occurs, converting the PET into PETG (Polyethylene terephthalate glycol).

3.3.2 Polymerization with Maleic Anhydride

- The PETG obtained from the glycolysis process is then transferred to another batch reactor equipped with a cooling jacket.
- MA is introduced into the reactor.
- The exothermic polymerization reaction takes place between PETG and MA, resulting in the formation of PETG-g-MA (Polyethylene terephthalate glycol-maleic anhydride). The extra heat is removed by cooling water in the jacket.
- Xylene is utilized as a reflux agent to facilitate the reaction and maintain optimal reaction conditions.
- The reaction requires occurs at 260℃ for 7-8 hours for complete polymerization.

3.3.3 Condensation of Water-Xylene Mixture

- As a byproduct of the reaction between PETG and MA, water is generated along with the desired product.
- The water-xylene mixture is condensed in a shell and tube heat exchanger, where heat is exchanged with a cooling medium (i.e., water).
- The condensed mixture is collected in a receiver or a separation unit to separate the water and xylene components for further treatment or recycling.

3.3.4 Styrenation

- The PETG-g-MA obtained from the polymerization reactor is transferred to a styrenation tank.

- The styrenation tank is initially cooled to a specific temperature range to optimize the subsequent mixing process.
- Styrene is added to the tank, and the PETG-g-MA is mixed thoroughly with styrene.
- This mixing process enhances the curing properties of the final product, preparing it for further applications.

3.3.5 Cooling

- The styrenated PETG-g-MA, now containing the desired properties, is then cooled down in another shell and tube heat exchanger.
- The heat exchanger facilitates the exchange of heat between the product and a cooling medium, ensuring the resin reaches the desired temperature for storage or packaging.

3.4 Post-Processing

After the polymerization step, the UPR undergoes various post-processing treatments to ensure the final product meets the required specifications. These treatments may include degassing, filtration, and additives incorporation. Degassing eliminates any trapped air or volatile components, which could cause defects in the final product. Filtration removes any impurities or solid particles that may have formed during the production process. Additionally, additives such as pigments, thickeners, or flame retardants may be incorporated into the resin to enhance specific properties or meet customer demands.

3.5 Quality Control

Throughout the production process, quality control plays a crucial role in ensuring the consistency and performance of the UPRs. Quality control measures involve sampling and testing at various stages, including raw material inspection, in-process analysis, and final product testing. Analytical techniques such as gas chromatography, gel permeation chromatography, and viscometry are employed to assess the chemical composition, molecular weight, viscosity, and other relevant parameters. Any deviations from the specified requirements prompt corrective actions to maintain product quality and process efficiency.

3.6 Process Optimization and Continuous Improvement

Continuous improvement of the UPR production process is vital for enhancing product quality, reducing costs, and increasing overall efficiency. Process optimization involves evaluating different parameters, such as reaction conditions, catalyst concentrations, and raw material selections, to identify opportunities for improvement. Techniques like statistical process control, design of experiments, and lean manufacturing principles can aid in process optimization efforts. By implementing these strategies, manufacturers can achieve higher yields, minimize waste, and optimize energy consumption, thereby ensuring a competitive edge in the market.

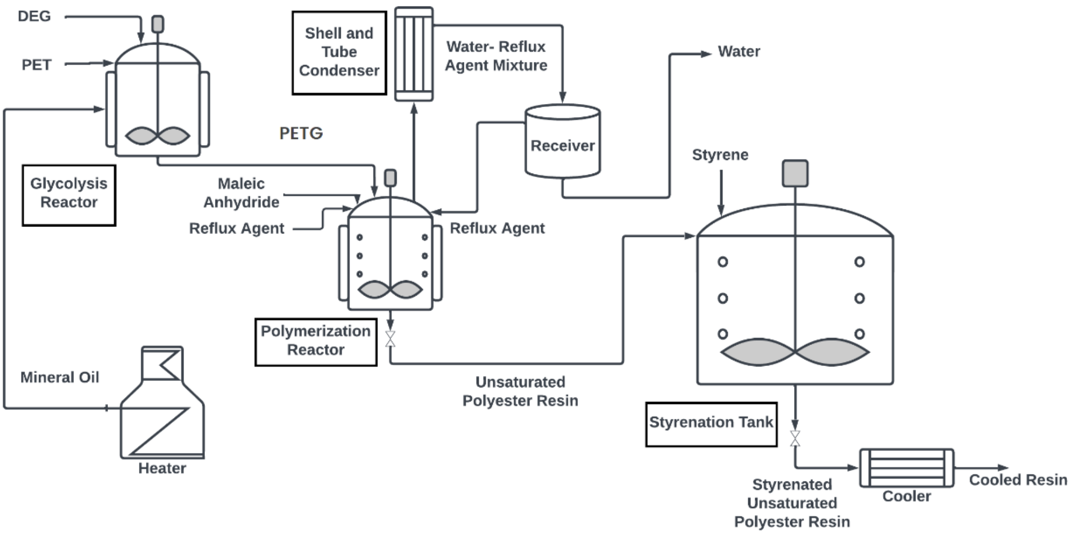


Figure 2 : Process Flow Diagram

CHAPTER 4

MASS BALANCE

Material balance is based on law of conservation of mass, which states that mass can neither be created nor destroyed and is always conserved in any process. Material balance, also known as mass balance, is a method of analyzing physical systems using the principle of mass conservation. Mass flows that would have been unknown or difficult to assess, can be identified by accounting for material entering and leaving a system. Material balances are frequently used in chemical engineering calculations, especially for equipment design such as determining flows into and out of a polymerization reactor. The general mass balance equation can be written as:

Accumulation within the system = (Mass into the system) – (Mass out of the system) + (Generation within the system) – (Consumption within the system)

4.1 Methodology

For the purpose of this project, material balance was performed to find out the values of major streams. Initial calculations were performed by hand and then refined and copied to MS Excel. Material balance was done, initially, on the whole system and then on major equipment including:

- Glycolysis reactor
- Polymerization reactor
- Styrenation tank

4.1.1 Overall Mass Balance

Table 1 : Overall Mass Balance

Components	In(kg/day)	Out(kg/day)

PET	15073	-
DEG	6000	-
PETG	-	21073
MA	7740	-
PETG-g-MA	-	26749
Styrene	14350	-
st-PETG-g-M	-	41096
Water	-	2124

4.1.2 Glycolysis Reactor

In glycolysis reactor, PET and DEG are combined. This is an endothermic reaction required heat provided by mineral oil which heats the mixture from 25C to 260C. The mixture, after leaving the glycolysis reactor, enters the polymerization reactor.

Table 2 : Mass Balance on Glyolysis Reactor

Inlet (kg/day)	**21073**	
Component	**Mass Fraction**	**Mass (Kg/day)**
PET	0.72	15073
DEG	0.28	6000

Outlet (kg/day)	**21073**	
Component	**Mass Fraction**	**Mass (Kg/day)**
PETG	1	21073

4.1.3 Polymerization Reactor

Reactants after leaving glycolysis reactor enter the polymerization reactor at

260℃ where reflux agent i.e., xylene and maleic anhydride enter this reactor at 25℃ and leave the polymerization reactor at 240℃. Here Reaction takes place and maleic anhydride added to introduce the unsaturation. UPR leaves at the bottom of reactor and mixture of water and xylene move towards condenser where water separated from xylene and reflux agent added back into reactor.

Table 3 : Mass Balance on Polymerization Tank

Inlet (kg/day)	**29138**	
Component	**Mass Fraction**	**Mass (Kg/day)**
PETG	0.72	21073
MA	0.26	7740
Xylene	0.01	325

Outlet (kg/day)	**29138**	
Component	**Mass Fraction**	**Mass (Kg/day)**
PETG-g-MA	0.92	26749
Water	0.07	2124
Xylene	0.01	325

4.1.4 Styrenation Tank

In this reactor styrene added in reactor 20-30% to enhance cross linking in UPR. At the end of this tank we get our final product at 80℃.

