A Technical and Economic Feasibility Study of:
Production of Polyethylene Terephthalate by Direct Esterification Using Pervaporation

PART I: The Report

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Chapter One

Background on Polyethylene Terephthalate

1.1 Historical Development

The first fiber–forming polyesters were prepared by Carothers and Hill in 1932 using the melt condensation of dicarboxylic acids and aliphatic diols [1]. Because of their low melting points and ready dissolution in organic solvents, these polymers were not considered to be significant advance. The development of polyester fibers having high melting points and more chemical resistance was possible through the use of terephthalic acid. This was discovered simultaneously in the early 1940s by Whinfield and Dickson at Calico Printers Association [2]. The technical development of PET fibers began after DuPont and ICI purchased the rights to the technology of Darcon and Terylene, respectively. A series of licensee arrangements by ICI led to the production of fiber in most industrialized countries. In Germany PET fiber was produced by Hoechst (Tervira) and Verreinigte Glanzstoff-Fabriken (Diolen). In addition to fiber spinning, the mid 1950s saw the increased significance of PET film (Mylar for DuPont and Hostaphan from Kalle) [2].

As a design material, polyethylene terephthalate was first commercialized in 1966 through the introduction of Arnite by Akzo. An injection-moldable PET was now commercial which, because of nucleating agents, had a crystallization rate that made economic injection molding possible. Afterward a number of firms brought injection-moldable PET to the market: Hostadur from Hoechst, Crastin from Ciba Geigy, and FR-PET from Teijin [2].

From the beginning of 1980s PET became a more significant force in the injection molding market as DuPont (Rynite) and Mobay (Pelton) introduced more readily processable products.

In 1990s polyester fiber amounted to 40 per cent of total man-made fibers. This growth may be attributed to polyester’s nearly optimum balance of properties; strength, blend ability, and dimensional stability. Further, it exhibits superior performance, is extremely versatile, has a great capacity for modification, and has a great capacity for modification, and is a low cost fiber [2].
1.2 Basic Principles of Polyethylene Terephthalate Formation

PET is generally produced via two different routes: Transesterification of dimethyl terephthalate (DMT) with ethylene glycol (EG) and direct esterification of purified terephthalic acid (TPA) with EG. The first stage of the two routes, known respectively as transesterification (ester interchange) and direct esterification, both produce a mixture of ethylene glycol ester of terephthalic acid. This mixture of linear oligomers (mainly bis-hydroxyethyl terephthalate BHET) is subjected to a further stage known as polycondensation that produces polyethylene terephthalate of fiber-forming molecular weight. Solid-state polymerization is required only for the production of bottles.

The first stage in the polymer synthesis is esterification, which results from the reaction of carboxylic group with an alcoholic group. Since these groups occur at the ends of bifunctional compounds, PET with a linear structure is produced. However, it is necessary during esterification for the compound that is eliminated (water or methanol) to be rapidly removed from the reaction mixture so that the equilibrium shifts preferentially in favour of the polycondensation product.

The second stage in the polymer synthesis is similar for both the ester interchange and direct esterification routes. A further catalyst is added to the mixture of linear oligomers, free glycol is distilled out by using very low pressure until the required molecular weight is attained. The most popular catalyst for this stage is antimony trioxide, although antimony pentoxide and germanium dioxide have also been used.

With the rising worldwide demand for polyethylene terephthalate, prospective PET producers are faced with a lot of decision; whether to use purified terephthalic acid or dimethyl terephthalate as the raw material, batch or continuous process, and whether to use the conventional process or to add some modifications to reduce the costs and increase the productivity.

1.3 Raw Material Selection

During 1970 DMT production exceeded that for TPA by more than three to one. In 1980s TPA production was about 53 percent of the total. The shift from DMT to TPA as the dominant raw material for PET production occurred for several reasons, the most important of which are quality, price, and overall PET production costs [3].

Purified terephthalic acid has become available for commercial scale production of polyester polymer with the development of Amoco’s process of bromine-promoted air oxidation of
p-xylene. From the view point of the producers there is no doubt now that the quality of the PET derived from TPA is equivalent to that derived from DMT [3].

Terephthalic acid gives a higher yield (15% over DMT) of polyester and therefore results in obvious savings in material cost. Thus, by pricing the acid the same as ester on a weight basis (policy established by Amoco) the difference amounts to approximately 2.5 percent per pound of PET fiber.

The capital to construct a PET facility based on TPA is reported to be at least 20 percent less than one based on DMT. This saving is attributed to many factors. In the direct esterification of TPA, the by-product is less costly to recover besides being less bothersome from a disposal standpoint as compared to methanol by-product from DMT process. Furthermore, a TPA process is capable of requiring less EG during the initial stages of the reaction. Currently PET producers operate in the range of 1.1-1.3 [1] moles of EG per mole of TPA with a 1 to 1 mole ratio perhaps becoming possible by introducing the pervaporation technology to the process in contrast to that at least 1.8 moles of EG per mole DMT. Hence there is less EG to be recovered when processing TPA, resulting in a lower investment for a glycol recovery and recycle system. Furthermore, the importance of using less glycol is that less diethylene glycol (DEG) is formed.

The time required to reach a given molecular weight is less with the free acid than with its dimethyl ester. This means that for a given capacity, a reduction in the reactor size is possible. Finally, the transesterification catalyst required by the DMT process is omitted when the process uses TPA. This minimizes adverse effects brought about by the catalyst residue in the polymer [3].

However, it is worthy to mention certain disadvantages of TPA as a raw material, TPA has a very low solubility in boiling EG at atmospheric pressure, so, it is necessary to raise the reaction temperature and pressure in order to obtain an adequate reaction rate. In addition, trace impurities can be responsible for undesirable discoloration of the polymer. And finally, not all TPA’s are capable of processing at the lower glycol-to-acid ratios. A TPA with specially "engineered" particle size is required [2].

Ethylene glycol is derived from ethylene by catalytic oxidation with air to ethylene oxide followed by acid hydrolysis. The EG must be pure and free from color-forming impurities and traces of strong acids or bases.

In the next chapters a process for PET production using pervaporation to shift the equilibrium in the esterification stage will be designed.
References


Chapter Two

Project Definition

2.1 Introduction

A principal objective of this chapter is to describe the project scope, the design basis, and the boundaries and the conditions for the feasibility study of polyethylene terephthalate production by direct esterification of terephthalic acid and ethylene glycol using pervaporation membrane reactor system to remove water that is produced in the esterification stage.

2.2 Project Scope

The scope of this project is to make a process design, technical and economical feasibility study for the production of polyethylene terephthalate by direct esterification of terephthalic acid and ethylene glycol using pervaporation to remove the esterification by-product, which is water (for original assignment, see Appendix A).

A hierarchical approach to conceptual design by Douglas (1988) [5] and the guidelines given by Van den Berg (2000) is followed in the process design part of this project. The idea behind this methodology is to find an optimum design using the minimum number of alternatives that needed to be considered in details. This methodology allows calculating equipment sizes and estimating costs as proceeding through the levels in the hierarchy, then if the potential profit becomes negative at some level a process alternative can be studied. The optimum process is selected based on technical and economical studies.

A process for the production of high-purity polyethylene terephthalate by direct esterification of terephthalic acid and ethylene glycol using distillation to remove the reaction by-product (water) is known. In this study, esterification-pervaporation as a membrane reactor system will be used to remove the by-product water from the reaction mixture in the esterification stage to shift the equilibrium reactions of esterification to increase the formation of diesters used to produce polyethylene terephthalate. Using pervaporation will remove water more efficiently, by which it might be possible to reduce the reaction time leading to a shorter batch time and/or a smaller process.
The total duration of this project would be approximately four months. During this period a complete process design will be made as well as an economic evaluation.

2.3 Design Basis

The design basis for the production of polyethylene terephthalate (PET) is given in Table (2.1). The choices made for the design basis are explained in sections 2.3.1 till 2.3.4.

Table (2.1) Design basis

<table>
<thead>
<tr>
<th>Description</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polyethylene Terephthalate Capacity</td>
<td>100,000 ton/year</td>
</tr>
<tr>
<td>Production Time</td>
<td>8,150 hours/year</td>
</tr>
<tr>
<td>Economic Lifetime</td>
<td>10 years</td>
</tr>
<tr>
<td><strong>Polyethylene Terephthalate Specifications</strong></td>
<td></td>
</tr>
<tr>
<td>Purity</td>
<td>&gt; 99.0 wt%</td>
</tr>
<tr>
<td>Physical State</td>
<td>Solid</td>
</tr>
<tr>
<td>Pressure</td>
<td>1 atm a (atmospheric)</td>
</tr>
<tr>
<td>Temperature</td>
<td>25°C (room temperature)</td>
</tr>
<tr>
<td>Maximum Concentration of Diethylene Glycol</td>
<td>&lt; 1.0 wt%</td>
</tr>
<tr>
<td>Moisture Contents</td>
<td>&lt; 0.4 wt%</td>
</tr>
<tr>
<td><strong>Water (By-Product) Specifications</strong></td>
<td></td>
</tr>
<tr>
<td>Purity</td>
<td>100 wt%</td>
</tr>
<tr>
<td>Physical State</td>
<td>Liquid</td>
</tr>
<tr>
<td>Pressure</td>
<td>1.0 atm a (atmospheric)</td>
</tr>
<tr>
<td>Temperature</td>
<td>25°C (room temperature)</td>
</tr>
<tr>
<td><strong>Ethylene Glycol (Raw Material) Specifications</strong></td>
<td></td>
</tr>
<tr>
<td>Purity</td>
<td>99.9 wt%</td>
</tr>
<tr>
<td>Physical State</td>
<td>Liquid</td>
</tr>
<tr>
<td>Pressure</td>
<td>1.0 atm a</td>
</tr>
<tr>
<td>Temperature</td>
<td>25°C</td>
</tr>
<tr>
<td><strong>Terephthalic Acid (Raw Material) Specifications</strong></td>
<td></td>
</tr>
<tr>
<td>Purity</td>
<td>99.99 wt%</td>
</tr>
<tr>
<td>Physical State</td>
<td>Solid</td>
</tr>
<tr>
<td>Pressure</td>
<td>1.0 atm a</td>
</tr>
<tr>
<td>Temperature</td>
<td>25°C</td>
</tr>
<tr>
<td>Location</td>
<td>The Netherlands</td>
</tr>
<tr>
<td>Project Type</td>
<td>Continuous</td>
</tr>
<tr>
<td>Utilities</td>
<td>Saturated steam (34 bar a @ 240.9 °C, 76 bar a @ 291.4°C, Cooling water (inlet: 25°C, outlet max. 45°C) Chilled water (inlet: 10°C, outlet max. 45°C) Electricity</td>
</tr>
</tbody>
</table>
2.3.1 Raw materials

This section describes the technical preparation of the main raw materials required to produce polyethylene terephthalate and their specifications.

2.3.1.1 Terephthalic acid

Polyethylene terephthalate is increasingly produced from very pure terephthalic acid. As mentioned in the previous chapter that terephthalic acid has some advantages over dimethyl terephthalate for the production of PET [4].

- lower price
- does not need catalyst like transesterification
- higher polycondensation speed
- no recovery of methanol necessary

Because of these benefits, the world production of terephthalic acid has been increasing, the world capacity for 1994 is 10.8 million tons compared to 5.3 million tons for dimethyl terephthalate [4].

