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DESIGN AND STUDY OF MANUFACTURING OF POLYESTER PLANT USING PTA AND MEG

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Abstract - *Polyester is a category of polymers which contain the ester functional group in their main chain. Although there are many polyesters, the term "polyester" as a specific material most commonly refers to polyethylene terephthalate (PET). A chemical reaction bonding monomers together to make a polymer is called polymerization. Polymers are substances whose molecules have high molar masses and are composed of a large number of repeating units. Pure Terephthalic Acid (PTA) and Mono Ethylene Glycol (MEG) are mixed to produce oligomer and water in the Esterification section. The oligomer is then pumped to polymerisation section after addition of chemicals namely catalyst, TiO2, DEG & glycol. The oligomer is converted to polymer through polymerisation reaction and is sent to spinning and the spin product is sent for drawing after which it is baled and cut. After cutting, the product is sent to warehouse. We started with the study of polyester and studies its manufacturing process available. We also formed out its application and uses and its supply and demand of polyester. Also advantages and disadvantages here with we come across the present demand in the market of polyester and the current supply rate of polyester. The proposed work in this project is the plant study and material balance of polyester plant installed in Reliance Industries Pvt. Ltd. in Patalganga, where we study the manufacturing of polyester by using its raw materials pure terephthalic acid and mono ethylene glycol. Also the production of polymer is a two step reaction process that is esterification and polycondensation. The production of polyester polymer is a two step reaction process i.e. Esterification and Polymerisation. Esterification is the formation of monomer and polycondensation is the formation of oligomer and polymer chain building. The esterification reaction is technically an acid –base reaction that forms salt and water. Terephthalic Acid (TPA) is the acid and Ethylene Glycol (EG) is the base and the monomer DiHydroxyEthyl Terephthalate, DHET is the salt with water also being a product of the reaction. Polycondensation is the actual "chain building" step in the making of polyester polymer. The reaction in order to proceed forward, requires the addition of a catalyst, typically antimony, as well as heat and vacuum. The chemical linkage between two molecules forming one large molecule.Material balance importance first step when designing a new process or analysing. They are almost always pre requisite to all other calculation in the solution of process engineering a material balance is an accounting for material. Thus material balance are often compared to the balancing of current account. They are used in industry to calculate mass flow rates of different stream entering or leaving chemical or physical process.*

Keywords: *Polyester, Pure Terephthalic Acid, Mono Ethylene Glycol, Esterification, Polycondensation*

1. INTRODUCTION

Polyester is a category of polymers which contain the ester functional group in their main chain. Although there are many polyesters, the term "polyester" as a specific material most commonly refers to polyethylene terephthalate (PET). Polyesters include naturally occurring chemicals, such as in the cutin of plant cuticles, as well as synthetics through step-growth polymerization such as polycarbonate and polybutyrate. Natural polyesters and a few synthetic ones are biodegradable, but most synthetic polyesters are not.Depending on the chemical structure, polyester can be a thermoplastic or thermoset; however, the most common polyesters are thermoplastics.Fabrics woven or knitted from polyester thread or yarn are used extensively in apparel and home furnishings, from shirts and pants to jackets and hats, bed sheets, blankets, upholstered furniture and computer mouse mats. Industrial polyester fibers, yarns and ropes are used in tyre reinforcements, fabrics for conveyor belts, safety belts, coated fabrics and plastic reinforcements with high-energy absorption. Polyester fiber is used as cushioning and insulating material in pillows, comforters and upholstery padding. Polyesters are also used to make bottles, films, tarpaulin, canoes, liquid crystal displays, holograms, filters, dielectric film for capacitors, film insulation for wire and insulating tapes. Polyesters are widely used as a finish on high-quality wood products such as guitars, pianos and vehicle/yacht interiors. Thixotropic properties of spray-applicable polyesters make them ideal for use on open-grain timbers, as they can quickly fill wood grain, with a high-build film thickness per coat. Cured polyesters can be sanded and polished to a high-gloss, durable finish.