Table 4 : Mass Balance on Styrenation Tank

Inlet (kg/day)	**41096**	
Components	**Mass Fraction**	**Mass (Kg/day)**
PETG-g-MA	0.650817598	26746
Styrene	0.349182402	14350

Outlet (kg/day)	**41096**	
Components	**Mass Fraction**	**Mass (Kg/day)**
PETG-g-MA-st	1	41096

CHAPTER 5

ENERGY BALANCE

After completing the necessary material balances, we proceeded to perform energy balances on the relevant equipment. As the proposed process consists solely of a sequence of unit operations, we simply relied on the energy values of the streams involved.

5.1 Glycolysis Reactor

Table 5 : Energy Balance on Glycolysis Reactor

		Temperature (°C)	**C_p** (KJ/Kg C)	**Mass** (Kg)	**Q** (KJ)
Inlet Conditions	PET	25	1.03	15073	388129.75
	DEG	25	2.306	6000	345900
				Total Q	734029.75
Outlet Conditions	PETG	260	1.95	21073	10684011
	Total Q				10684011
	Total Heat				1596000

	Mineral Oil Inlet	350	1.81		
	Mineral Oil Outlet	100	1.69		
	Total Amount of Mineral Oil Required			53200	

5.2 Polymerization Reactor

Table 6 : Energy Balance on Polymerization Reactor

		Temperature (^{o}C)	**C$_p$** (KJ/Kg C)	**Mass** (Kg)	**Q** (KJ)
Inlet Conditions	PETG	260	1.95	21073	10684011
	MA	25	1.21	7740	234135
	Xylene	25	2.2	325	17875
				Total Q	10936021
Outlet	PETG-g-MA	240	1.9	26746	12196176

Conditions	Water	240	4.77	2124	2431555.2
	Xylene	240	2.8	325	218400
	Total Q				14846131.2
	Total Heat				14846.1312
	Water Inlet	30	4.18		
	Water Outlet	100	4.22		
	Total Amount of water Required.			85500	

5.3 Heater

Table 7 : Energy Balance on Heater

		Temperature (°C)	**C_p** (KJ/Kg C)	**Mass** (Kg)	**Q** (KJ)
	Mineral Oil Inlet	25	1.67	53200	2221100
	Mineral Oil	350	1.81	53200	33702200

	Outlet				
				Total Q	31481100

5.4 Condenser

Table 8 : Energy Balance on Condenser

		Temperature (°C)	**C_p** (KJ/Kg C)	**Mass** (Kg)	**Q** (KJ)
Inlet Conditions	Reactor Outlet	240	4.5	2449	
	Water	30	4.18	89213.57143	
Outlet Conditions	Condenser Outlet	70	3.9	2449	
	Water	100	4.22	89213.57143	
	Heat Removed				249798
	Total Amount of water Required.			85500	

5.5 Styrenation Tank

Table 9 : Energy Balance on Styrenation Tank

		Temperature (°C)	C_p (KJ/Kg C)	**Mass** (Kg)	**Q** (KJ)
Inlet Conditions	PETG-g-MA	240	1.9	26746	12196176
	Styrene	25	1.75	14350	627812.5
Outlet Conditions	PETG-g-MA-st	85	1.91	41096	6671935.6
	Water Inlet	30	4.18		
	Water Outlet	100	4.22		
	Total Amount of Water			14328.21429	

	Required			
	Total Heat Removed from PETG-g-MA			40119

5.6 Cooler

Table 10 : Energy Balance on Cooler

		Temperature (^{o}C)	**C_p** (KJ/Kg C)	**Mass** (Kg)	**Q** (KJ)
Inlet Conditions	PETG-g-MA-st	85	1.91	41096	
	Water	20	4.18	82192	
Outlet Conditions	PETG-g-MA-st	25	1.87	41096	
	Water	80	4.2	82192	
	Total Amount of Water Required			82192	

	Total Heat Removed from PETG-g-MA-st			98630.4

CHAPTER 6

EQUIPMENT DESIGN CALCULATIONS

6.1 Design of Shell and Tube Condenser

Shell and tube condenser is used to cool down the water-Xylene vapor mixture arising from the polymerization reactor. It is a 1-1 shell tube pass exchanger with the vapor mixture in the tubes and cold water in the shell side. We have designed this shell & tube heat exchanger using Kern's Method.

6.1.1 Physical Properties of Fluids & Allocation

Table 11 : Tube Side Physical Properties

Tube Side	
Fluid	**Water-Xylene Mixture**
Temperature (Inlet) (C)	240.00
Temperature (Outlet) (C)	80.00
Cp (inlet) (kJ/kg-C)	4.50
Cp (outlet) (kJ/kg-C)	3.96
Cp (average) (J/kg-K)	4.23
Enthalpy (inlet) (KJ/kg)	1080.00
Enthalpy (outlet) (KJ/kg)	316.80
Density (average) (kg/m^3)	1037.00
Viscosity (average)(Kg/ms)	0.00026
Thermal Conductivity (average) (W/mK)	0.07
Mass Flow Rate (Kg)	2449.00

Table 12 : Shell Side Physical Properties

Shell Side	
Fluid	**Water**
Temperature (Inlet) (C)	25.00
Temperature (Outlet) (C)	90.00

Cp (inlet) (kJ/kg-C)	4.18
Cp (outlet) (kJ/kg-C)	4.22
Cp (average) (kJ/kg-C)	4.20
Enthalpy (inlet) (KJ/kg)	104.50
Enthalpy (outlet) (KJ/kg)	379.80
Density (average) (kg/m^3)	997.00
Viscosity (average)(Kg/ms)	0.002
Thermal Conductivity (average) (W/mK)	0.64
Mass Flow Rate (Kg/day)	81382.15

Table 13 : Heat Transfer Equation

Total Heat removed (Q) (MJ/day)	211.59
Total Heat removed (Q) (kJ/day)	211593.60
Total Heat removed (Q) (J/s)	2449.00
Let's Assume U (W/m^2K)	1.60
T1 (C)	150.00
T2 (C)	55.00
LMTD	94.69
Area (m^2)	16.17

6.1.2 Size Specifications

Table 14 : Size Specifications

Tube OD (inch/m)	0.03810
Surface Area per tube in meters(m^2/m)	0.02000
Length of tube (m)	16.00000
Surface Area per tube (m^2)	0.32000
Number of tubes	**50.51577**
di (m)	0.016
do (m)	0.038
Nt	50.516
Type of Pitch	Square Staggered
Pitch (m)	2.5do
No of Passes	1.000
Db (Bundle Diameter) (m)	2.35

Shell-Bundle Clearence (mm)	50.00
Shell Diameter (IDs) (m)	2.40

6.1.3 Tube Side Analysis

Table 15 : Tube Side Analysis

Flow Area per tube (m^2)	**9.94E-06**
Total Flow Area (m^2)	5.02E-04
Mass Velocity (Kg/m^2.s)	5.65E+01
Velocity (m/s)	5.45E-02
Reynolds Number	3.39E+03
Prandtl Number	1.60E-02
hi	1.79E+01
hio (W/m^2-K)	7.38E+00

6.1.4 Shell Side Analysis

Table 16 : Shell Side Analysis

Number of baffles	22.222
Baffle spacing (m)	**0.720**
Flow Area of Shell (m^2)	0.346
Mass Velocity (Kg/m^2.s)	65.411
Equivalent Diameter (m)	0.027
Velocity (m/s)	0.066
Reynolds Number	876.023
Baffle cut	0.450
Jh	**0.100**
Prandtl Number	0.013
ho	490.506
Uc	7.270
Rd (Steam)	0.000
Rd (Cracked Gas)	0.000
Ud	7.255