Terephthalic acid is produced mainly by the Amoco process, then the raw terephthalic acid, containing 4-carboxybenzaldehyde as the main contaminant, is purified by hydrogenation and crystallization. The final terephthalic acid has a purity of 99.99 wt% [4].

To produce light-colored and high molecular weight PET, the following demand, incorporating values established by the American Public Health Association (APHA), are made on terephthalic acid as shown in Table (2.2) with a typical particle size distribution lies between 50 and 600 µm [4].

Table (2.2) Purified terephthalic acid specifications for PET production [4].

<table>
<thead>
<tr>
<th>Specification</th>
<th>Limit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ash content</td>
<td>≤ 15 ppm</td>
</tr>
<tr>
<td>Metals</td>
<td>≤ 10 ppm</td>
</tr>
<tr>
<td>Fe, Ca, Al, Na, K</td>
<td>≤ 2 ppm</td>
</tr>
<tr>
<td>Co, Mo, Cr, Ni, Ti, Mg</td>
<td>≤ 1 ppm</td>
</tr>
<tr>
<td>4-carboxybenzaldehyde</td>
<td>≤ 25 ppm</td>
</tr>
<tr>
<td>Water content</td>
<td>≤ 0.5%</td>
</tr>
</tbody>
</table>
Table (2.3) contains some important physical properties of purified terephthalic acid.

Table (2.3) Physical properties of purified terephthalic acid [9].

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molecular weight, g/mol</td>
<td>166.14</td>
</tr>
<tr>
<td>Melting point, °C</td>
<td>427</td>
</tr>
<tr>
<td>Triple point, °C</td>
<td>427</td>
</tr>
<tr>
<td>Specific gravity at 25 °C, g/mL</td>
<td>1.522</td>
</tr>
<tr>
<td>Specific heat J/(kg.K)</td>
<td>1202</td>
</tr>
<tr>
<td>Sublimation point, °C</td>
<td>404</td>
</tr>
<tr>
<td>Heat of combustion at 25 °C, kJ/mol</td>
<td>-3198</td>
</tr>
<tr>
<td>Heat of formation at 25 °C, kJ/mol</td>
<td>-816</td>
</tr>
<tr>
<td>Heat of sublimation, kJ/mol</td>
<td>142</td>
</tr>
</tbody>
</table>

2.3.1.2 Ethylene glycol

Ethylene glycol is produced industrially by the reaction of ethylene oxide with excess water. The typical product distribution between the products of this reaction, which are ethylene glycol, diethylene glycol, and triethylene glycol, is a mass relation of 30:4:1 respectively [4]. The glycols are separated by purification under vacuum in distillation columns connected in series.

To produce light-colored, high molecular weight PET, demands are made on ethylene glycol as shown in Table (2.4).

Table (2.4) Ethylene glycol specifications for PET production [4].

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Purity</td>
<td>≥ 99.9 wt%</td>
</tr>
<tr>
<td>Water content</td>
<td>≤ 0.05%</td>
</tr>
<tr>
<td>Diethylene glycol content</td>
<td>≤ 0.03 – 0.04%</td>
</tr>
<tr>
<td>Ash content</td>
<td>≤ 0.005 g/100 ml</td>
</tr>
<tr>
<td>Iron content</td>
<td>≤ 0.05 ppm</td>
</tr>
<tr>
<td>Acid content as acetic acid</td>
<td>≤ 0.005%</td>
</tr>
<tr>
<td>Acetaldehyde content</td>
<td>≤ 7 ppm</td>
</tr>
<tr>
<td>Density at 20 °C</td>
<td>1.1151 – 1.116 g/cm³</td>
</tr>
<tr>
<td>UV permeability</td>
<td></td>
</tr>
<tr>
<td>at 220 nm</td>
<td>≥ 70%</td>
</tr>
<tr>
<td>at 275 nm</td>
<td>≥ 90%</td>
</tr>
<tr>
<td>at 350 nm</td>
<td>≥ 98%</td>
</tr>
</tbody>
</table>
Table (2.5) includes some important physical properties of ethylene glycol.

**Table (2.5) Physical properties of ethylene glycol [7,8].**

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molecular weight, g/mol</td>
<td>62.07</td>
</tr>
<tr>
<td>Specific gravity at 20 °C, g/ml</td>
<td>1.1135</td>
</tr>
<tr>
<td>Heat of vaporization at 101.3 kPa, kJ/mol</td>
<td>52.24</td>
</tr>
<tr>
<td>Specific heat, J/(g.K)</td>
<td></td>
</tr>
<tr>
<td>as liquid, 19.8 °C</td>
<td>2.406</td>
</tr>
<tr>
<td>as ideal gas, 25 °C</td>
<td>1.565</td>
</tr>
<tr>
<td>Autoignition temperature, °C</td>
<td>400</td>
</tr>
<tr>
<td>Heat of combustion at 25 °C, kJ/mol</td>
<td>-1189.595</td>
</tr>
<tr>
<td>Heat of formation at 25 °C, kJ/mol</td>
<td>-392.878</td>
</tr>
<tr>
<td>Heat of fusion, kJ/mol</td>
<td>11.63</td>
</tr>
<tr>
<td>Critical constants</td>
<td></td>
</tr>
<tr>
<td>temperature, °C</td>
<td>446.55</td>
</tr>
<tr>
<td>pressure, kPa</td>
<td>6515.73</td>
</tr>
<tr>
<td>volume, L/mol</td>
<td>0.186</td>
</tr>
<tr>
<td>compression factor</td>
<td>0.2671</td>
</tr>
<tr>
<td>Viscosity, mPa.s (cP)</td>
<td></td>
</tr>
<tr>
<td>at 0 °C</td>
<td>51.37</td>
</tr>
<tr>
<td>at 40 °C</td>
<td>9.20</td>
</tr>
</tbody>
</table>

### 2.3.2 Product

The main product in this process is the Polyethylene terephthalate. However, water is produced as a polycondensation by-product with no important economical value.

Polyethylene terephthalate (PET) is a polycondensation polymer. It is most commonly produced from a reaction of ethylene glycol (EG) with either purified terephthalic acid (TPA) or dimethyl terephthalate (DMT), using a continuous melt-phase polymerization process. In many cases, melt phase polymerization is followed by solid-state polymerization.

This polymer is the most common thermoplastic polyester. It is often called just “polyester”, which often causes confusion. PET is a hard, stiff, strong, dimensionally stable material that absorbs very little water. It has good gas barrier properties and good chemical resistance except to alkalis (which hydrolyze it). Its crystallinity varies from amorphous to fairly high crystalline. It can be highly transparent and colorless but thicker sections are usually opaque and off-white (Salaeh A. Jabarin, 1996).
PET is widely known in the form of thermally stabilized films used for capacitors, graphics, film base and recording tapes etc. It is also used for fibres for a very wide range of textile and industrial uses. Other applications include bottles and electrical components.

Many analysts estimate PET growth at an annual rate of 7% through 2003. According to purchasing survey data, PET spot pricing currently average about 59 ¢/lb. Prices have risen steadily in 1999, when PET spot prices averaged about 51 ¢/lb. Since the third quarter 1999, PET prices have risen an average of 8 ¢/lb (Buyer’s News, Sep 2000).

2.3.3 Chemical fundamental of PET production

The two most important syntheses of PET are based on the reaction of ethylene glycol (EG) with either purified terephthalic acid (TPA) or its ester dimethyl terephthalate (DMT). Early PET production was based solely on the ester, but, with the advent of purified terephthalic acid on a commercial scale in 1964 [3], it became possible to implement processes based on the acid. As mentioned in chapter one that, using pure acid as a raw material has a lot of advantages over using its ester. The first step of the two routes, known respectively as transesterification (ester interchange) and direct esterification, both produce a mixture of ethylene glycol ester of terephthalic acid.

In the second step the obtained BHET undergoes polycondensation at higher temperature to form the polyester PET, while glycol is removed. An advanced polycondensation in the solid state just below the melting temperature of the polyester is necessary to obtain very high molecular weights [4].

2.3.3.1 Esterification process

Since TPA has a very low solubility in boiling glycol at atmospheric pressure, it is necessary to raise the reaction temperature and pressure in order to obtain an adequate reaction rate. Adequate rates are obtained at 240-260 °C and above atmospheric pressure, usually 4 atm. The reaction is self-catalyzed by the carboxylic acid groups. Usually, the glycol: terephthalic acid molar ratio is 1.1 to 1.3:1 [3], the initial reaction product is a mixture of linear oligomers, mostly BHET, in addition to water as by product according to this reaction [1].

\[
\begin{align*}
\text{HOOC-} & \text{COOH} + 2 \text{HOCH}_2\text{CH}_2\text{OH} & \text{pressure} \rightarrow \\
& 2 \text{H}_2\text{O} + \text{HOCH}_2\text{CH}_2\text{OOCCOOCH}_2\text{CH}_2\text{OH} & \text{heat}
\end{align*}
\]

\[(2.1)\]
The volatile product of direct esterification is water, which is distilled out of the reactor to force the reversible reaction toward completion.

2.3.3.2 Polycondensation

The second step in PET synthesis is similar for both the ester interchange and direct esterification routes. A further catalyst is to be added to the mixture of linear oligomers, free glycol is distilled out according to reaction (2.2) [1], and the temperature is raised until it reaches 260-290. The pressure is reduced as rapidly as possible without causing carry-over due to foaming, and polymerization is carried out finally at a pressure below 1 mm Hg until the required molecular weight is attained [3,6].

\[
\begin{align*}
&\text{n HOCH}_2\text{CH}_2\text{OOCCOOCH}_2\text{CH}_2\text{OH} \xrightarrow{\text{catalyst, heat}} \text{HOCH}_2\text{CH}_2\text{OH}^n \text{OCH}_2\text{CH}_2\text{CO} (n-1) \text{OCH}_2\text{CH}_2\text{OH}
\end{align*}
\]

(2.2)

The most popular catalyst for this stage is antimony trioxide, although antimony pentoxide and germanium dioxide has also been used.

The polycondensation reaction is reversible as it is shown in reaction (2.2), so it is important to remove the glycol produced from the system as quickly as possible. In most polymerization reactors, the rate of attainment of high molecular weight is diffusion-controlled rather than chemically controlled, and it is useful to minimize the diffusion path by maximizing the surface: volume ratio and the rate of generation of free surface.

There are two types of polycondensation, the melt and the solid polycondensation. The melt polycondensation of PET, carried under common industrial conditions, leads to products with a molecular weight of 15,000-25,000 [4]. Certain injection molding and extrusion applications require high quality, high molecular weight polyesters with improved mechanical and thermal properties. PET with a molecular weight of more than 30,000 can rarely be prepared under conditions of melt polymerization because of the long reaction times and because at high polycondensation temperature, thermal degradation occurs more rapidly than formation. Higher molecular weight PET can be obtained more easily by polycondensation in the solid phase below the PET’s melt temperature because at the lower temperatures, the speed of formation is higher than the speed of degradation.

A major side reaction that can take place in addition to the previous main reactions is the formation of diethylene glycol (DEG). The formation of this side product is important in preparing PET. The amount of DEG in PET molecules influences many important properties of the polymer;
for instance, temperature and light stability, and melting point, which decreases by about 5 °C for each percent increase in DEG concentration. Above all, the esterification reaction is the most important stage in the formation of DEG [10].