There are both naturally occurring and synthetic polymers. Among naturally occurring polymers are proteins, starches, cellulose, and latex. Synthetic polymers are produced commercially on a very large scale and have a wide range of properties and uses. The materials commonly called plastics are all synthetic polymers. Polymers are formed by chemical reactions in which a large number of molecules called monomers are joined sequentially, forming a chain. In many polymers, only one monomer is used. In others, two or three different monomers may be combined. Polymers are classified by the characteristics of the reactions by which they are formed. If all atoms in the monomers are incorporated into the polymer, the polymer is called an addition polymer.

ABABABABAB………. Chain

-A- + -B- → -AB-

-AB- + -AB- → -ABAB-

ABAB- + ABAB- → ABAB-

ABAB- + ABAB- → ABAB ABAB

The ends on - A- form a strong chemical bond to the different ends on –B-

Van der waal forces hold the long molecules to each other in a uniform crystalline structure. All the long molecules hold together to make a very strong material. Synthetic fibre made from polymer is ofen handled like cotton .cut synthetic fibre, called staple is combined and twisted to make long fibres that are lined up with each other . even though the filaments are very thin the van der waal forces hold them together.

2. Material and Methods:

Materials: RAW MATERIALS USED:

Polyester is a synthetic polymer made of purified terephthalic acid (PTA) or its dimethyl ester dimethyl terephthalate (DMT) and monoethylene glycol (MEG). With 18% market share of all plastic materials produced, it ranges third after polyethylene (33.5%) and polypropylene (19.5%).

The main raw materials are described as follows:

- Purified terephthalic acid – PTA

Synonym: 1,4benzenedicarboxylic acid,

formula; $C_6H_4(COOH)_2$, mol weight: 166.13

- Dimethylterephthalate – DMT

Synonym: 1,4benzenedicarboxylic acid dimethyl ester

formula $C_6H_4(COOCH_3)_2$, mol weight: 194.19

- Mono Ethylene Glycol – MEG

Synonym: 1,2ethanediol

formula: $C_2H_6O_2$, mol weight: 62,07

To make a polymer of high molecular weight a catalyst is needed. The most common catalyst is antimony trioxide (or antimony tri acetate):

Antimony trioxide – ATO

Molecular weight: 291.51 Sum formula: Sb_2O_3

In 2008, about 10,000 tonnes Sb_2O_3 were used to produce around 49 million tonnes polyethylene terephthalate.

Synthesis

Synthesis of polyesters is generally achieved by a polycondensation reaction. See "condensation reactions in polymer chemistry". The general equation for the reaction of a diol with a diacidis :

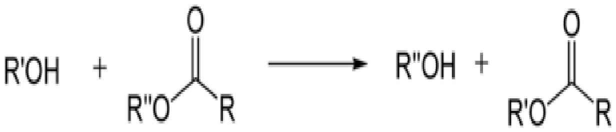
$(n+1)\ R(OH)_2 + n\ R'(COOH)_2 \rightarrow HO\ _nROH + 2n\ H_2O$

Azeotrope esterification

In this classical method, an alcohol and a carboxylic acid react to form a carboxylic ester. To assemble a polymer, the water formed by the reaction must be continually removed by azeotrope distillation.

Alcoholic transesterification

Transesterification



Acylation (HCl method)

The acid begins as an acid chloride, and thus the polycondensation proceeds with emission of hydrochloric acid (HCl) instead of water. This method can be carried out in solution or as an enamel.

Silyl method

In this variant of the HCl method, the carboxylic acid chloride is converted with the trimethylsilyl ether of the alcohol component and production of trimethylsilyl chloride is obtained

Acetate method (esterification)

Silyl acetate method

Ring-opening polymerization

Aliphatic polyesters can be assembled from lactones under very mild conditions, catalyzedanionically, cationically or metallorganically. A number of catalytic methods for the copolymerization of epoxides with cyclic anhydrides have also recently been shown to provide a wide array of functionalized polyesters, both saturated and unsaturated.