6.1.5 Pressure Drop – Tube Side

Table 17 : Pressure Drop - Tube Side

Reynolds Number	3394.56
Np (Number of passes)	4.00
(L) length of one tube (m)	6.10
di (m)	0.02
ut (Velocity Tube side) (m/s)	0.05
Density (kg/m^3)	1037.00
Jf	**0.0041**
dP (pressure drop) (Pa)	**93.53**
dP (pressure drop) (PSI)	**0.01**

6.1.6 Pressure Drop – Shell Side

Table 18 : Pressure Drop - Shell Side

Reynolds Number	876.02
Np (Number of passes)	1.00
(L) length of one tube (m)	6.10
(Lb)Baffle Spacing	0.72
de (m)	0.03
ds (m)	2.40
ut (Velocity Tube side) (m/s)	0.07
Density (kg/m^3)	997.00
Jf	**0.02**
dP (pressure drop) (Pa)	**245.14**
dP (pressure drop) (PSI)	**0.04**

6.2 Design of Furnace

A furnace is used to heat the mineral oil flowing through the heating jacket of the glycolysis reactor. We have designed the furnace using Lobo & Evans method.

6.2.1 Assumptions and Requirements

Mineral Oil:

Table 19 : Mineral Oil Properties

Inlet Temperature (C)	25	**Heat Capacity (J/kg C)**	2085
Outlet Temperature (C)	250	**Heat Capacity (J/kg C)**	2248

Table 20 : Overall Quantities

Quantity	Unit	Value
Total Required Heat Duty	kJ/day	31481100
Efficiency (assumed)	%	75
Fuel name (selected)		Natural Gas
Caloric Value of fuel	kJ/kg	54300
Temp of inlet air (assumed)	˚C	25
TUBES SIZE (3inch - 40 schedule no.)		
Outer Diameter	m	0.0889
Thickness		0.0057404
Centre-to-centre distance		
Pitch	m	0.21
Exposed Tube Length(selected)	m	10
Heat Capacity for air	kJ/kg-K	1
Heat Capacity for flue gases	kJ/kg-K	1.218
Average Flux for Radiant Section	(BTU/hr ft^2)	11000
Q air	kJ/hr	136803.976

6.2.2 Furnace Tubes

The outer diameter of the tubes and their length is assumed first and then we'll do further calculations to see if our design is valid or not.

Table 21 : Furnace Tube Specifications

Furnace Tubes	
OD (Inches)	5
Pitch (inches)	8.5
Exposed tube length (ft)	25

6.2.3 Flue Gas Temperature

Depending upon the average flux that we've assumed for the radiant section & the tube surface temperature we'll find out the temperature of the flue gases using the graph.

Table 22 : Flue Gas Temperature

Average Flux for Radiant Section (BTU/hr ft^2)	11000
Tube Surface Temperature ($°F$)	500
Flue Gas Temperature (over Bridge wall) ($°F$)	**1660**

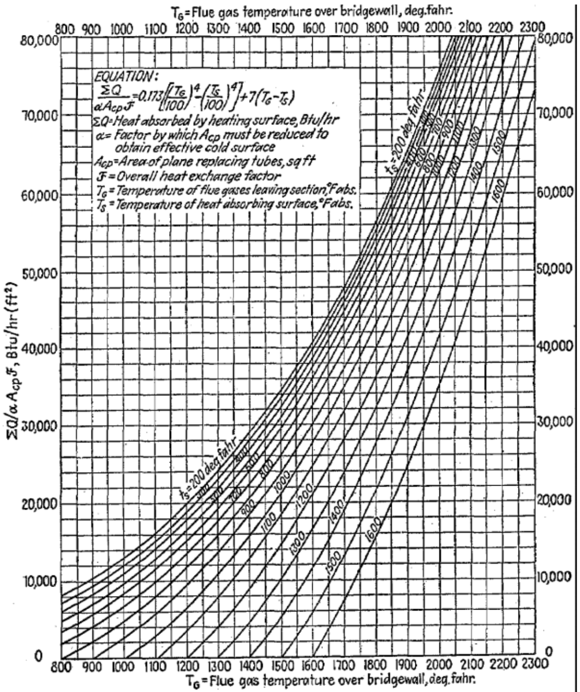


Fig. 19.14. Radiant-section heat flux.

Figure 3 : Radiant Section Heat Flux

6.2.4 Total Heat

$$\frac{\Sigma Q}{A_{cp}\alpha_{cp}} = 2\text{*Average Flux}$$

Overall exchange factor (f) = 0.57

$$\frac{\Sigma Q}{A_{cp}\alpha_{cp} f} = 38596\ (\text{BTU/hr ft}^2)$$

Table 23 : Total Heat Liberated

Heat Liberated by Fuel (QF) (kJ/hr)	41974800
Quantity of Fuel (METHANE) Required (kg/hr)	773

Air Required for Combustion (kg/hr)	14476
Percentage Excess Air	25%
Air Required for Effective Combustion (kg/hr)	18095
Heat of Air at 77F (QA)	136803
QF+QA (kJ/hr)	42111603
QW=0.2*QF	
QW (Heat loss through Furnace Walls) (kJ/hr)	839496
Qnet=QF+QA-QW (kJ/hr)	**41272107**
Specfic Heat Capacity of Flue Gas (kJ/kg.R)	0.68
QG (Heat out in Flue Gas)	6992423
Q=Qnet-QG	**34279684**

6.2.5 Number of Tubes

$$Nt = \frac{Q}{(Average\ flux)*(Surface\ Area\ per\ Tube)}$$

Table 24 : Number of Tubes

Surface Area/tube	6.594

Estimated Number of Tubes	**472**
Equivalent Cold Plane Surface Area /tube (Acp) (m^2)	992

Now, finding the α factor using the graph

Table 25 : a and Dimensions

α	**0.937**
αcp*Acp (m^2)	930
Width (m)	2.8
Height (m)	1.9
Bridgewall Height (m)	53.2