2.3.4 Reaction information

The reaction mechanisms and kinetics of the direct esterification process are examined in many open sources. The rate parameters in our process are based on the published work of Kang and Lee [10] for the esterification stage and that of Gupta and Kumar [2] for the polycondensation stage.

The complete set of reactions considered in producing polyethylene terephthalate (PET) by direct esterification of ethylene glycol (EG) and terephthalic acid (TPA) can be divided into three categories, water formation, polycondensation, and diethylene glycol formation reactions. Since Flory’s principle of equal reactivity has been successfully applied to many polymerization reactions including that of PET, in this principle, all like functional groups behave similarly and can be as the reactants, whereas the polymer chain segment between or beside these groups are considered as a kind of solvent. Table (2.6) shows the various reactions of functional groups in the PET formation by direct esterification. In this table, $k_i$ (i = 1-8) are the “effective” rate constants and $K_i$ (i = 1-7) are the equilibrium constants. Reactions 1-4 are the esterification reactions, and reactions 5 and 6 are the polycondensation reactions. Reactions 7 and 8 are the side reactions leading to the DEG formation. Although several reaction mechanisms have been proposed to describe the DEG formation reaction, the mechanisms are lumped together in reactions 7 and 8.

All components considered in the reactions set are listed in Table (2.7), where five different oligomeric segments are defined: tEG, tTPA, bEG, bTPA, and bDEG (“t” and “b” represent the “terminal functional group, end-group segment” and the “bound monomer repeating unit” respectively).
Table (2.6) Reaction scheme of reactions considered in this project [2,10].

<table>
<thead>
<tr>
<th>No.</th>
<th>Reactions</th>
<th>Rate Constants (forward, reverse)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>EG + TPA → tEG + tTPA + W</td>
<td>$k_1$, $k_1/K_1$</td>
</tr>
<tr>
<td>2</td>
<td>EG + tTPA → tEG + bTPA + W</td>
<td>$k_2$, $k_2/K_2$</td>
</tr>
<tr>
<td>3</td>
<td>tEG + TPA → bEG + tTPA + W</td>
<td>$k_3$, $k_3/K_3$</td>
</tr>
<tr>
<td>4</td>
<td>tEG + tTPA → bEG + bTPA + W</td>
<td>$k_4$, $k_4/K_4$</td>
</tr>
<tr>
<td>5</td>
<td>tEG + tTPA + tEG → bEG + tTPA + EG</td>
<td>$k_5$, $k_5/K_5$</td>
</tr>
<tr>
<td>6</td>
<td>tEG + bTPA + tEG → bEG + bTPA + EG</td>
<td>$k_6$, $k_6/K_6$</td>
</tr>
<tr>
<td>7</td>
<td>2 EG → DEG + W</td>
<td>$k_7$, $k_7/K_7$</td>
</tr>
<tr>
<td>8</td>
<td>tEG + tEG → bDEG + W</td>
<td>$k_8$</td>
</tr>
</tbody>
</table>

Table (2.7) Molecular structure of the considered components [10].

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
<th>Molecular Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>TPA</td>
<td>Terephthalic acid</td>
<td>HOOC -- COOH</td>
</tr>
<tr>
<td>EG</td>
<td>Ethylene glycol</td>
<td>HOCH₂CH₂OH</td>
</tr>
<tr>
<td>W</td>
<td>water</td>
<td>H₂O</td>
</tr>
<tr>
<td>tEG</td>
<td>EG end group</td>
<td>HOCH₂CH₂O</td>
</tr>
<tr>
<td>tTPA</td>
<td>TPA end group</td>
<td>HOOC -- CO</td>
</tr>
<tr>
<td>bEG</td>
<td>EG repeat units</td>
<td>~ OCH₂CH₂O</td>
</tr>
<tr>
<td>bTPA</td>
<td>TPA repeat units</td>
<td>~ OC -- CO</td>
</tr>
<tr>
<td>bDEG</td>
<td>Diethylene glycol repeat unit</td>
<td>~ OCH₂CH₂OCH₂CH₂O</td>
</tr>
</tbody>
</table>

For solving the material balance equations, the kinetic parameters for both the esterification and the polycondensation stages for all reactions have to be known. From previous works, it can be assumed that the reactivity of the acid end group on TPA is equivalent to that on an oligomer chain (tTPA) while the reactivity of the hydroxyl end group on EG is different from the half-esterified EG (tEG), i.e., $k_1 = k_2$ and $k_3 = k_4$. In the reverse esterifications, water attacks an ester link, splitting the polymer molecule into two smaller molecules. Similarly, it can be assumed that $(k_1/K_1) = (k_2/K_2)$ and $(k_3/K_3) = (k_4/K_4)$ [10].
The rate constants are dependent on temperature, catalyst type, and catalyst concentration. According to previous works, it can be assumed that the constants for the acid-catalyzed esterification and polycondensation can be written as [10]:

\[
k_i = A_i C_{\text{acid}} e^{-\frac{E_i}{RT}} \tag{2.3}
\]

Where \( A_i \) is the preexponent factor (L/mol^2/min); \( E_i \), the activation energy; \( R \), the gas constant; \( T \), the temperature in K; and \( C_{\text{acid}} \), the total acid concentration. \( C_{\text{acid}} \) is defined as the concentration of the dissolved TPA and t-TPA in the liquid phase of the reaction mixture free from the undissolved TPA.

For the values of the equilibrium constants, \( K_1 = K_2 \) and \( K_3 = K_4 \), and the rate constants, \( k_i \), \( i = 1, 2, 3, 4 \), the results of an experimental work by Otton and Ratton were used for the first stage of the process which is esterification. The values of these parameters are shown in Table (2.8) [10].

Several workers have studied the kinetic parameters of the esterification and polycondensation reactions in the polycondensation stage of the process in the presence of antimony trioxide as a catalyst. The literature shows a wide variation in the reported values. It is generally believed that this arises because the vapor-liquid equilibrium of ethylene glycol required in correctly interpreting the rate data is subject to considerable uncertainty. There has been a simulation study by Ravindranath and Mashelkar, which has used the rate constants estimated from the data of Yokoyamo et al. This simulation claims to predict the performance of the a PET plant in operation, and in view of this, the values of the rate constants, as reported in Table (2.8) and explained by equation (2.4) (\( A_i \) is the frequency factor (L/mol min)) [2], have been used for the polycondensation stage of this project.

\[
k_i = A_i e^{-\frac{E_i}{RT}} \tag{2.4}
\]

The side reactions of both steps, esterification and polycondensation, are the same. However, the esterification is the most important step in the formation of DEG during PET synthesis through the direct esterification process. The kinetic parameters of reaction (7) has been published by Chen and that for reaction (8) by Chang et al. following equation (2.4), as shown in Table (2.8) are used in this project for both stages of the process.
Table (2.8) Rate constant parameters and equilibrium constants [2,10].

<table>
<thead>
<tr>
<th>Reaction number</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Activation energy, ( E_i )</strong></td>
<td>18</td>
<td>18</td>
<td>18</td>
<td>18</td>
<td>18</td>
<td>18</td>
<td>43.32</td>
<td>29.8</td>
</tr>
<tr>
<td><strong>Frequency factor, ( A_i )</strong></td>
<td>4.68 E 5</td>
<td>4.68 E 5</td>
<td>2.34 E 5</td>
<td>2.34 E 5</td>
<td>3.64 E 5</td>
<td>3.64 E 5</td>
<td>6.17 E 11</td>
<td>2.17 E 9</td>
</tr>
<tr>
<td><strong>Equilibrium constant, ( K_i )</strong></td>
<td>2.5</td>
<td>2.5</td>
<td>1.25</td>
<td>1.25</td>
<td>0.5</td>
<td>0.5</td>
<td>8</td>
<td>--</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Polycondensation stage of the process</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Activation energy, ( E_i )</strong></td>
</tr>
<tr>
<td><strong>Frequency factor, ( A_i )</strong></td>
</tr>
<tr>
<td><strong>Equilibrium constant, ( K_i )</strong></td>
</tr>
</tbody>
</table>

2.3.5 Solubility of terephthalic acid

In addition to the kinetic parameters, the solubility of TPA in EG is required. TPA has a limited solubility in EG, but it is more soluble in BHET. The solubility of TPA in ethylene glycol and BHET has been studied by several workers and can be correlated by the following empirical equation:

Solubility of TPA in ethylene glycol [2]

\[
\ln c = 1.19 - 1240 / T
\]  

(2.5)

Solubility of TPA in BHET [2]

\[
\ln c = 1.90 - 1420 / T
\]  

(2.6)

where \( c \) is the concentration of TPA in moles/kg of the solution and \( T \) is in °K. It can easily be seen from the above equations that the solubility of TPA in BHET is larger than it is in ethylene glycol.

Kang et al. [10] concluded that the solubility of TPA has no effect on the reactions at high conversions where all the solid TPA molecules are dissolved and consumed for the reactions; they concluded that the solid-liquid mass transfer of TPA is not the rate limiting.

Yamada et al. [16,17,18,19, and 20] assumed that the rate of dissolution of TPA is fast. The rate determination step, therefore, is not the dissolution of TPA, but the reaction of TPA, and he proved that by doing experimental work [18,20].
2.4 Conclusions

- The scope of this project is to make a process design, technical and economical feasibility study for the production of polyethylene terephthalate by direct esterification of terephthalic acid and ethylene glycol using membrane reactor technology to remove the esterification by-product, which is water.

- It is decided to follow a hierarchical approach to conceptual design by Douglas (1988) [5] and the guidelines given by Van den Berg (2000) in the process design part of this project.

- It is decided to use pervaporation membrane reactor that will remove water more efficiently by which it might be possible to reduce the reaction time leading to a shorter batch time and/or a smaller process.

- The design basis for the production of polyethylene terephthalate (PET) is discussed.

- Description of the technical preparation of the main raw materials required to produce polyethylene terephthalate and their specifications is discussed.

- Chemical fundamentals of PET production by TPA and EG are discussed including, esterification process, polycondensation process, reaction information, and the solubility data of TPA in EG and BHET.

- The rate of dissolution of TPA is fast. The rate determination step, therefore, is not the dissolution of TPA, but the reaction of TPA.
References


Chapter Three

Project Organization

3.1 Introduction

This chapter presents the planning and the scheduling for the plant design project of Polyethylene Terephthalate (PET) production. The tree diagram and the work diagram discussed in section 3.1 and 3.2 show the structure of the project and the sequence of all project activities.

3.2 Tree Diagram

The tree diagram is an organization flow chart. It shows the main project goal and the accompanying activities in order of priority. The main goal is split up in three main sub-goals. These main sub-goals are in turn divided in several sub-goals. Figure (3.1) presents the overall tree diagram of the PET project.

The main goal of the project is to prepare a technical and an economic feasibility study for the production of Polyethylene Terephthalate by direct esterification using pervaporation. The three main sub-goals required to achieve the main goal are project definition, technical process design and economic evaluation. Most boxes will be given in more details in the corresponding chapter.

3.2 Work Diagram

All the design activities are scheduled and summarized in the work diagram shown in Figure (3.2). This diagram comprises the sequence of the project tasks mentioned in the tree diagram. Every stage in the project is ended with an evaluation based on economic, technical, environmental, safety and social constraints. Most boxes will be given in more details in the corresponding chapter.