The chemical linkage between the two molecules forming one larger molecules is called an ester poly ester means a polymer with many ester group .That is an ester group joins every linkage of the TPA and EG molecules thus ,the name polyester.

Poly condensation is actual "chain building "step in the making of polyester polymer. The glycol end of reacted monomer and 'oligomers' react and continue build large sized molecules. As each glycol end react with another one of the glycol is formed as vapour .each combination is a monoer. Two units make a dimer .The units make at trimer .Ans so on .The number of units ,n, in a polymer molecule is defined as "DP" meaning degrees of polymerization .

EG-TPA-EG + EG-TPA-EG = TPA-EG-TPA-EG

Monomer Monomer Dimer

Cross-linking

Unsaturated polyesters are thermosetting resins. They are generally copolymers prepared by polymerizing one or more diol with saturated and unsaturated dicarboxylic acids (maleic acid, fumaric acid...) or their anhydrides. The double bond of unsaturated polyesters reacts with a vinyl monomer mainly the styrene, resulting in a 3-D cross-linked structure. This structure acts as a thermoset. The cross-linking is initiated through an exothermic reaction involving an organic peroxide, such as methyl ethyl ketone peroxide or benzoyl peroxide[10].

METHODS OF PRODUCTION OF POLYESTER

Process Description for Manufacturing of Partially Oriented Yarn (POY)

Pure Terephthalic Acid (PTA) and Monoethylene Glycol (MEG) are mixed to produce Oligomer and water in the Esterification section. The oligomer is then pumped to polymerisation section after addition of chemicals namely catalyst, TiO_2, DEG & Glycol. The oligomer is converted into polymer through polymerisation reaction and is sent to spinning for converting it into Partially Oriented Yarn. The water generated in the process is sent to Effluent Treatment Plant.

Process Description for Manufacturing of Polyester Staple Fibre (PSF):

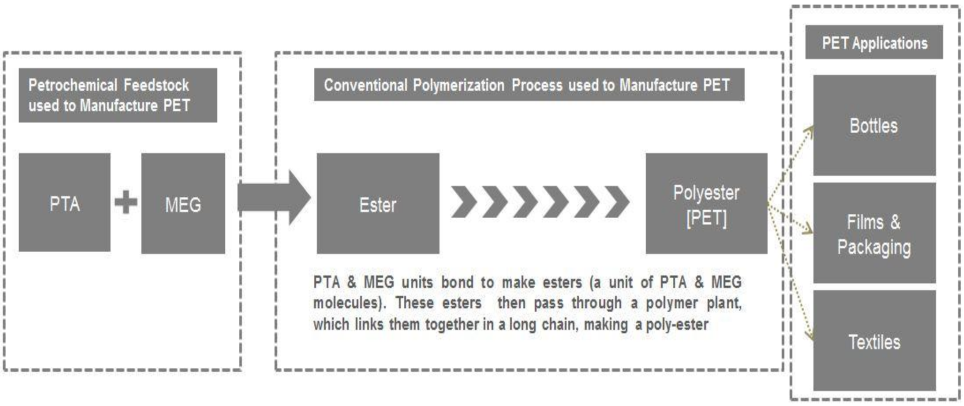
Pure Terephthalic Acid (PTA) and Mono ethylene Glycol (MEG) are mixed to produce Oligomer and water in the Esterification section. The oligomer is then pumped to polymerisation section after addition of chemicals namely catalyst, TiO_2, DEG & Glycol. The oligomer is converted to polymer through polymerisation reaction and is sent to spinning and the spin product is sent for drawing after which it is baled and cut. After cutting, the product is sent to warehouse. The waste water generated in the process is sent to Central Effluent Treatment Plant - II.