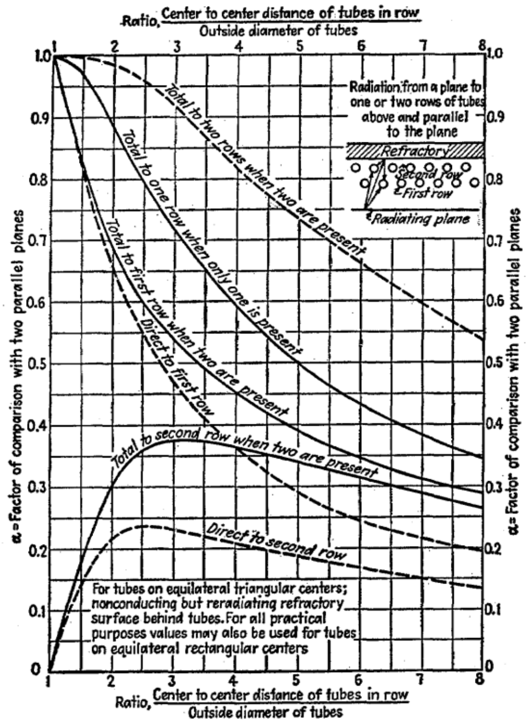


Figure 4 : Effectiveness of Furnace

6.2.6 Mean Beam Length

$$L = \tfrac{2}{3}\sqrt[3]{\text{volume}}$$

Mean Beam Length (m) (L)	**11.82**

Calculated overall exchange factor = 0.53

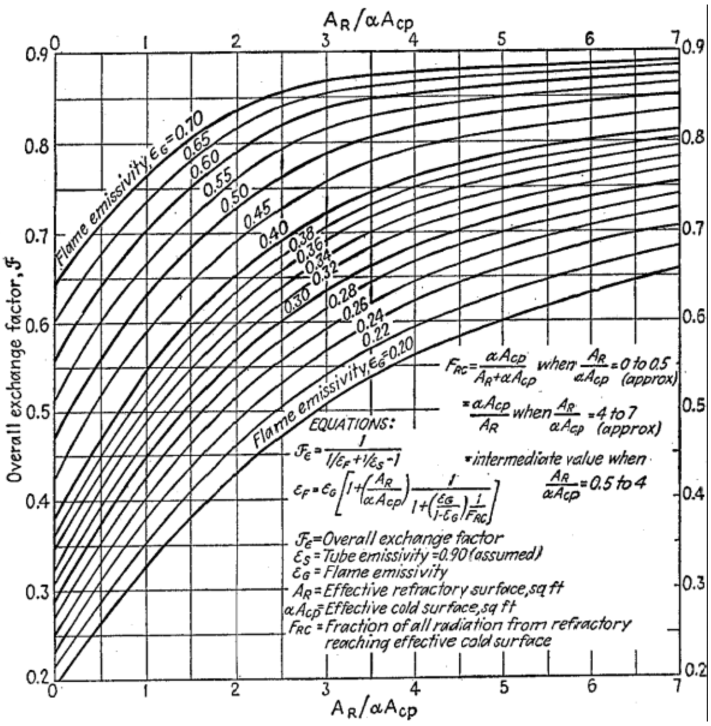


Figure 5 : Overall Exchange Factor

6.2.7 Calculated Flux

$\frac{\Sigma Q}{A_{cp}\alpha_{cp}f}$ = 64670.74 BTU/hr ft^2

6.3 Design of Glycolysis Reactor

The glycolysis reactor is where PET undergoes chemical recycling by reacting with DEG to make PETG.

6.3.1 Volume Calculations

Table 26 : Volume Calculations

Volume Calculations			
Component	**Mass (Kg/day)**	**Density (Kg/m^3)**	**Volume (m^3/day)**
PET	15073	1380	10.92246377

DEG	6000	1120	5.357142857
Volume of Above Reactants			**4.883881988**
Total volume			**21.16348861**

6.3.2 Length and Diameter Calculations

Table 27 : Length and Diameter

Length & Diameter Calculations	
Parameters	**Value (m)**
Reactor Diameter	2.53
Reactor length	3.8

6.3.3 Area of Reactor

Table 28 : Reactor Area

Area of reactor		
Parameter	**Formula**	**Value (m^2)**
Cylinder Area	A_c = 2πrh	30
Torispherical Disc Area	A_t = π/4*(1.47*D)^2	6.46
Overall Area	**A_r = A_c + A_t**	**36.46**

6.3.4 Heat Load

Table 29 : Heat Load

Heat Load		
Parameter	**Formula**	**Value (KJ)**
Heat Load	Q=mcpΔT	9.6*10^6

6.3.5 Overall Data

Table 30 : Overall Data

Overall Data	
Parameters	**Values**
Volume	21.2m^2
Length	3.8m
Diameter	2.53m
Area	36.46m^2
Batch time	7/8 hr
Heat Load	9.6*10^6 KJ

CHAPTER 7

SIMULATION AND INSTRUMENTATION

7.1 Simulation

Aspen HYSYS is a powerful process simulation software commonly used in the chemical engineering industry to model and optimize various processes. To perform a simulation on Aspen HYSYS, you generally follow these steps:

1. Define the Process: Start by defining the components, streams, and equipment in your process.
2. Specify Thermodynamic Models: Aspen HYSYS requires you to select appropriate thermodynamic models for your process.
3. Configure Equipment: Set up the equipment in your process by specifying their properties, operating conditions, and connections to streams.
4. Define Stream Properties: Assign the appropriate properties to each stream in your process, such as temperature, pressure, flow rate, composition, and enthalpy.
5. Run the Simulation: Once you have set up your process, you can run the simulation. Aspen HYSYS will use the specified models, equipment configurations, and stream properties to calculate the behavior of the process.
6. Analyze Results: After the simulation is complete, you can analyze the results to understand the behavior of your process.
7. Optimize and Modify: If needed, you can modify your process parameters or equipment configurations to optimize the performance of your system.

7.1.1 Overall Process Flowsheet

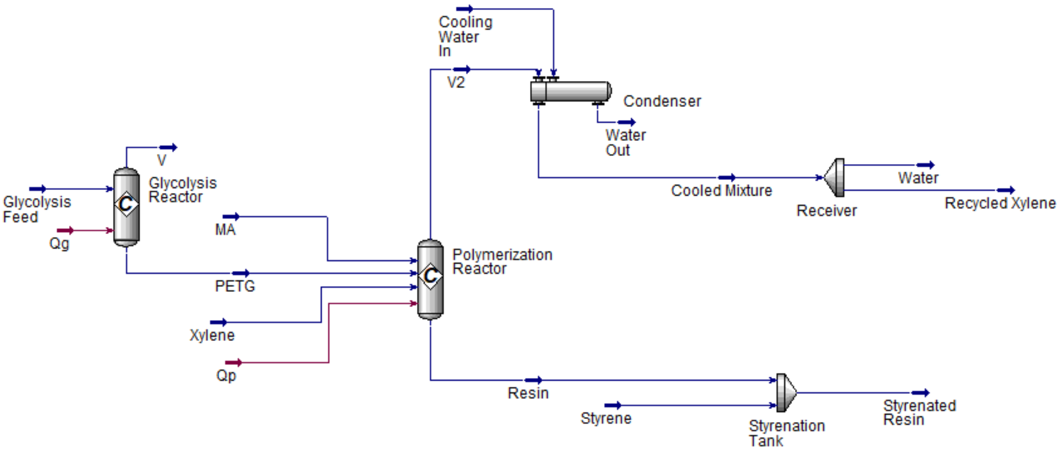
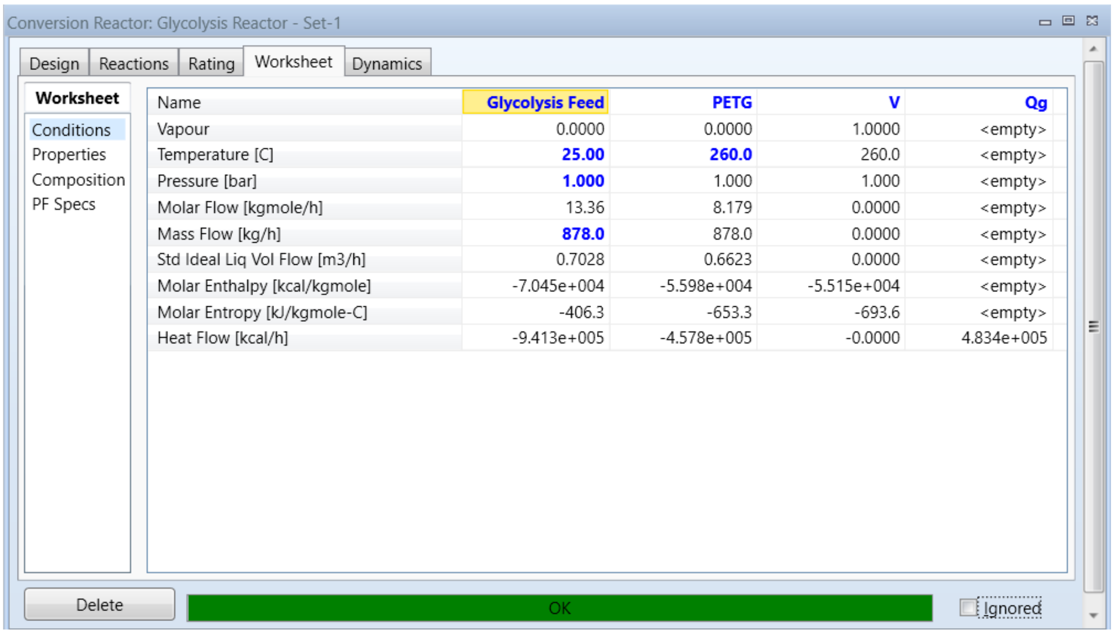