The project starts with the definition of the scope and the design basis to formulate the demands of the project. Together with the process constraints, the first economic evaluation is carried out using black box evaluation. When the outcome of the evaluation is positive, a
conceptual flow sheet is made. Here process alternatives are developed and tasks are coupled to functional sections.

The conceptual flowsheet is used as a basis for the index flowsheet. In this part the process equipment are selected and preliminary material and energy balances for unit ratios are done. Using the index flowsheet a process flowsheet is made on the basis of modeling and optimization results of the unit operations.

The required utilities and possibilities of heat integration are considered. The design and dimensions of the process equipment are determined. The main process control is designed and P&ID is made. Finally the process is evaluated with respect to safety, environment and economics.

![Figure (3.1) Tree diagram of the PET project.](image-url)
3.3 Conclusions

- Planning and scheduling for the feasibility study of the production of PET by direct esterification using pervaporation is done
- The necessary activities needed to achieve this study are determined
- The sequence of the project tasks is determined.

Reference

Berg, H. van den, “Process Plant Design”, Course material, University of Twente, (2000)
Chapter Four

Conceptual Flowsheet

4.1 Introduction

In this chapter a conceptual design of the production of polyethylene terephthalate by direct esterification is made. The design methodology of Douglas is followed. First, the raw materials terephthalic acid and ethylene glycol react to produce the BHET oligomer and water as by-product, then BHET and its oligomers convert to polyethylene terephthalate and ethylene glycol. Second, the reactor effluents have to be separated. Special attention is given to the synthesis of the reaction section.

The process constraints and the black box form the basis for more detailed design of the plant. The main functional sections, which are required in order to obtain the desired product, are defined. Then, the main sections are divided into sub sections, which are needed to accomplish the specific tasks within the main functional sections.

4.2 Work Organization

4.2.1 Tree diagram

The tree diagram, which depicts construction of the conceptual flowsheet, is shown in Figure (4.1). The goal of this diagram is to determine the functional sections and the overall mass balance. The choice of process alternatives depends on choices of reaction system, recycle and separation structure, which predict the overall yield, utility requirement, equipment cost and other technical and economic variables.

Figure (4.1) Tree diagram of the conceptual flowsheet
4.2.2 Work diagram

The work diagram, which depicts construction of the conceptual flowsheet, is shown in Figure (4.2). The conceptual design is based on the design methodology of Douglas (1988) [5]. The methodology decomposes the design problem into a hierarchy of decisions.

The methodology starts with the decision of whether the process is continuous or batch. The previous decision is the basis for the input-output structure that includes the black box evaluation. After approving, the recycle structure of the process is determined including possible process alternatives. Alternatives are rejected based on technical, economic or other reasons. The most feasible process alternative is selected to work out in more details.

Figure (4.2) Work diagram of the conceptual flowsheet
4.3 Introduction to the Design Method of Douglas

Douglas conceptual design methodology [5] is based on five hierarchical decisions levels; starts with batch over continuous process selection and ends with heat-exchanger network. The levels of this methodology can be summarised as follows:

1. Level 1: Batch versus continuous.
2. Level 2: Input-output structure of the flowsheet.
3. Level 3: Recycle structure of the flowsheet.
4. Level 4: General structure of the separation system.

One great advantage of this methodology to design is that it allows calculating of the equipment sizes and estimating costs after proceeding through the levels in the hierarchy. Then if the potential profit becomes negative at some level, a process alternative can be taken into account or project design termination can be done without having a complete solution of the problem. Another advantage of the procedure arises from the fact that decisions can be made about the structure of the flowsheet at various levels.

This approach of conceptual design has one disadvantage that it doesn’t take into account the possibility that at an early stage of the design, different functionality (e.g; unit operations) can be integrated and thereby overlooking interesting process alternatives.

4.4 Level 1: Batch versus Continuous

At level 1 a decision is made whether the process will be operated batchwise or continuously. Characteristics for batch process are given by Biegler et al. (1997):

1. The process has to be operational within a few months to enter the market and ensure sufficient share.
2. A few days of production are needed for a year’s supply.
3. Limited design information.
4. The expected lifetime of the product is one or two years.
5. The value of the product overwhelms its manufacturing cost.
According to the batch process characteristics given above, a decision of batch process selection can’t be taken, other guidelines have to be considered in PET process selection to be batch or continuous.

Other guidelines for the decision making are given by Douglas (1988) [5], which can be summarised in two points:

1. Production rate.

Plants having a capacity of greater than 45,000 ton/year are usually continuous, whereas plants having a capacity of less than 450 ton/year are normally batch types.

2. Operational problems.

Some reactions are so slow that batch reactors are the only reasonable alternative. Similarly, some materials foul equipment so rapidly that the equipment must be shut down and cleaned at frequent intervals.

The capacity of the plant is selected to be 100,000 ton/year because of high demand of PET. Based on this capacity, it is clear that continuous process can be selected.

According to operational problems, PET can be produced, by direct esterification of TPA and EG, by both batch and continuous processes. Minimising batch cycle time and producing consistent product are the major concerns for batch mode processes. In a continuous process for PET production, fast and stable response of a polymerization process to disturbances is essential, otherwise a significant amount of off-spec product may be produced. A modified and well done control scheme may improve and stabilize the process response, which, in turn, reduces off-spec product caused by unstable processes. The PET continuous process application demonstrates the use of dynamic modelling to improve operation stability of a continuous PET reactor system.

To be clearer in our selection, complete comparison, including advantages and disadvantages of a continuous process versus batch based on the plant size (economics) and the product flexibility is done.

i. With the continuous process, uniform process conditions and constant volume are possible. Furthermore, it is possible to maintain the right temperature in the right vessel and thus reduce degradation and/or speed up the reaction [7].
ii. The heating elements are smaller in the continuous process as there are no peak loads as required in the batch process [7].

iii. In the batch process, the complete polycondensation reaction is carried out in one reactor and the process conditions in this reactor are completely different at the beginning of the polycondensation from those at the end. At the beginning of polycondensation the viscosity of the product is not high initially and the reaction is not mass-transfer controlled. But, at the end of polycondensation the reaction becomes mass transfer controlled. With the continuous process, it is possible to design the reactors so that various requirements at each stage of the process are satisfied [7].

iv. In contrast to the batch process, which poses difficult non-steady state control problems, the continuous process is at steady state except during start-up. This results in a better possibility for complete automation of the process [7].

v. With continuous process, more advantage can be taken of the “scale effect” that is possible with the batch process [7].

vi. In the continuous process there is a possibility of better constant product characteristics, in particular carboxyl end group, hydroxyl end group and diethylene content [7].

vii. In the continuous process, a certain degree of polymerization takes place in the esterification reactors train resulting in the evolution of ethylene glycol. Then the evaporated EG is recycled to that reactors train that cause reduction of EG/TPA mole ratio from 2 for batch process to about 1.1-1.3 [7].

Based on the previous discussion, continuous process for the production of PET is selected.

4.5 Level 2: Input-Output Structure of the Flowsheet

This level considers the number of raw materials and product streams, and their overall relation to the process. It is assumed in this level that the only product is polyethylene terephthalate in addition to water as by-product, and no losses of raw materials and product occur. The black box evaluation is made in this level to decide the feasibility of this project.
4.5.1 Raw materials and product streams

The compositions of the different feed and product streams are given in section 2.3.1. Since the purity of the commercial ethylene glycol used in PET formation is 99.9%, and that for the purified terephthalic acid is 99.99%, purity of 100% for raw materials can be assumed in the black box evaluation. Section 2.3.1 gives the full specifications of the commercial raw materials. Several by-products can be formed through PET formation; the most important one is diethylene glycol that has strong effect on the PET properties which means that it is found in very low percentage in our final product PET (0.4 wt%). Based on this it can be assumed in this level that our final product has 100% purity.

4.5.2 Reaction and catalysts

There are a number of alternative reaction paths to produce the polyethylene terephthalate. It is generally produced via two different routes; dimethyl terephthalate (DMT) – ethylene glycol (EG), and terephthalic acid (TPA) – EG. Since high purity of TPA was commercially available at low price, it has become economically more useful than the other routes [8]. (for more details see chapter one).

The complete set of reactions producing PET by direct esterification of EG and TPA is given in Table (2.6). The direct esterification reaction produces the monomer bis-hydroxyethyl terephthalate (BHET) [1].

\[
\text{TPA} + 2 \text{EG} \xrightarrow{\text{BHET} + 2 \text{H}_2\text{O}}
\]

(4.1)

The produced monomer has two functional groups; carboxyl group (COOH) and hydroxyl group (OH). It goes through step-growth polymerization, where the growth of the molecules occurs through the reaction of the two functional groups [1].

\[
\text{n BHET} \xrightarrow{\text{PET}_n + (n-1) \text{EG}}
\]

(4.2)

The direct esterification reaction is conducted at an elevated temperatures, generally in the range of 240-260 °C, and under elevated pressures in the range of 1 – 8 bar. The polymerization (polycondensation) reaction is generally conducted at a temperature in the range of 260-290 °C, and under a reduced pressure up to 1 torr [3].
PET prepared using a homogeneous antimony catalyst systems is more resistant to thermal and thermooxidative degradation than other catalyst systems containing manganese, cobalt or zinc [8].

### 4.5.3 Number of product streams

The components that leave the reactor system are polyethylene terephthalate, water, unreacted ethylene glycol, unreacted terephthalic acid, catalyst and impurities (see section 4.6). The impurities and by-products, other than water, are neglected. In Table (4.1) the destinations of the main components are given. Unreacted EG and TPA are recycled to prevent losses of raw materials.

Table (4.1) Destinations of components of the reactor effluent

<table>
<thead>
<tr>
<th>Component</th>
<th>Destination</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethylene glycol</td>
<td>Recycle</td>
</tr>
<tr>
<td>Catalyst</td>
<td>Waste*</td>
</tr>
<tr>
<td>Poly(ethylene terephthalate)</td>
<td>Primary product</td>
</tr>
<tr>
<td>Water</td>
<td>Waste</td>
</tr>
</tbody>
</table>

* Since it is a homogeneous catalyst

### 4.5.4 Black box evaluation

The black box of the process is shown in Figure (4.3). The process is represented in the form of a box with the raw materials as feed streams and the products as output streams. In the black box calculations the following assumptions are made;

- No impurities are presented in the feed streams,

- 100% conversion of reactants, (for more details, see Section 4.6)

- 100% solubility of TPA in EG and reaction mixture, (for more details, see Section 4.6)

- The amounts of by-products other than water are neglected, and

- No losses of valuable materials (rather than the rule of thump of greater than 99% Recoveries).

- The produced PET has a molecular weight of 19,000 g/mol
An estimate of the overall mass balance for a production rate of 100,000 tons of poly(ethylene terephthalate) per year and an operating time of 8,150 hours per year is given in Table (4.2).