Process Description for Manufacturing of Polyester Staple Fibre Fill (PSFF)

Polymer waste (Hard waste and Soft waste) and Monoethylene Glycol (MEG) are mixed to produce Oligomer and water in the Esterification section. The oligomer is then pumped to polymerisation section after addition of chemicals namely catalyst, TiO_2, DEG & Glycol. The oligomer is converted to polymer through polymerisation reaction and sent to spinning and spin product is sent for drawing after which it is baled and cut. After cutting, the product is sent to warehouse. The waste water generated in the process is sent to Central Effluent Treatment Plant - II. In Glycol recovery column, Ethylene Glycols are recovered from top as Product and Glycol Residues are obtained from the bottom as by product.

Process Description for Manufacture of Polyethylene Terephthalate (PET):

Pure Terephthalic Acid (PTA) and Mono Ethylene Glycol (MEG) are mixed to produce oligomer and water in the esterification section. The oligomer is then pumped to polymerisation section after addition of chemicals namely catalyst, TiO_2, DEG & Glycol. The oligomer converted into polymer through polymerisation reaction and is sent to chippers for making polyester chips. The waste water generated in the process is sent to Central Effluent Treatment Plant - II. The polymer chips are post polymerized in the “Solid State Polymerization” section. The chips are packed in polypropylene bags in an automatic chips bagging system[8].



Process description

1. Raw Material Preparation and Feed:
    a. Terephthalic Acid (TPA)

TPA powder is purchased in 1000kg bags and unloaded into a storage silo by means of a pressurized inert gas transfer system. The powder is then metered with a screw conveyor into a slurry mix tank where it is mixed with heated glycol in ratio of 2:1.

b. Ethylene Glycol

The glycol that is mixed with the TPA in slurry mix tank is a combination of virgin and recovered glycol. The glycol is accumulated and fed from an agitated tank through filters and into one of two centrifugal pumps installed in parallel. Ratio of glycol to TPA is controlled by a signal from a densitometer which resetsthe magnetic flow meter. The flowrator also measures and records the glycol flow. The temperature of the glycol being fed to the slurry mix tank is approximately 160^{o}C.

c. TPA Slurry

The mixing of TPA and glycol (slurry) is a continuous process and is controlled automatically by ratio control of the raw material fed streams. From the slurry mix tank the slurry is fed to the slurry hold tank which supplies the metering pumps feeding slurry into the esterifier through injection nozzles.

2. Esterification:

The reaction of the TPA and the glycol mixture is accomplished in the esterifier, which is a combination of a side arm heat exchanger and a vapour separator. The slurry is injected into the bottom of the heat exchanger and natural circulation of the slurry/oligomer mixture up through the heat exchanger heats the slurry from approximately 100^{o}C to 295^{o}C, causing the reaction to take place. H_2O formed in the reaction, excess glycol and small amounts of oligomer is taken off the top of the vapour separator through a heated vapour line into a H_2O separation column where the H_2O and glycol vapors are condensed and separated. The H_2O is fed into an air stripped column which removes acid aldehyde and other by-products before it is fed to a process sewer. The glycol is collected in a hotwell, filtered, cooled and pumped back into the bottom of H_2O separation column. The excess glycol is pumped to the recovered glycol hold tank for use in making slurry.

The product of the esterifier is oligomer which is fed to the reaction vessel with metering pumps.

3. Polymerization:

a. General:

The C.P., which consists of two polymerization vessels, further reacts the oligomer to form polyester polymer of the desired viscosity, luster and color suitable for spinning. The process involves removing excess glycol to link up polymer chains. This is accomplished by subjecting the polymer to progressively lower pressure and higher temperatures in the (Up Flow Pre-Polymeriser) UFPP and the finisher.

b. Oligomer Line, Catalyst, Delustrant and Titration Glycol

Oligomer is pumoped from the esterification through a cooler which reduces the oligomer temperature to about 275 c n preparation for injection titanium (Tio2)

And antimiony trioxide (Sb2O 3). TIo2 is a Delustrabt and is meterd into the oligomer as a 20% slurry to provide 0.3 % tio2 in polymer . Sb2O 3 is metered in at a 5% solution to provide about 300 ppm in polymer .