Figure 6 : Overall Process Simulation on Aspen HYSYS

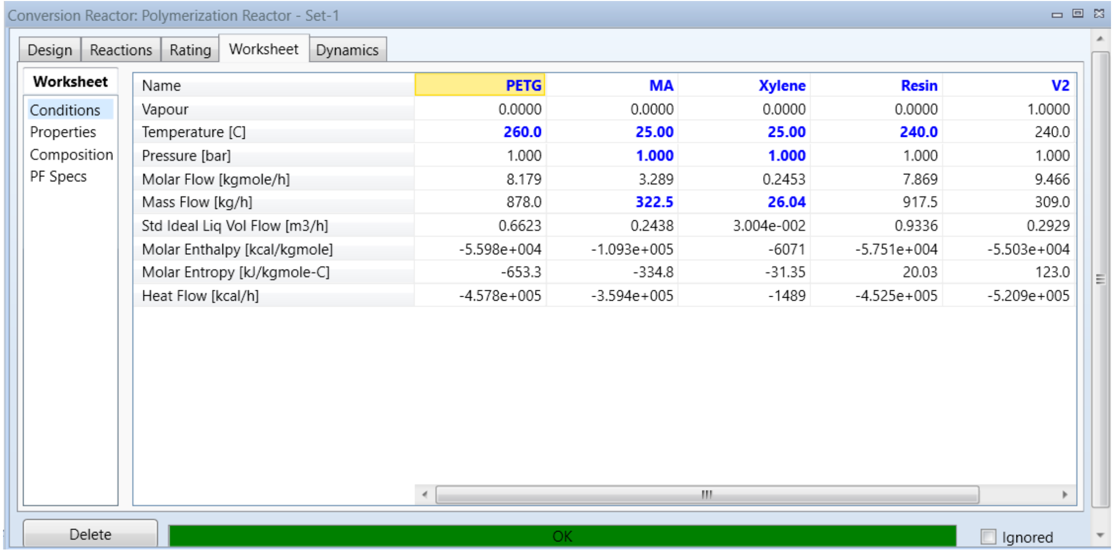
7.1.1.1 Glycolysis



Name	Glycolysis Feed	PETG	V	Qg
Vapour	0.0000	0.0000	1.0000	<empty>
Temperature [C]	25.00	260.0	260.0	<empty>
Pressure [bar]	1.000	1.000	1.000	<empty>
Molar Flow [kgmole/h]	13.36	8.179	0.0000	<empty>
Mass Flow [kg/h]	878.0	878.0	0.0000	<empty>
Std Ideal Liq Vol Flow [m3/h]	0.7028	0.6623	0.0000	<empty>
Molar Enthalpy [kcal/kgmole]	-7.045e+004	-5.598e+004	-5.515e+004	<empty>
Molar Entropy [kJ/kgmole-C]	-406.3	-653.3	-693.6	<empty>
Heat Flow [kcal/h]	-9.413e+005	-4.578e+005	-0.0000	4.834e+005

Figure 7 : Glycolysis Reactor Worksheet

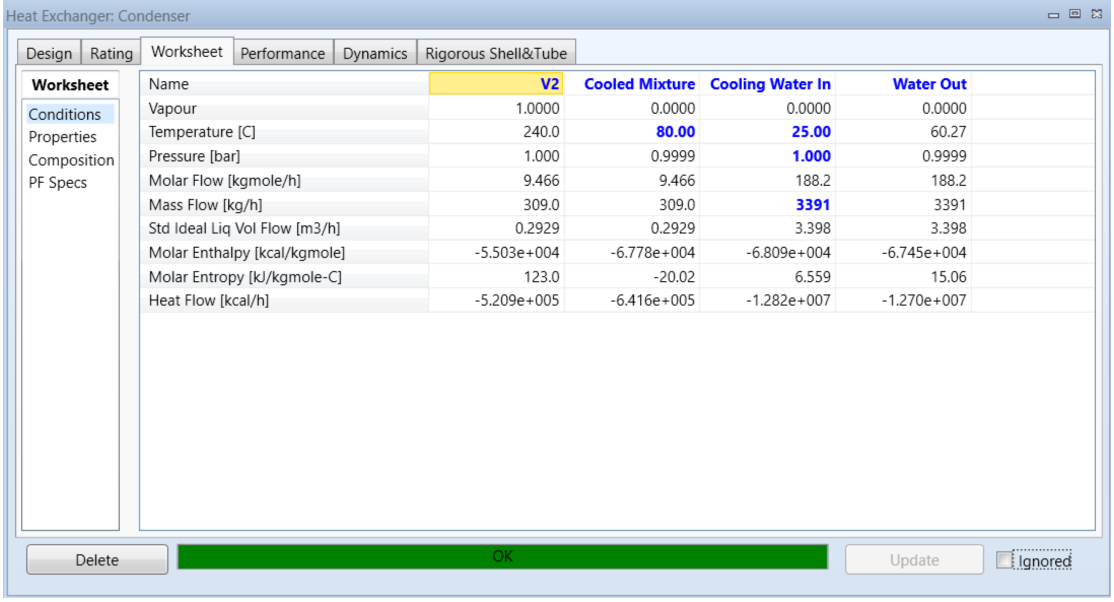
7.1.1.2 Polymerization



Name	PETG	MA	Xylene	Resin	V2
Vapour	0.0000	0.0000	0.0000	0.0000	1.0000
Temperature [C]	**260.0**	**25.00**	**25.00**	**240.0**	240.0
Pressure [bar]	1.000	**1.000**	**1.000**	1.000	1.000
Molar Flow [kgmole/h]	8.179	3.289	0.2453	7.869	9.466
Mass Flow [kg/h]	878.0	**322.5**	**26.04**	917.5	309.0
Std Ideal Liq Vol Flow [m3/h]	0.6623	0.2438	3.004e-002	0.9336	0.2929
Molar Enthalpy [kcal/kgmole]	-5.598e+004	-1.093e+005	-6071	-5.751e+004	-5.503e+004
Molar Entropy [kJ/kgmole-C]	-653.3	-334.8	-31.35	20.03	123.0
Heat Flow [kcal/h]	-4.578e+005	-3.594e+005	-1489	-4.525e+005	-5.209e+005

Figure 8 : Polymerization Reactor Worksheet

7.1.1.3 Condensation



Name	V2	Cooled Mixture	Cooling Water In	Water Out
Vapour	1.0000	0.0000	0.0000	0.0000
Temperature [C]	240.0	**80.00**	**25.00**	60.27
Pressure [bar]	1.000	0.9999	**1.000**	0.9999
Molar Flow [kgmole/h]	9.466	9.466	188.2	188.2
Mass Flow [kg/h]	309.0	309.0	**3391**	3391
Std Ideal Liq Vol Flow [m3/h]	0.2929	0.2929	3.398	3.398
Molar Enthalpy [kcal/kgmole]	-5.503e+004	-6.778e+004	-6.809e+004	-6.745e+004
Molar Entropy [kJ/kgmole-C]	123.0	-20.02	6.559	15.06
Heat Flow [kcal/h]	-5.209e+005	-6.416e+005	-1.282e+007	-1.270e+007

Figure 9 : Condenser Worksheet

7.2 Instrumentation

In process control, there are three main types of variables that are important to consider: controlled variables, manipulated variables, and disturbance variables. These variables play different roles in the control and operation of a process. Here's an explanation of each:

- **Controlled Variables**

Also known as process variables or controlled parameters, these are the variables that you want to maintain or control at a specific setpoint or target value. Controlled variables represent the key properties or conditions of the process that need to be regulated to ensure optimal performance. Examples of controlled variables include temperature, pressure, level, flow rate, pH, concentration, etc. The control system continuously measures the controlled variables and adjusts the manipulated variables to keep them at the desired setpoint.