<table>
<thead>
<tr>
<th>Component</th>
<th>In [kg/kg PET]</th>
<th>In [ton/yr]</th>
<th>Out [kg/kg PET]</th>
<th>Out [ton/yr]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethylene glycol</td>
<td>0.33</td>
<td>33,000</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Terephthalic acid</td>
<td>0.86</td>
<td>86,000</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Poly(ethylene terephthalate)</td>
<td>-</td>
<td>-</td>
<td>1.00</td>
<td>100,000</td>
</tr>
<tr>
<td>Water</td>
<td>-</td>
<td>-</td>
<td>0.19</td>
<td>19,000</td>
</tr>
<tr>
<td>Total</td>
<td>1.19</td>
<td>119,000</td>
<td>1.19</td>
<td>119,000</td>
</tr>
</tbody>
</table>

The process has to achieve the following constraints:

- Keep unreacted raw materials ethylene glycol and terephthalic acid in the process,

- Water must meet the environmental regulations before disposal, otherwise it should be purified, and

- The process operation must be safe for the employees, civilians and the environment.
Based on the mass balance calculations of the black box, the zero economic potential is calculated. It is defined as follows (Asselberg, 2000);

$$\text{EP}_0 (\text{US$/yr}) = \text{Product Value + By-product Value} - \text{Raw Material Cost} \quad (4.3)$$

As stated previously, the amounts of by-products other than water are assumed to be zero. Table (4.3) shows the prices of the different chemicals and the zero economic potential calculation of the PET process.

Table (4.3) Prices of chemicals of the PET process [9].

<table>
<thead>
<tr>
<th>Chemical material</th>
<th>Price (US$/ton)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethylene glycol</td>
<td>310</td>
</tr>
<tr>
<td>Terephthalic acid</td>
<td>507</td>
</tr>
<tr>
<td>Polyethylene terephthalate</td>
<td>948</td>
</tr>
</tbody>
</table>

Using data in Table (4.2) and Table (4.3) the zero economic potential is calculated as shown in Table (4.4)

Table (4.4) Overall mass balance and zero economic potential of the PET process.

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>EG</td>
<td>33,000</td>
<td>-</td>
<td>310</td>
<td>- 10.23</td>
</tr>
<tr>
<td>TPA</td>
<td>86,000</td>
<td>-</td>
<td>507</td>
<td>- 43.60</td>
</tr>
<tr>
<td>PET</td>
<td>-</td>
<td>100,000</td>
<td>948</td>
<td>+ 94.80</td>
</tr>
</tbody>
</table>

$$\text{EP}_0 = 40.97$$

Table (4.4) shows that the zero economic potential is about 41 million US$/yr at an annualized production rate of 100,000 ton/yr. The total sales revenue (TSR), which are the price of the total annual production rate, are estimated to be 94.8 million US$/yr. The TSR equal the earning before tax and the total annual investment cost. If the earning before tax is assumed to be 25% of the TSR, then the total variable and fixed production cost (total annual investment cost) is allowed to be 71.1 million US$/yr. The economic lifetime of the project is assumed to be 10 years and the depreciation is assumed to be 10% of the total annual investment cost.

To verify this result, a turnover ratio (TOR) of 1-2 per year is assumed, then a rough estimate of the fixed capital investment (FCI) can be obtained. (Asselberg, 2000)
From this relation the FCI is estimated to be in the range of 47.4-94.8 million US$. This rule of thumb confirms that the estimated total investment cost is realistic and about 71.1 million US$ should be available for the investment.

4.6 Level 3: Recycle Structure of the Flowsheet

After taking a decision on the input-output structure of the flowsheet, the next level of detail is added. The decisions that fix the recycle structure of the flowsheet are given below. Each of these decisions is discussed in detail [5].

1. How many reactors are required? Should some components be separated between the reactors?
2. How many recycle streams are required?
3. Is it necessary to introduce any reactant in excess to the reactor system?
4. Is a gas-recycle compressor required? How does it affect the costs?
5. Should the reactor be operated adiabatically, with direct heating or cooling, or is a diluent or heat carrier required?
6. Is it necessary to shift the equilibrium conversion? How?
7. How do the reactor costs affect the economic potential?

4.6.1 Number of reactor systems

The process of PET production by direct esterification consists mainly of four stages: esterification, prepolymerization, melt polycondensation, and solid-state polycondensation, but since the number average molecular weight of our final PET is 19,000, three stages are sufficient. In the first stage, bis-hydroxyethyl terephthalate (BHET) (and some of its linear oligomers) is prepared by direct esterification process, through which EG and pure TPA are reacted to form BHET and water as by-product according to this esterification reaction [1]:

\[
\text{HOOC} \quad \text{COOH} + \ 2 \ \text{HOCH}_2\text{CH}_2\text{OH} \underset{\text{pressure}}{\overset{\text{heat}}{\rightarrow}} \ 2 \ \text{H}_2\text{O} + \ \text{HOCH}_2\text{CH}_2\text{OOCCOOCH}_2\text{CH}_2\text{OH} \quad \text{(BHET)}
\]
In the second stage, BHET (and some of its oligomers) emerging from the first stage is polymerized in a prepolymerization reactor up to a degree of polymerization of approximately 30. The product is then passed onto the third stage where it is polymerized to a degree of polymerization of about 100 using high vacuum and a special agitation system. In both stages BHET is converted into PET producing EG as by-product, according to this polycondensation reaction [1]:

$$n \text{HOCH}_2\text{CH}_2\text{OOC COOCH}_2\text{CH}_2\text{OH} \xrightarrow{\text{catalyst, heat}} (n-1) \text{HOCH}_2\text{CH}_2\text{OH} + \text{OCH}_2\text{CH}_2\text{OOC COH}$$

(PET) (4.7)

The undesirable side reactions will not be taken into account in mole and mass balance calculations at this level.

The first esterification reactor system operates at temperatures of 240-260 °C and pressure ranging from one to several atmospheres (usually 4.0 atm) [3], but the polycondensation reactor system operates at higher temperatures and lower pressure in the presence of a catalyst.

Based on the previous discussion, it is clear that two reactor systems would be required for the PET production process.

It is good to mention here that mass and mole balance calculations can’t be done in a correct way because of the complexity of the system like, the solubility of TPA in EG and the produced oligomers, vapor-liquid equilibrium of volatile components (water and EG), the reactions set in the esterification and polycondensation stages, and the effects of mass transfer limitations of EG on the reactions set in the polycondensation stage.

### 4.6.2 Number of recycle streams

In the first reactor system and based on the esterification reaction shown in Section 4.6.1, the formed water vapor has to be removed to shift the reaction to the right direction to form more BHET that is required for the polymerization reaction. Since the reaction occurs at temperature higher than the boiling temperature of EG, some fed EG would be evaporated.

The evaporated water and EG flows to one or more separation units which separate EG from the water. The separated EG can be recycled directly to the esterification reactor system.

In the second reactor system of polymerization reaction shown in Section 4.6.1, the formed EG and the evaporated water flows to one or more separation units which separate EG
from water. The separated EG can be recycled directly to the esterification reactor system or the mixing tank before the esterification reactor system.

The temperature of the first stream is closed to that of the second one, but the pressure is totally different, for the first one it is above atmospheric pressure and for the second one is high vacuum. That means that these two streams can't be mixed with each other or separated in one separation system.

Based on the previous discussion two recycle streams would be used for the two reactor systems (the actual number of streams is based on the number of reactors in each reactor system that can be determined by simulation).

4.6.3 Excess reactant

Since TPA has a very low solubility in EG and esterification is an equilibrium reaction, it is necessary to increase the amount of EG fed to the reactor to increase the rate of the esterification reaction, which means that excess amount of EG is required. This will not be economical in terms of high price of EG, which means that simulation and optimization has to be done to determine the excess amount of EG. It is found in literature that in the continuous process, the optimum molar feed ratio of EG/TPA is 1.1-1.3 [2,3,4] for the conventional process. It is expected to reduce this ratio by using the pervaporation separation technology in the esterification stage.

4.6.4 Equilibrium limitations

Due to the fact that esterifications are equilibrium reactions, high yields can be obtained when a large excess of EG reagent is used. Alternatively, the reaction can be forced toward completion by the removal of the by-product (water). In order to overcome this problem, it is essential to make judicious choices about process equipment and operating conditions based on understanding of the these processes. There are two options to shift the equilibrium of the esterification reactions:

1. Using pervaporation separation technology.
2. Using reactive distillation system.

4.6.4.1 hybrid process of an esterification reaction coupled with pervaporation.

There is currently a great deal of interest in the development and use of alternative non-conventional techniques that allow using of systems that combine the reaction and separation in a
single process in order to increase the efficiency of the esterification reactions. However, the use of membranes coupled to a reactor is a technique of practically undeveloped potential. This is mainly due to the lack of suitable membranes, in other words, membranes with a good permeability and resistance to the solvents that take part in the chemical reaction in addition to the temperature of the reaction.

Pervaporation is a technique that allows the fractionation of liquid mixtures through a membrane and which is mainly used for the dehydration of organic compounds. These membranes are designed to work optimally with mixtures in which the water concentration is low. In this way, the use of pervaporation in order to eliminate the product of a reaction “in situ” can increase its efficiency.

This is the case of equilibrium reactions in which water is obtained as one of the products. Among these reactions are those of esterification, in which the reaction rate can be increased by integrating a pervaporation module into the system. This will eliminate the water as displacing the equilibrium and thus increasing the conversion forms it.

The use of pervaporation coupled to the esterification reaction increases the conversion considerably, 100% being possible. Several articles have been published studying a hybrid process of esterification-pervaporation but, very little have been published on a pervaporation-type membrane reactor.

In general, there are two basic process types combining a reactor and a pervaporation unit. These can be distinguished as illustrated in Fig (4.4).

![Fig (4.4) Basic layout of pervaporation-reactor hybrid processes. Reactor with (a) internal pervaporation unit, and (b) external pervaporation unit.](image)

Waldburger et al. (1994) [10] studied the acetic acid/ethanol esterification reaction in a recycle continuous flow reactor using a commercial PVA membrane. Acetic acid and ethanol were mixed...
in a reservoir and then recycled through the membrane reactor. After the whole reservoir had been recycled three times at 80 °C the reactor conversion achieved was 98.7%.

Kita and co-workers (Kita et al., 1988 [11]; Okamoto et al., 1991 [12], 1992 [13], 1993 [14]) also reported on the use of pervaporation and vapor permeation reactors in esterification reactions. In their pervaporation experiments. They used a batch reactor and a flat disk membrane consisting of various polymers like polyimide, Nafion, Chitosan, etc. The reactions studied were the esterification of oleic acid with ethanol, the reaction of phenol with acetone and the esterification of acetic acid with ethanol. Complete conversion was reported.

Y. Zhu et al. (1996) [15] studied the esterification reaction between acetic acid and ethanol in a continuous flow pervaporation membrane reactor utilizing a polymeric/ceramic composite membrane. During the membrane reactor experiments, removal of the water from the membrane tubeside resulted in reactor conversions which exceeded the calculated equilibrium conversions for a region of experimental conditions.

Domingues et al. (1999) [16] studied the coupling of a pervaporation module to a discontinuous esterification reactor using a commercial GFT membrane and analysing its possible application on an industrial level. The reaction chosen for the pervaporation study was that of esterification of benzyl alcohol with acetic acid. The results showed 96% selectivity in water and 99% conversion.

Dams and Krug [17] analysed pervaporation–aided esterification processes. Three different layouts were analysed for the connection of the pervaporation unit using hydrophilic PVA membranes with the reactor as shown in Fig (4.5).