Titration glycol is added to the oligomer toreact with the carboxyl to less than 7000 to insure proper carboxyl level in the polymer leaving the finisher .

c. UFPP

The UFPP recive s oligomer from the TPA reactor through a Dowtherm heated shell and tubes heat exchange which supplies the heaqt to vaporise glycol evolved in the pre-polymerizer .the heat reduced pressure ,surface area generation and action of catalyst remove approximately 97 %of the excess glycol.

On reaching the top tray of the UFPP ,the pre-polymer and glycol vapour are separated by a bubble cap with the pre-polymer flowing out of the vessel through the 16 th plate process outlet and the vapour exhausted away by the vaccume system .On exiting the UFPP the pre-polymer gravity flows through a level valve equipped loop seal to the finisher .

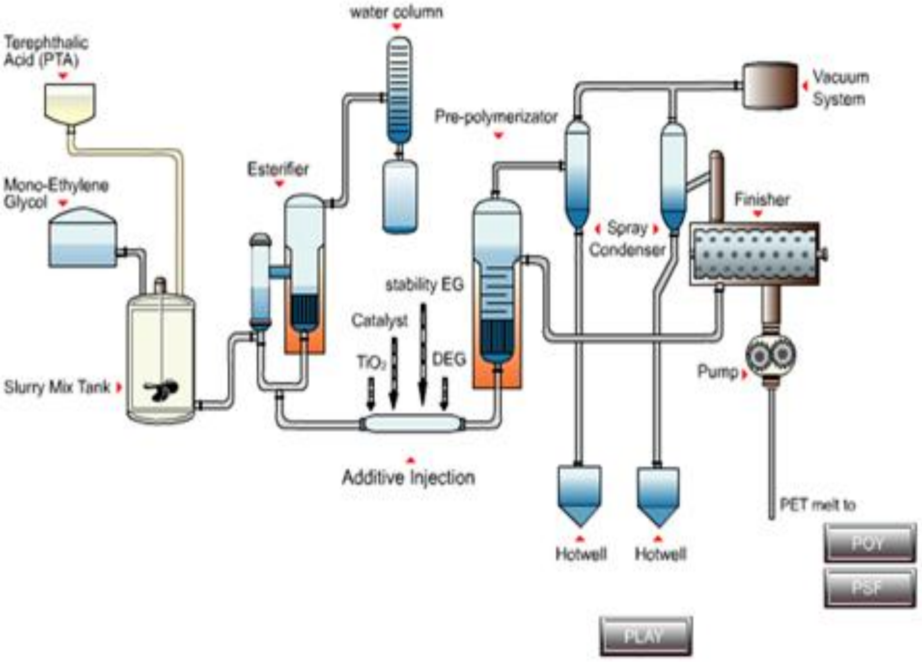
d. Finisher

The finisher is horizontal ,cylindrical vessel with a full length ,screen type agitator to achive maximum surface generation . the vessel is operated at about 290 and 2 mm hg absolute pressure .the remaining excess glycol (2-3%) is removed in the finisher and the polymer viscosity is increased to about 2500 poise suitable for spinning .Glycol removed from the vessel is condensed in a spray type condenser and goes to a separate hotwell and glycol circulation system.

Virgin glycol is added to dilute the finisher off glycol which is high in solids and contain moisture which could effect the recovery jets. Glycol bleed –off from this is hotwell is sent to the UFPP hotwell to maintain the level.

e. Polymer Gear Pump

The finised , high viscosity ,polymer is pumped with a gear pump from the finisher to the spinning machine through a Dowtherm heated transfer line . the gear pumped is cooled with liqupdDowther and the polymer is pumped isothermally at approximately 85kg/cm2 pressure.