- **Manipulated Variables**

These are the variables that the control system can adjust or manipulate to influence the values of the controlled variables. Manipulated variables are typically controlled by actuators or control devices, such as control valves, pumps, heating elements, etc. The control system calculates the appropriate changes to the manipulated variables based on the measured values of the controlled variables and the desired setpoint. By adjusting the manipulated variables, the control system aims to bring the controlled variables to their target values. Examples of manipulated variables include the opening of a control valve to adjust flow rate, the speed of a pump to control pressure, the position of a damper to regulate airflow, etc.

- **Disturbance Variables**

Disturbance variables are external factors or influences that can impact the behavior of the process and cause deviations in the controlled variables. These variables are usually beyond the control of the process operator. Disturbances can be changes in feed composition, variations in ambient temperature, fluctuations in utility supply, equipment malfunctions, etc. The control system needs to account for these disturbances and adjust the manipulated variables accordingly to minimize their impact on the controlled variables. Robust control strategies and feedback control algorithms are often employed to compensate for disturbances and maintain stability and performance.

In a feedback control system, the control loop continuously measures the controlled variables, compares them to the setpoint, calculates the necessary changes to the manipulated variables, and takes action to bring the process back to the desired conditions. This ongoing control action helps maintain the process within the desired operating range despite disturbances and uncertainties.

7.2.1 Temperature Control Loop

In the feedback control system, a temperature measurement, T-OUT is measured on temperature transmitter TT, is obtained, and fed into a feedback temperature controller (TC) based on the PID (Proportional - Integral - Derivative) algorithm. The TC compares the measured temperature with the desired temperature set-point and computes the necessary control action. This control action determines whether the control valve should be opened more or less.

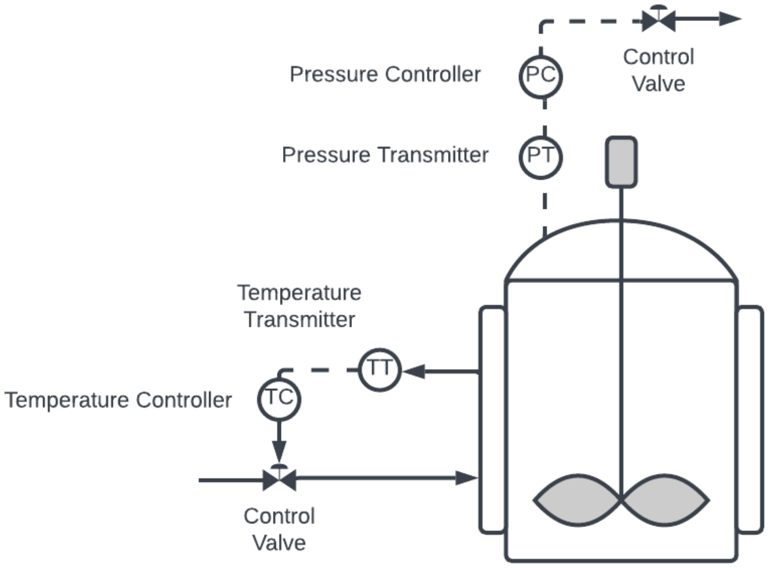


Figure 10 : Control Loops

7.2.2 Pressure Control Loop

A pressure feedback control loop is a control system that regulates and maintains a desired pressure setpoint in a process. In this control loop, the pressure is measured using a pressure transducer (PT) and the resulting signal is sent to a pressure controller. The pressure controller then compares the measured pressure with the desired setpoint and generates a control signal. This control signal is used to adjust a control element, typically a relief valve, to open or close in order to control the pressure within the desired range in the reactor.

CHAPTER 8

COST ESTIMATION AND ECONOMIC ANALYSIS

8.1 Purchase Cost of Equipment (PCE)

8.1.1 Specifications and Materials

Table 31 : Equipment Specifications

Equipment	Specification	Material of Construction
PET Storage Tank	Volume = 500m^3, Cone roof	Carbon Steel
DEG Storage Tank	Volume = 500m^3, Cone roof	Carbon Steel
MA Storage Tank	Volume = 500m^3, Cone roof	Carbon Steel
Xylene Storage Tank	Volume = 500m^3, Cone roof	Carbon Steel
Styrene Storage Tank	Volume = 500m^3, Cone roof	Stainless Steel
st-PETG-g-MA Storage Tank	Volume = 500m^3, Cone roof	Carbon Steel
Glycolysis Reactor	Volume: 15 m3	Carbon Steel
Polymerization Reactor	Volume: 21 m3	Carbon Steel
Styrenation Tank	Volume: 25 m3	Carbon Steel
Condenser	Area: 41 m2	SS-SS
Cooler	Area: 48 m2	SS-SS
Furnace	Heat Capacity = 365 Kw, Box Type	Carbon Steel

8.1.2 Cost

Table 32 : Equipment Costs

Equipment	Equipment Cost
PET Storage Tank	$ 70,171.59
DEG Storage Tank	$ 70,171.59
MA Storage Tank	$ 70,171.59
Xylene Storage Tank	$ 70,171.59
Styrene Storage Tank	$ 95,857.22
st-PETG-g-MA Storage Tank	$ 70,171.59
Glycolysis Reactor	$ 200,619.00
Polymerization Reactor	$ 235,547.00
Styrenation Tank	$ 261,082.00

Condenser	$	147,000.00
Cooler	$	202,800.00
Furnace	$	110,000.00
PCE	**$**	**1,603,763.19**

8.2 Plant Purchase Cost (PPC)

Using the factors for solid-fluid operations:

Table 33 : Plant Purchase Cost

f1 (Equipment erection)	0.45	
f2 (Piping)	0.45	
f3 (Instrumentation)	0.15	
f4 (Electrical)	0.1	
f5 (Buildings, process)	0.1	
*f6 (Utilities)	0.45	
*f7 (Storages)	0.2	
*f8 (Site development)	0.05	
*f9 (Ancillary buildings)	0.2	
f10 (Design and Engg.)	0.25	
f11 (Contractor's fee)	0.05	
f12 (Contingengency)	0.1	
PPC	**$**	**5,051,854.04**

8.3 Required Investments

Table 34 : Capital Investments

FCC	**$**	**7,072,595.66**
Working Capital	**$**	**1,060,889.35**
Total Investment Required	**$**	**8,133,485.01**

8.4 Operating Costs

Operating Time of Plant (d/y)	347

8.4.1 Fixed Operating Costs

Table 35 : Fixed Operating Costs

Maintenance (3% of FC)	$	212,177.87
Operating Labour	$	30,000.00
Plant Overheads (40% of OL)	$	12,000.00
Labortary (20% of OL)	$	6,000.00
Capital Charges (2% of FC)	$	141,451.91
Insurance (1% of FC)	$	70,725.96
Local Taxes (1% of FC)	$	70,725.96
Total	**$**	**543,081.70**

8.4.2 Variable Operating Costs

PET Scrap

Table 36 : Variable Operating Costs

Feed Rate		15.073	tonnes/day
Feed Price	$	500	/tonne
Total Feed Price/day	$	7,537	/day
Feed Price/Yr	$	2,615,166	/yr

DEG

Feed Rate		6	tonnes/day
Feed Price	$	800	/tonne
Total Feed Price/day	$	4,800	/day
Feed Price/Yr	$	1,665,600	/yr