The first layout illustrated in Fig (4.5,a) combined an esterification of process with a distillation column and pervaporation unit. In the esterification vessel, ethanol reacted with an acid to form an ester and water. The vapour phase of this process was recycled by distillation to recover the unreacted ethanol. While the top product of the distillation column with 87 wt% ethanol and 13 wt% water was further treated by pervaporation, the bottom product of the column was water. The pervaporation unit further concentrated the ethanol to 98 wt%. The ethanol-rich retentate stream was recycled to the reaction vessel.
The second layout, as seen in Fig (4.5,b) was characterized by the circulation of the liquid reaction mixture from the esterification process. This layout achieved high conversion rate combined with low energy consumption. Furthermore, there was no limitation due to the alcohol-water azeotrope. However, the permeate quality necessitated a permeate disposal process. Additionally high membrane stability was required. Finally, reduced effectiveness of the pervaporation could not be avoided, as a low water concentration was required inside the reactor to accelerate the reaction process.

In the third layout, as shown in Fig (4.5,c). The pervaporation unit was used to dehydrate a circulated stream evaporated from the reaction mixture. This layout was advantageous due to the acid- and ester-free permeate obtained, no exposure of the membrane to concentrated acids and high boilers, reduced the energy requirement, and improved effectiveness compared to the first concept.

An economic comparison with the conventional process combining a reactor with distillation revealed that the second layout dehydrating the liquid phase of the reactor by pervaporation
achieved the lowest energy costs being only 7% of the conventional process. The third layout dehydrating the vapour phase by pervaporation may reduce energy costs by 78% compared to the conventional process. Even for the first layout, the energy costs were 58% lower. The same results were observed by comparing the investment costs. It was concluded that the key advantage of the conventional process was its established reliability compared to the alternatives, whilst the first layout seemed to be useful for a plant expansion. The two other alternatives should be taken into considerations if a new plant is projected.

Bruschke et al [17] analysed different process layouts. They found that both a batch process and a continuous cascade process with recycling would lead to high investment costs. Therefore, they proposed the alternative process layout shown in Fig (4.6) combining batch and cascade operation.

![Diagram](image)

**Figure (4.6) Pervaporation-based esterification hybrid process combining batch and cascade operation [17].**

In their layout, the first chemical reactor was operated in batch mode, and the reaction product was recycled by the first pervaporation unit to reduce the water contents without significant concentration changes. The second pervaporation unit was used to completely dehydrate a bleed stream from the first pervaporation unit. This stream was then further processed in the second reactor that was similar to the first, also being combined with two pervaporation units for recirculation and dehydration. It was possible to achieve a conversion rate of 97% and final water concentration of less than 0.5 wt% this process has been reported on the application for a medium size esterification plant. The plant was operated in batch mode for the production of various esters. The construction of a larger plant using the hybrid process combining batch and cascade operation was scheduled.

Till now there are no published studies on using pervaporation-esterification reactor hybrid process for the esterification of EG and TPA. This may be due to the solid state of TPA and the related operational problems in addition to the non-availability of a suitable membrane for the pervaporation unit. In this case, the concept of pervaporation-esterification reactor hybrid process
can be applied after dissolving the solid TPA into the reaction mixture before it is fed to the membrane reactor by using a CSTR of high residence time (enough for total dissociation of TPA) before the pervaporation unit(s). By this application, in addition to the shifting in the reaction equilibrium, considerable savings can also be made in the amount of EG as there is no need for a large amount of EG to shift the equilibrium. Finally, such a process reduces the overall energy consumption, the cycle time in the PET process, and EG/TPA ratio.

4.6.4.2 reactive distillation system

Reactive distillation is an attractive chemical processing technique that combines reaction and separation in a single vessel. Reactive distillation can increase the conversion of an equilibrium limited reaction by continuously removing products from reactants, increase the selectivity in some multi-reaction systems, reduce operating costs by creating a natural heat integration between reaction and separation, and reduce capital costs by lowering the number of unit operations involved in a chemical production process.

The Reactive Distillation (RD) approach combines the reaction step and separation step into a single reactive distillation step. The products are formed in a reactive distillation column and simultaneously removed from the reaction zone by distillation. The required reactants are recycled inside the column and by-products can be removed out from the distillation column. Since the products are continuously removed in the RD approach the chemical equilibrium restrictions of the traditional processes can be avoided and much higher conversion and often selectivity and yield can be achieved.

Ketan et al. (1999) [6] studied the synthesis of prepolymerization stage in a reactive distillation system. They represented a systematic procedure to synthesize feasible process alternatives for the prepolymerization stage in PET production from DMT and TPA with EG. They studied the input and output specifications, the representation of kinetic scheme, the phase and reaction equilibrium, the reactive phase diagrams, and the feasible process flow sheet and operating conditions.

The feasible process flow sheets, based on their article, are:

- CSTR with separator.
- Cascade of CSTRs with separator.
- Flowsheet configurations involving reactive distillation:
  1. Reactive distillation column fed through reboiler.
2. Reactive Distillation columns with recycle streams.
3. Reactive distillation column with product recycle.
4. Reactive distillation column fed through intermediate reboiler
5. Reactive distillation column with distributed addition of solid TPA.

They found that the solid TPA has to be completely dissolved in the solution fed to the reactive distillation column to avoid handling solids in a distillation column to prevent fouling and related operational difficulties. In addition to that, temperature and pressure on each tray of the column should not allow precipitation of TPA.

In the first case they tried to dissolve the solid TPA into the reaction mixture before it is fed to the column by using a CSTR before the column. This reactor acts as the reboiler for the distillation column. Solid TPA and EG are fed to the reboiler then, the liquid and vapor streams from the reboiler form the feed to the distillation column. Water is removed from the top and the prepolymer product is removed from the bottom tray.

In the case of the reactive distillation with recycle stream, they did modifications involved changing the stream destination to make it feasible in the desired range of operating temperature and pressure. Then they recycled a part of the prepolymer product to ensure complete dissociation of the solid TPA.

They found that using reactive distillation system would reduce the residence time, feed ratio of EG/TPA, increase the conversion by shifting the equilibrium, and reducing the costs of recycling EG in the conventional process.

Same concept can be used for the esterification stage. In that article they didn't differentiate between esterification and polycondensation in the prepolymerization stage. Based on that the prepolymerization, like esterification stage, is used to prepare a short-chain polymer that forms the feed to the polymerization stage.

In this project, using pervaporation will be studied. We recommend studying PET process using reactive distillation system in the esterification stage that will reduce the capital cost by reducing the number and the size of reactors and separators, and shift the equilibrium that means reducing EG/TPA ratio.
4.6.5 Selection of catalyst type

In the direct esterification step, the carboxylic groups of TPA catalyze the reaction and no added catalyst is required. Higher temperature and pressure increase the reaction rate.

Selection of a suitable catalyst for the polycondensation step synthesis is very critical for production of high grade of PET. The literature suggests numerous catalysts, but few of them have gained commercial acceptance. A good catalyst should accelerate the polycondensation reaction, it should have good stability in the reaction medium and it should not promote side reactions.

Polycondensation catalysts are insensitive to acid end groups, but their catalytic activity is known to increase as the concentration of hydroxyl end groups decreases. During the polycondensation stage, antimony trioxide or antimony triacetate catalysts are commonly used in the industry. A few manufacturers use germanium oxide, but reportedly it is not as effective as antimony compounds.

Rafler et al. (1974), Tomita (1976a,b), Kamatani and Konagaya (1978), Kamatani et al. (1980) studied the mechanism of polycondensation reactions and concluded that the reaction proceeds by the nucleophilic attack of hydroxyl end groups, upon the ester carbonyl groups. The polycondensation catalysts facilitate the co-ordination of metal ion to the ester carbonyl bond which increases the polarity of this bond and facilitates the nucleophilic attack. In the initial stages of polycondensation, antimony compounds readily form stable compounds containing hydroxyl groups and can’t react with carbonyl groups of esters. Therefore, the catalytic activity of antimony compounds is less at high concentration of hydroxyl end groups observed in the initial stages of polycondensation (Stevenson, 1969). As the polycondensation progresses, the concentration of hydroxyl end groups decreases and the co-ordination of the carbonyl groups to antimony catalyst becomes possible. Therefore, the activity of the antimony catalysts increases as the polycondensation proceeds [18].

Antimony catalyst (antimony trioxide Sb$_2$O$_3$) as a polymerization agent is selected for the polycondensation stage since it is the most common one, and since most of the published kinetics of polycondensation are based on antimony trioxide (Sb$_2$O$_3$).

4.7 Level 4: Separation System Synthesis

The synthesis of the desired product PET is carried out in two reaction steps; esterification and polycondensation. EG and TPA are firstly esterificated into bis-hydroxyethyl
terephthalate (BHET). Secondly, the BHET and some of its oligomers is polymerized to produce PET and EG as by-product. Because of the low solubility of TPA in EG; the molar feed ratio of EG to TPA is normally greater than one. It is found in literature that the optimum ratio for continuous processes is 1.15.

The temperature is between 240 and 260 °C, and the operating pressure is 1-8 bar in the esterification section while, 260-290 °C and less than 30 mm Hg in the polycondensation section. The normal boiling points of EG and water are 197 °C and 100 °C, respectively. Consequently, continuous evaporation of the reactant EG and the by-product water is occurring in the two reaction systems. The rate of evaporation decreases as the operating pressure increases.

At this level a separation system is synthesized to separate water from the linear oligomers, EG, and TPA (l) mixtures that exit from the esterification reactors and water from EG vapor streams that exit from the polycondensation reactors.

4.7.1 Separating system selection

The methodology of Douglas divides the separation system into a vapor recovery system and a liquid recovery system. The streams needed to be separated at the operating conditions of the reactor systems are liquids and vapors.

The output stream(s) from the esterification reaction system(s) include water that have to be separated in order to shift the equilibrium reaction in this section. Water has to be separated from the EG-W vapor mixture that exit from the polycondensation reaction system, then EG has to be recycled to the esterification reaction system, due to its high cost.

The process for PET production that is studied in this project is totally different than the conventional processes especially in the esterification section. In the conventional processes, there are two-product streams exit from each reactor in the esterification reaction system, which means that vapor recovery of EG is required. For this part of separation, distillation was used since there is no azeotrope for EG-water mixture based on the vapor-liquid equilibrium data.

For the modified and intensified process that is studied in this project, there is only one stream that exits from each esterification reactor from which water has to be removed in order to shift the equilibrium reaction in the next reactor that follows the first reactor. The possible techniques, for separating water from the oligomer, EG, and TPA mixture, are given in Table (4.4).
Table (4.4) Techniques for separation of water from the oligomer, EG and TPA mixtures.