BY Product And Side Reactions

The esterification and polycondensation reactions one two theoretical steps of the polymerization process. But of course nothing in the real world is that simple. What actually happens in the CP during the polymerization process is quite complicated. Many events occur besides these two reaction steps. As we already mentioned the esterifier makes oligomer with dimers and trimersetc and not pure monomer. Cyclic trimers are formed .theestefier also make half esters that is not all of the TPA carboxyl ends react to form an ester linkage . there are many by products and side reactions occurring including the formation of DEG , acetaldehyde and many other volatile organic compounds or VOC'S . All the reaction in the CP are reversible. Some of these can cause serious problemsduring polymerization process and must be deal with in the the design of the CP and its operation in order to make the desirable final product in a safe manner.

4. ENERGY BALANCE

Energy Balance for Heat Exchanger

Heat required to heat slurry from $80^{\circ}C$ to $285^{\circ}C$

Heat taken by PTA (Q_1)	2123858.93 kJ/hr
Heat taken by EG (Q_2)	2926313.12 kJ/hr
Heat taken by H_2O (Q_3)	245052.56 kJ/hr
Total Heat Load	11764789.88 kJ/hr

Energy Balance ForVapour Separator

Heat taken for EG vaporization (at $285^{\circ}C$	1523561kJ/hr
Heat taken for H_2O vaporization (at $285^{\circ}C$	0 kJ/hr
Total heat load	1523561.18 kJ/hr

UFPP PREHEATER

Heat required to heat oligomer from 247° C to 288°C

Heat taken by PTA (Q1)	29606.59 kJ/hr
Heat taken by EG (Q2)	79744.85 kJ/hr
Heat taken for PTA dissolution	259784.21 kJ/hr
Total heat load	1290095.25 kJ/hr

5. COST ESTIMATION

PLANT CAPACTIY AND PRODUCTION PROGRAMME

1. Plant Capacity

Based on the expected demand for polyester yarn as presented earlier, and the planned technology, the envisaged plant is set to produce 245ton/day, taking about 15% of the 2018's estimate.

2. Production Program

The program is scheduled based on the consideration that the envisaged plant will work 275 days in a year in 2 shifts, where the remaining days will be holidays and for maintenance. During the first year of operation the plant will operate at 75 percent capacity and then it grows to 85 percent in the 2nd year. The capacity will reach to 100% in the 3rd year and so on.

PRODUCTION COST

The annual production cost at full operation capacity is estimated at Rs. 73.09 million. The cost of raw material account for 78.47% of the production cost. The other major components of the production cost are financial cost, depreciation, utility, and marketing and distribution, which account for 2.59%, 3.77%, 12.28% and 0.96% respectively. The remaining 1.93% is the share of labour, repair and maintenance, labour overhead and administration cost.

Raw Material and Inputs	54354	78.47
Utilities	8975	12.28
Maintenance and repair	543	0.74
Labour direct	521	0.71
Labour overheads	104	0.14
Administration Costs	250	0.34
Land lease cost	0	0.00
Cost of marketing and distribution	700	0.96
Total Operating Costs	68447	93.65
Depreciation	2752	3.77
Cost of Finance	1891	2.59
Total Production Cost	73089	100.0

Annual Production Cost At Full Capacity(13).

6. **Conclusions**:

Our chemical engineering project design was aimed to bring forth an integrated detailed design for “Manufacturing of polyester by using PTA and MEG”. This project covered several aspects of the plant’s design including firstly a literature background on the production of polyester through different routes. Rigorous comprehensive mass and energy balances were done through several areas of the plant including the reaction area. The task was the detailed design and sizing of the plant’s equipment including the three major units in the plant; the reactor, the absorber and the distillation column. The final task was to estimate the economical feasibly of the polyester manufacturing process. The guidance and support from our mentor Prof. Suryawanshi is much appreciated, and the knowledge he passed on to us is something to cherished, so for that we express our deep gratitude.

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