MA

Feed Rate		7.7	tonnes/day
Feed Price	$	800	/tonne
Total Feed Price/day	$	6,160	/day
Feed Price/Yr	$	2,137,520	/yr

Xylene

Feed Rate	0.325	tonnes/day
Feed Price	$ 1,100	/tonne
Total Feed Price/day	$ 358	/day
Feed Price/Yr	$ 124,053	/yr

Styrene

Feed Rate	14.35	tonnes/day
Feed Price	$ 1,250	/tonne
Total Feed Price/day	$ 17,938	/day
Feed Price/Yr	$ 6,224,313	/yr

Miscellaneous Operating Material (5% of Maintenance Cost)	$ 10,608.89	
Cooling Water Required	170	tonnes/day
Cooling water price	$ 0.50	/tonne
Cooling water price	$ 85.00	/day
Cooling Water Price/ year	$ 29,495.00	/yr
Electric Power Required	34560	MJ/day
Electric Power Required	11992320	MJ/yr
Cost of electricity	$ 179,884.80	/yr
TVC		**$ 12,986,639.19**
Direct Production Cost (FOC+TVC)		**$ 13,529,720.89**

8.5 Revenue Generated

Table 37 : Revenue

Product	**Production (tonnes/yr)**	**Price ($/tonne)**	**Revenue Generated**
st-PETG-g-MA	15000	$ 1,200.00	$ 18,000,000.00
	Total Revenue /yr	**$ 18,000,000.00**	
	Total Profit/ yr	**$ 4,470,279.11**	
	Total Profit/ day	**$ 12,882.65**	

8.6 Payback Period

Table 38 : Net Present Worth Over 10 Years

No. of Years (k)	Cash Inflow	Cash Outflow	Net Cash Flow	Net Present Worth (10%, k)
0	-	$ 8,133,485.01	$ (8,133,485.01)	$ (8,133,485.01)
1	$ 18,000,000.00	$ 13,529,720.89	$ 4,470,279.11	$ 4,063,890.10
2	$ 18,000,000.00	$ 13,529,720.89	$ 4,470,279.11	$ 3,694,445.55
3	$ 18,000,000.00	$ 13,529,720.89	$ 4,470,279.11	$ 3,358,586.86
4	$ 18,000,000.00	$ 13,529,720.89	$ 4,470,279.11	$ 3,053,260.78
5	$ 18,000,000.00	$ 13,529,720.89	$ 4,470,279.11	$ 2,775,691.62
6	$ 18,000,000.00	$ 13,529,720.89	$ 4,470,279.11	$ 2,523,356.02
7	$ 18,000,000.00	$ 13,529,720.89	$ 4,470,279.11	$ 2,293,960.02
8	$ 18,000,000.00	$ 13,529,720.89	$ 4,470,279.11	$ 2,085,418.20
9	$ 18,000,000.00	$ 13,529,720.89	$ 4,470,279.11	$ 1,895,834.72
10	$ 18,000,000.00	$ 13,529,720.89	$ 4,470,279.11	$ 1,723,486.11

Table 39 : Payback Period

No. of Years (k)	Cumulative Present Worth
0	$ (8,133,485.01)
1	$ (4,069,594.91)
2	$ (375,149.37)
3	**$ 2,983,437.49**
4	$ 6,036,698.28
Payback Period	**3 Years**

CHAPTER 9

HAZOP ANALYSIS

9.1 HAZOP on Polymerization Reactor

Polymerization of PETG with MA is an exothermic reaction, so a lot of heat is generated and it's necessary to have all the parameters checked and they must be maintained at a defined level.

Table 40 : HAZOP on Polymerization Reactor

Project name: Design of Unsaturated Polyester Resin Plant						Date: 25/5/23
Process: Exothermic Polymerization reaction of PETG with MA to make PETG-g-MA						
Section: Polymerization Reactor						
Item	**Study node**	**Process parameters**	**Deviations (Guide words)**	**Possible Causes**	**Possible Consequences**	**Action Required**
1A	**Polymerization Reactor**	**Agitation**	No	Failure of Agitation Motor	Uneven Distribution of Monomer	Cut-off Monomer Feed
				Electric Supply Cut-off	Localized Polymerization Reactions	Standard Operating Procedures
				Operator Negligence	Runaway Reaction	Implementation of Alarm System
					Contours/ Hot-spots Formation	Fail-Close Monomer Feed Valve
					Monomer Concentration Build-up	
1B			More/Higher	Stirrer Motor Controller Fails	None	None

				Stirrer Motor Controller Calibration Error		Calibration of motor Controller (Not Significant)
1C			Less/Lower	Stirrer Motor Controller Fails	Poor Distribution of Monomer	Place controller on critical instrumentation list
				Stirrer Motor Controller Calibration Error	Monomer Concentration Build-up	Calibration of motor Controller (Significant)
				Motor Work Life Exceeded	Runaway Reaction	Manipulate the flow of Monomers using Control valve
1D			Part of	No/Less Agitation	HDPE Quality decreases	Maintain Agitation at design value
					Monomer Chain Length decreases	
1E			Reverse	See 1A		
1F			Sooner	Neglecting Operating procedure order	Splashing of Monomer	Follow Operating Procedures
						Training Operators
1G			Later	See 1A	See 1A	See 1A.2
2A	**Cooling Jacket**	**Flow**	No	No water supply	Runaway Reaction (No-Cooling)	Backup Water Storage Tank & Low levels alarm Indicator
				Water pump breakdown		Backup Water Pump with bypass &

						automatic switch
				Blockage in the cooling Coil		Scheduled Servicing of Cooling Coils
				Malfunctioning of the Control Valve		Install high temperature alarm systems
						Install Fail-open type valve
2B			High	Control valve fails open	Reactor Cools	Instruct Operators
					Concentration of Monomer builds-up	Update Procedures
					Possible Runaway Reaction on heating	Reduce/cut-off the monomer feed rate
2C			Low	Blockage in the cooling Coil	Less Cooling	See 2A.3
				Controller failure or Calibration error	Heat build-up	Place controller on critical instrumentation list
				Low water head available/diminishing	Possible Runaway Reaction	See 2A.1
2D			As well as	Contamination of Water Supply	Possible Scaling or fouling of coils	See 2A.3
2E			Part of	Same as 2D		
2F			Reverse	See 2A	Runaway Reaction (No-Cooling)	Install high temperature &low flow alarm systems
				Backflow of water due to		Installation of Check

				high back pressure		valves for unidirectional flow
2G			Sooner	Neglecting Operating procedure order	See 2B	Instruct Operators & Update Procedures
2H			Later	Neglecting Operating procedure order	Runaway Reaction (No-Cooling)	Instruct Operators & Update Procedures
3A	**Polymerization Reactor**	**Temperature**	Low	Control valve fails open	Reactor Cooled	Monomer Cut-off/ flow rate Control valve
				Neglecting Operating procedure order	Concentration of Monomer built-up	Regulate the cooling water flow rate
				Flow of water sooner than required	Possible Runaway Reaction on heating	Instruct Operators & Update Procedures
3B			High	Cooling Water failure	Polymerization Reaction Runaway	Install Fail-open type valve for cooling coils
				Concentration of Monomer built-up		Ensure enough water supply in the backup
				Not enough cooling water flow rate		Monomer Cut-off system with alarm system
				Failure of Monomer flow rate control		Design CSTR with Cooling Jacket along with coils

9.2 HAZOP on Shell and Tube Condenser

Shell and tube Condenser is a heat exchanger used to condense the vapor mixture od water-xylene that exits the polymerization reactor.