<table>
<thead>
<tr>
<th>Rating</th>
<th>Technique</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>+</td>
<td>Distillation</td>
<td>It is a proven technology for the recovery of the vapor of the esterification reactor system. It gives perfect separation and effective for large capacities, but it is not used for the separation of water from the oligomers mixture that exit from each esterification reactor in this modified process because of fouling problems.</td>
</tr>
<tr>
<td>--</td>
<td>Absorption</td>
<td>Can not be used because of:</td>
</tr>
<tr>
<td></td>
<td></td>
<td>- None of the two components is a gas at ambient conditions.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>- High temperature of the vapor mixture (250-300 °C)</td>
</tr>
<tr>
<td>--</td>
<td>Adsorption</td>
<td>Can not be used because of the expected plugging problems in addition that it is not proven technology even for the conventional process.</td>
</tr>
<tr>
<td>+++</td>
<td>Membrane separation</td>
<td>- Energy saving</td>
</tr>
<tr>
<td></td>
<td>(Pervaporation)</td>
<td>- Perfect separation by which enhancement of the reaction occurs in the next reactor that follows the membrane unit.</td>
</tr>
<tr>
<td></td>
<td>- inorganic membrane</td>
<td>- Availability of the membrane that can handle the acidity and high temperatures problems.</td>
</tr>
<tr>
<td>--</td>
<td>- organic membrane</td>
<td>Can not be used because of high temperatures that cause thermal degradation of the membrane material.</td>
</tr>
<tr>
<td>--</td>
<td>Extractive distillation</td>
<td>It is not a proven technology. Generally used for azeotropic mixtures.</td>
</tr>
</tbody>
</table>

Membrane technology (pervaporation) is used for removal of water from aqueous-organic mixtures. Recently, this technology has been applied for the dehydration of ethylene glycol in the commercial production of EG by direct oxidation of ethylene. EG do not form an azeotrope with water, but the separation of EG-water ranks as the eighth most energy intensive distillation process in the chemical industry. Pervaporation has low energy consumption and selective separation; this is the reason for using it there as an alternative.

In our process, pervaporation as a membrane separation technique is used because of low operating costs (energy-saving technique), availability of the membranes that can handle the operating conditions and have high permeability and selectivity of water, and using this technique will give approximately pure stream from water by which enhancement of the esterification reaction occurs.
Since the vapor from the polycondensation reactor system is at high vacuum, in addition that the fraction of water in the output stream is very small, distillation is not used. The vapor from the polymerization reactor system is recovered using a cascade of spray condensers. The spray condensers recover most of the EG generated by the reactions. The ethylene glycol recovered in the spray condensers may be further purified or recycled directly, depending on the product grade. Other alternatives including their disadvantages are explained in Table (4.5).

Table (4.5) Techniques for separation of water from EG vapor.

<table>
<thead>
<tr>
<th>Rating</th>
<th>Technique</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>-</td>
<td>Distillation</td>
<td>It is not a proven technology for the recovery of the vapor of the polycondensation reaction system.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>- High vacuum</td>
</tr>
<tr>
<td></td>
<td></td>
<td>- Very low fraction of water</td>
</tr>
<tr>
<td>++</td>
<td>Condensation</td>
<td>It is a proven technology for the recovery of the vapor of the polycondensation reactor system. It gives perfect separation and effective for large capacities</td>
</tr>
<tr>
<td>--</td>
<td>Absorption</td>
<td>Can not be used because of:</td>
</tr>
<tr>
<td></td>
<td></td>
<td>- None of the two components is a gas at ambient conditions.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>- High temperature of the vapor mixture (250-300 °C)</td>
</tr>
<tr>
<td>--</td>
<td>Adsorption</td>
<td>It is not proven technology.</td>
</tr>
<tr>
<td></td>
<td>Vapor Permeation</td>
<td>- Perfect separation.</td>
</tr>
<tr>
<td>+</td>
<td>- inorganic membrane</td>
<td>- Not proven in industry.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>- Needs very high vacuum in order to cause a gradient force to separate water from EG mixtures (less than 0.5 torr)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>- The amount of water that has to be separated is traces.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>- The energy requirement costs are comparable to that of condensation.</td>
</tr>
<tr>
<td>--</td>
<td>- organic membrane</td>
<td>Can not be used because of high temperatures that cause thermal degradation of the membrane.</td>
</tr>
<tr>
<td>--</td>
<td>Extractive distillation</td>
<td>It is not a proven technology. Generally used for azeotropic mixtures.</td>
</tr>
</tbody>
</table>

4.8 Main Functional Sections

Polyethylene terephthalate (PET) is produced by direct esterification of ethylene glycol (EG) and purified terephthalic acid (TPA). The conceptual flowsheet is shown in Figure (4.7). The
solid TPA is mixed with excess EG to form a solid-liquid paste, the paste is introduced to the first reaction system.

Two reaction systems are required in the PET process. The first reaction system is the esterification system, which is needed for the production of the BHET and water as by-product. The by-product water is separated from the first reactor of the esterification reaction system using pervaporation separation system to shift the equilibrium in the second reactor of the esterification system by removing the by-product (water).

The second reaction system is the polymerization reaction system. This system is required for the conversion of the BHET into the desired PET polymer. The by-product EG is separated from the evaporated EG-water mixture and then recycled to the esterification reactor system.

The separation systems are required to separate the by-product (water) in the esterification system and EG from EG-water vapor mixtures produced from the polycondensation system. A storage section is required for storing the product. Table (4.6) summarize the main functional sections, their numbers and tasks.

Table (4.6) Main functional section, their numbers and tasks.

<table>
<thead>
<tr>
<th>Number</th>
<th>Name</th>
<th>Task</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>Feed section</td>
<td>Raw material supply</td>
</tr>
<tr>
<td>200</td>
<td>Esterification section</td>
<td>Production of the monomer BHET</td>
</tr>
<tr>
<td>300</td>
<td>Polymerization section</td>
<td>Conversion of the monomer into the desired PET polymer</td>
</tr>
<tr>
<td>400</td>
<td>Vapor recovery section</td>
<td>Separation (condensation) of EG from water and recycle EG to the esterification section</td>
</tr>
<tr>
<td>500</td>
<td>Product storage section</td>
<td>PET storage</td>
</tr>
</tbody>
</table>

The connection between the main functional sections forms the conceptual flowsheet as shown in Figure (4.7). The conceptual flowsheet is used as a basis for developing the index flowsheet and the process flowsheet in chapters five and six, respectively.

The overall mole and mass balance calculations of the conceptual flowsheet are done using a Mathcad program, and shown in Table (4.6 and 7). The following assumptions are made:

- Continuous steady-state process.
- No impurities are presented in the feed streams.
- 100% solubility of TPA in EG and reaction mixture in the first reaction system.
• 99% conversion for the esterification reactions that occur in the first reaction system.
• 100% conversion for the polymerization reactions that occur in the second reaction system.
• 99% separation of water from the reaction mixture by using pervaporation technology combined with the first reaction system.
• The molecular weight of the produced PET is 19,000 g/mol.

![PET Conceptual Flowsheet](image)

**Table (4.6) Overall mass balance of the conceptual flowsheet (kg/h).**

<table>
<thead>
<tr>
<th>Stream No.</th>
<th>EG (kg/hr)</th>
<th>TPA (kg/hr)</th>
<th>BHET (kg/hr)</th>
<th>Water (kg/hr)</th>
<th>PET (kg/hr)</th>
<th>Total (kg/hr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3990</td>
<td>0</td>
<td>0</td>
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<tr>
<td>4</td>
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<tr>
<td>5</td>
<td>79.8</td>
<td>106.8</td>
<td>16180</td>
<td>22.94</td>
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<td>16390</td>
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<td>2271</td>
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<tr>
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<td>22.94</td>
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<td>4013</td>
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<tr>
<td>8</td>
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<td>106.8</td>
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<td>0</td>
<td>12270</td>
<td>12377</td>
</tr>
<tr>
<td>9</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>22.94</td>
<td>0</td>
<td>23</td>
</tr>
</tbody>
</table>
Table (4.7) Overall mole balance of the conceptual flowsheet (kmol/h).

<table>
<thead>
<tr>
<th>Stream No.</th>
<th>EG (kmol/hr)</th>
<th>TPA (kmol/hr)</th>
<th>BHET (kmol/hr)</th>
<th>Water (kmol/hr)</th>
<th>PET (kmol/hr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>64.29</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>0</td>
<td>64.28</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>3</td>
<td>64.28</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>4</td>
<td>128.57</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>5</td>
<td>1.286</td>
<td>0.643</td>
<td>63.64</td>
<td>1.273</td>
<td>0</td>
</tr>
<tr>
<td>6</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>127.3</td>
<td>0</td>
</tr>
<tr>
<td>7</td>
<td>64.28</td>
<td>0</td>
<td>0</td>
<td>1.273</td>
<td>0</td>
</tr>
<tr>
<td>8</td>
<td>0</td>
<td>0.643</td>
<td>0</td>
<td>0</td>
<td>0.6458</td>
</tr>
<tr>
<td>9</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>1.273</td>
<td>0</td>
</tr>
</tbody>
</table>

4.9 Conclusions and Recommendations

4.9.1 Conclusions

- Organization of this chapter is done using tree diagram and work diagram of the conceptual flowsheet (Van den Berg, 2000).

- Douglas conceptual design methodology is followed in this project starting with batch versus continuous, then, black box evaluation (Van den Berg, 2000), recycle structure of the flowsheet, and ending with general structure of the flowsheet.

- A decision of considering PET process in this project as a continuous process is taken based on several points of view, specially, the production rate and the operational problems.

- Black box evaluation is done using to produce 100,000 ton/yr PET of 19,000 g/mol based on the assumptions of 100% conversion and separation, then the zero economic potential (Aselberg, 2000) is calculated. It is found that this economic potential is about 41 million US$/yr, based on which, the decision is taken to complete studying this process.

- The recycle structure of the flowsheet is studied by determining the number of reaction systems, the number of recycle streams, excess reactant, the equilibrium limitations, and the catalyst type selection.

- It is decided to consider two reaction systems, one for the esterification stage and another one for the polycondensation stage. This decision is taken based on the operating conditions and the necessity of using catalyst in the polycondensation stage.
• Number of recycle streams is also studied. It is decided to consider one recycle system of stream(s) for the polycondensation reaction system. This decision is based on the different operating pressure of the two streams.

• It is found in literature that in the continuous process, the optimum molar feed ratio of EG/TPA is 1.1-1.3 for the conventional process. It is expected to reduce this ratio to 1.0 as close as possible by using the pervaporation system in the esterification stage.

• Due to the fact that esterifications are equilibrium reactions, high yields can be obtained when a large excess of EG reagent is used. Alternatively, the reaction can be forced toward completion by the removal of the by-product (water). In order to overcome this problem, there are two options to shift the equilibrium of the esterification reactions: using pervaporation-esterification hybrid process or using reactive distillation system. In this project, pervaporation-esterification hybrid process option will be studied.

• Pervaporation-esterification hybrid process will be used between each two esterification reactors in order to shift the equilibrium of the reaction and reduce the ratio of EG/TPA as described in section 4.6.4.1

• Distillation system is chosen to separate the EG-water vapor mixture exiting from the esterification reactor system, and spray condensers system for the polycondensation reactor system.

4.9.2 Recommendations

• We recommend studying PET process using reactive distillation system in the esterification stage that will reduce the capital cost by reducing the number and the size of reactors and separators, and shift the equilibrium that means reducing EG/TPA ratio.

• We recommend studying PET process using vapour permeation technology instead of pervaporation technology, or hybrid process of both of them to remove the by-product water from the esterification output streams.

• After studying the ability of using reactive distillation system and vapor permeation technology, comparison with that of pervaporation-esterification hybrid process, the latest is recommended based on the cycle time of the process and the economical bases.
References


Chapter Five

Index Flowsheet

5.1 Introduction

The functional sections and the conceptual flowsheet of the PET process were developed in chapter four. In this chapter, the process overall data based on the functional sections and unit operations will be given.