Table 41 : HAZOP on Condenser

Project name: Design of Unsaturated Polyester Resin Plant						Date: 25/5/23
Process: Exothermic Polymerization reaction of PETG with MA to make PETG-g-MA						
Section: Shell and Tube Condenser						
Item	**Study node**	**Process parameters**	**Deviations (Guide words)**	**Possible Causes**	**Possible Consequences**	**Action Required**
1A	**Water-Xylene Vapor Mixture**	**Flow**	No	Breakage/Crack in heat exchanger tubes	Vapors mixed with steam - possible chances of fire	Installation of volatile content detectors with alarm
				Blockage in heat exchanger tubes	No water produced - Upsets Downstream Process	Scheduled Maintenance of Tubes (Critical)
				Failure of Feed to Reactor		Install low flow meter detectors with alarm indication
				Malfunctioning of Control Valve at inlet stream		Manual Control Valve with bypass stream
1B			Higher	Control Valve Fail-Open	High Flow Vapor Mixture - Upsets Downstream Process	Add lock procedure for valve on malfunctioning
				Pressure of vapor mixture increases		Install high flow alarm

1C			Less/Lower	Partial Failure of Reactor Feed	Low Flow Vapor mixture - Upsets Downstream Process	Low Flow Alarm indicator
				Valve at inlet Partially Opened		Add lock procedure for valve on malfunctioning
				Leakage in Heat exchanger tubes	Vapor mixture mixed with steam - possible chances of fire	Installation of volatile content detectors with alarm
1D			As well as	Vapor mixture leaks into steam	Possible chance of Fire & Contamination	Maintenance of tubes & volatile detectors
1E			Reverse	High Downstream Pressure	Backflow of Vapor mixture leading to high pressures in tubes	Install Check Valves for Unidirectional Flow
					Bursting of Heat Exchanger Tubes	Install High pressure alarm indicator
1F			Sooner	Inlet Valve Opened too early	Possible Downstream Upset	Follow Operating Procedures
						Check Criticality of Downstream Process
1H			Later	Inlet Valve Opened too late	Possible Downstream Upset or Buildup of pressure	Follow Operating Procedures & See 1F.2
2A		**Temperature**	Low	Low temperature inlet of vapor mixture	Composition changes (more xylene)	Increase duty of reactor
2B			High	Vapor mixture pressure	Decomposition in Cracked gas	Pressure regulating system with

				increases	Downstream process upset - Quenching stages duty increased	alarm
				Valve malfunctioning at inlet of water supply inlet		Add lock procedure for valve on malfunctioning

CONCLUSION

Results

- PETG-g-MA yield of 96.4% based on PET is achieved according to our design and calculations.
- Production of st-PETG-g-MA per annum based on our design and calculations is approximately 15,000 Tonnes.
- Considering the economic analysis, the payout period comes out to be 3 years therefore the project is commercially viable on an industrial scale at the current production rate.
- By utilizing recycled PET as a raw material for unsaturated polyester resins (UPRs), the project actively contributes to reducing plastic waste.
- Incorporating recycled PET into UPRs promotes a circular economy model by giving new life to post-consumer plastic waste. The project demonstrates a sustainable and resource-efficient approach that minimizes reliance on virgin materials and maximizes material reuse.
- The use of recycled PET in UPRs reduces the overall environmental footprint associated with plastic production. It decreases energy consumption, greenhouse gas emissions, and waste generation compared to the production of UPRs from virgin materials.
- The project highlights the value and potential of transforming plastic waste into high-quality UPRs. This waste valorization approach helps divert plastic from landfills or incineration and transforms it into valuable products, contributing to a more sustainable waste management system.
- The growing global demand for sustainable materials presents significant export opportunities. The project's focus on UPRs made from recycled PET positions it well to meet this demand and target export markets seeking environmentally friendly solutions.
- By offering UPRs derived from recycled PET, the project differentiates itself in the market, providing a competitive edge by aligning with

environmentally conscious consumers and businesses. This unique selling point can lead to increased market share and business growth.

- Utilizing recycled PET as a raw material reduces the need for virgin petrochemical resources. It conserves valuable natural resources and contributes to the efficient utilization of existing materials, supporting a more sustainable and responsible approach to resource management.
- The project's focus on environmental sustainability and circular economy principles can attract collaboration and support from stakeholders, including government agencies, environmental organizations, and investors. This engagement can enhance project visibility, funding opportunities, and partnerships.
- Implementing a project that prioritizes environmental impact and circular economy practices enhances the project's image and brand reputation. It demonstrates a commitment to sustainability, attracting customers, investors, and partners who value responsible and eco-friendly solutions.
- The project's success in developing and exporting UPRs made from recycled PET can contribute to economic growth by creating new market opportunities and generating employment in recycling, manufacturing, and related industries.

Scope for Future Advancements

Future advancements in the utilization of unsaturated polyester resins (UPRs) offer exciting scopes across various domains. These advancements include the development of advanced UPR formulations with improved mechanical strength, chemical resistance, thermal stability, and UV resistance, as well as the exploration of sustainable raw materials for UPR production, such as bio-based or renewable sources. Further advancements can be expected in recycling and circular economy practices, including improved recycling processes for post-consumer UPR products and the development of closed-loop systems that maximize the reuse of UPRs within specific industries. Integration of nanotechnology into UPR formulations can result in the development of nanostructured UPRs with enhanced properties, such as improved mechanical strength, electrical conductivity, thermal conductivity, and barrier properties, opening up new applications in fields like electronics, energy storage, and coatings. Advancements in additive manufacturing or 3D printing technology can enable the direct fabrication of complex UPR-based structures with tailored properties, leading to advancements in rapid prototyping, customization, and the production of intricate geometries. The future may also witness the development of multifunctional UPR composites with self-healing capabilities, sensing abilities, or improved fire resistance, expanding their applications in infrastructure, transportation, and electronics. Integration of advanced digital design tools and simulation techniques can optimize UPR-based product development processes, enabling efficient design iterations and reducing time-to-market. UPRs can find applications in sustainable packaging solutions, and future advancements may involve the development of UPR-based materials with improved barrier properties, biodegradability, and recyclability, addressing the challenges associated with single-use plastics. Tailoring UPR formulations and processing techniques to specific industry requirements will lead to industry-specific applications in automotive, construction, marine, and renewable energy sectors, enabling improved performance and increased adoption. Integration of smart technologies, such as IoT sensors or embedded electronics, into UPR-based products can enable functionalities like structural health monitoring and real-time data collection, advancing the development of smart composites and intelligent structures. Through ongoing research, innovation, and collaboration, UPRs have the potential to evolve, expand their applications, and contribute to sustainable and high-performance solutions in a wide range of industries.

REFERENCES

[1] [Coulson _ Richardson’s Chemical Engineering] R K Sinnott - Chemical Engineering Design, Fourth Edition Chemical Engineering Volume 6 (Vol.6 2005, Butterworth-Heinemann)

[2] D. W. Green and R. H. Perry, Perry's Chemical Engineers' Handbook, 2007.

[3] H. Vaness and H. Smith, Thermodynmics for Chemical Engineers, McGraw-Hill Press, 2001.

[4] D.Q. Kern, Process Heat Transfer, Tata Mn Graw Hill, 1951.

[5] Kinetics of poly(ethylene terephthalate) fiber glycolysis in ethylene glycol (Feifei Chen)

[6] Process Simulation of Bis (2- hydroxyethyl) terephthalate and Its Recovery Using Two–stage Evaporation Systems (Raheem)

[7] Chemical Kinetics, Simulation, and Thermodynamics of Glycolytic Depolymerization of Poly(ethylene terephthalate) Waste with Catalyst Optimization for Recycling of Value Added Monomeric Products (A. S. Goje)

[8] Glycolysis of Poly(Ethylene Terephthalate) Using Biomass-Waste Derived Recyclable Heterogeneous Catalyst (Samson Lalhmangaihzuala)