The objective of this chapter is to develop the index flowsheet. This flowsheet shows the number of the main process equipment and their interconnections. In addition to that, it indicates the operational costs based on the unit ratios of the utilities.

In this chapter the work organization is discussed initially. After that, process design data, flowsheet interconnectivity and selection of the operating conditions will be discussed. Finally, an evaluation for the index flowsheet is given.

5.2 Work Organization

5.2.1 Tree diagram

The index flowsheet is based on the conceptual flowsheet and the simulation results. The equipment in the functional sections of the process flowsheet has to be selected based on industrial proven technology and technical capabilities. The process design data are gotten from the design basis and the flowsheet simulation. The equipment and their interconnections in addition to the process design data are shown in the index flowsheet. Figure (5.1) shows the tree diagram of the index flowsheet.
The work diagram, which depicts the construction of the index flowsheet, is shown in Figure (5.2). The equipment and their interconnectivity are selected for the functional sections in the conceptual flowsheet. The equipment are selected based on literature recommendations. After that, preliminary operating conditions for the process are determined.

The process design data are gotten from the design basis and the flowsheet simulation, which require knowledge of aspen plus and polymer plus. The number or type of equipment may change according to the flowsheet simulation. Finally, the index flowsheet is drawn.
5.3 Index Flowsheet

The index flowsheet is shown at the end of this chapter (folded page). In this flowsheet, the type and number of the equipment is shown.

5.3.1 Process design data

Table (5.1) shows the source of the process design data in the index flowsheet.

<table>
<thead>
<tr>
<th>Process design data</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>Design production rate</td>
<td>Design basis</td>
</tr>
<tr>
<td>Product and raw materials specifications</td>
<td>Design basis</td>
</tr>
<tr>
<td>Unit ratios</td>
<td>Aspen plus and polymer plus simulation</td>
</tr>
<tr>
<td>Reactions</td>
<td>Design basis</td>
</tr>
<tr>
<td>Product and recycle</td>
<td>Aspen plus and polymer plus simulation</td>
</tr>
<tr>
<td>Waste stream</td>
<td>Aspen plus and polymer plus simulation</td>
</tr>
<tr>
<td>Ambient design criteria</td>
<td>Design basis</td>
</tr>
</tbody>
</table>

Table (5.2) shows that about 3.4 MUS$ per year is needed for the utilities. The prices are updated using Marshall and Swift Equipment Cost Index for the third quarter of year 2000. The zeroth-order economic potential estimated in chapter four ($EP_0 = 41$ MUS$/yr)$ is based on

<table>
<thead>
<tr>
<th>Utility</th>
<th>Unit Ratio (per 1 metric ton of PET)</th>
<th>Price (kUS$/unit)</th>
<th>Cost per year (kUS$/yr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electricity (kWh)</td>
<td>4.48</td>
<td>8.47</td>
<td>37.9</td>
</tr>
<tr>
<td>Cooling water (kg)</td>
<td>0.79</td>
<td>0.001</td>
<td>0.00079</td>
</tr>
<tr>
<td>Chilled water (kg)</td>
<td>0.04</td>
<td>0.008</td>
<td>0.00032</td>
</tr>
<tr>
<td>Saturated steam (kg)</td>
<td>34 bara</td>
<td>1198</td>
<td>2.32</td>
</tr>
<tr>
<td></td>
<td>76 bara</td>
<td>135.5</td>
<td>3.86</td>
</tr>
<tr>
<td></td>
<td>Total</td>
<td></td>
<td>Total = 3,340</td>
</tr>
</tbody>
</table>

(1) Coulson and Richardson, 1999
(2) Douglas, 1988
product price and raw materials cost. After knowing the utility cost the zeroth-economic potential can be adjusted by deducting the utility cost. This new economic potential is called the first-order economic potential (Asselberg, 2000). EP1 equals to 37.6 MUS$/yr. It can be concluded that the design is still feasible and the process design will be continued.

5.3.2 Flowsheet interconnectivity

The interconnectivity of the flowsheet is shown in Figure (5.3). The functional sections of the conceptual flowsheet (boxes with dashed lines) are split up. The gray-colored boxes distinguish the unit operations in every functional section. Every box represents a chemical conversion, a physical separation or both, which has to be performed in a process equipment. The next section describes functions of the functional sections and their equipment.

Figure (5.3) Functional sections and unit operations of the PET process
5.4 Selection of Operating Conditions and Equipment

This section illustrates the choice of operating conditions and equipment of the PET process. Appendix E shows an overview of the selected operating conditions of the main equipment.

5.4.1 Feed preparation section (S-100)

The goal of this section is to mix the solid terephthalic acid (TPA) with ethylene glycol (EG) and to control the mole ratio between them. Solid TPA at room temperature has a limited solubility in EG and the polymer solution even at relatively high temperatures. Further, the dissolution rate of TPA may be limited by the solid-liquid mass transfer rate.

It is desirable to operate the reactor in the esterification stage with an excess of EG to increase the solubility of TPA and to increase the conversion of the reactions. However, the use of excess EG is not economical because of the large energy requirements of EG vaporization and condensation in addition to the high cost of the EG. Therefore, this is a good reason to determine the optimal mole feed ratio of EG to TPA through simulation.

The addition of a pervaporation membrane as unit operation instead of distillation in the conventional processes has two advantages. First, it increases the conversion of EG due to the complete removal of the water from the reaction mixture. Second, it decreases the losses of EG which decreases the optimum mole feed ratio of EG to TPA.

5.4.2 Esterification section (S-200)

The goal of this section is the esterification of TPA with EG. The product of the esterification reactors is composed of short-chain oligomers with some residual monomers. The main oligomer in the product is bis-hydroxyethyl terephthalate (BHET). However, the rate of the esterification reaction is low since it is a reversible reaction. Consequently, to produce BHET in high proportion it is required that, the overall reaction is driven in the forward direction through either using excess of EG or fast removal of the condensation product, water (Gupta and Kumar, 1987). The degree of polymerization in this section is in the range 1-10 (Jie Zhang et. al., 1998). However, the degree of polymerization is very sensitive to the water content and the glycol-acid ratio in the reactor.
Typically, the primary esterification reactor is operated at a pressure of 1-8 bar and a temperature of 240-260 °C. At lower temperatures the reactions do not progress appreciably in addition to the low solubility of TPA in the oligomer. At higher temperatures the rate of formation of undesired products such as DEG increases (Ravindranath and Mashelkar, 1986) and the reactor performance is limited by the solid-liquid mass-transfer rate (David A. Trebly, 1999). Consequently, The performance of the reactor is highly non-ideal since the apparent reactor volume depends on the amount of solid TPA. Typical residence times of the primary estifier ranges from one to four hours, where as the secondary and tertiary esterifier residence time on the order of an hour (Polymer Plus Manual). The output of the primary esterifier is sent to the pervaporation membrane section to remove the esterification by-product (water).

The oligomer from the pervaporation membrane is fed to the secondary esterifier, which is usually operated close to atmospheric conditions with temperatures slightly higher than the primary esterifier. At higher pressures the conversion of TPA decreases while below that the loss of EG increases (Gupta and Kumar, 1987). The output liquid mixture of the secondary and tertiary esterifier is sent to pervaporation membranes to remove the esterification by-product (water).

Several types of reactors are commonly used for carrying out these reactions, each have their own advantages and disadvantages. The following table summarizes their characteristics (Gupta and Kumar, 1987)

| Table (5.3) Characteristics of common reactors used in the esterification section, (Gupta and Kumar, 1987) |
|---|---|---|---|
| Plug Flow Reactor (PFR) | Continuous Stirred Tank reactor (CSTR) |
| Advantages | Disadvantages | Advantages | Disadvantages |
| - High Reynolds numbers (turbulent flow) | - Lack of agitation | - Overcomes mixing problem | - Wide residence time distribution |
| - Uniform velocity across the reactor | - Problems with high viscous products | - Good heat transfer characteristics | - Can not attain high conversions |
| | | - Controlled wall deposit using appropriate stirrers | |

At room temperature TPA has limited solubility in the esterification solution, even at relatively high temperatures. The solid-liquid mass transfer may limit the dissolution rate of TPA, especially if the average particle size is large, or when the reactor operates at high temperature and pressure. To maintain a well-mixed condition in the esterification reactors, a stirred tank reactor is normally used in industry (Gupta and Kumar, 1987).
The preliminary operating conditions are selected based on literature recommendations. These conditions will be modified according to the simulation and sensitivity analysis on the process. The selected operating conditions for this section are shown in Table (5.4)

<table>
<thead>
<tr>
<th></th>
<th>Primary Esterifier</th>
<th>Secondary esterifier</th>
<th>Tertiary esterifier</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature</td>
<td>240-260°C</td>
<td>240-260°C</td>
<td>240-260°C</td>
</tr>
<tr>
<td>Pressure</td>
<td>1-8 bar</td>
<td>Close to atmospheric pressure</td>
<td>Close to atmospheric pressure</td>
</tr>
<tr>
<td>Residence Time</td>
<td>1-4 hr</td>
<td>Order of 1 hr</td>
<td>Order of 1 hr</td>
</tr>
</tbody>
</table>

The temperature in this section is restricted to 240 °C due to the use of silica membranes in the pervaporation section which can operate at temperature up to 240 °C (Sulzer Technical Review, 2000) as explained in section 5.4.3.

### 5.4.3 Pervaporation section (S-400)

The goal of this section is to remove the water produced from the esterification reaction mixture. These reactions are equilibrium–limited, so removal of co-product water is important for maximizing yield, throughput and product purity.

The pervaporation membrane section should withstand the operating conditions in the esterification section. Polymer membranes are well established and have a good operating record, as long as they are operated within their limitations. At high temperatures the polymer membrane is degraded and consequently, ceramic membrane is needed. An initial focus was Zeolite-A membranes, which have pores small enough to pass water molecules, but not molecules such as EG. Unfortunately, Zeolite-A membranes are very sensitive to even the slight acidity. Although composite membranes are acid-resistant, fluxes are modest and operation temperature is restricted to below 110 °C (Sulzer Chemtech, 2000).

Sulzer Chemtech Membrane Systems has developed tubular ceramic membranes externally coated with amorphous silica. These membranes can be operated for pervaporation and vapor permeation. It withstands high temperatures up to 240 °C, high pressures up to 35 bar and wide range of acidity.

The liquid reaction mixture passes through a microporous silica pervaporation membrane (Sulzer Chemtech, 2000). In this kind of microporous membranes the selectivity is based on preferential adsorption of one of the components, which is in this case water, and the flux is governed by a surface diffusion regime (L. Cot et al., 2000). Figure (5.3) shows the configuration of the selected ceramic membrane (Sulzer Chemtech, 2000).
5.4.4 Polymerization section (S-300)

The goal of this section is to manufacture the fiber grade polyethylene terephthalate (PET) by subjecting the BHET to the following three stages of polymerization:

Low polymerization stage is typically composed of a simple CSTR. It operates at a medium vacuum pressure (50-500 Torr). This stage strips off most of the excess EG and water remaining in the polymer. In most plants, the polymer intrinsic viscosity in the low polymerizer is 0.2 dL/g and the low polymerizer behaves ideally. At higher viscosity levels, the low polymerizer becomes increasing mass-transfer limited, (David A. Trebly, 1999). In this stage the degree of polymerization increases up to 30 (Ravindranath and Mashelkar, 1986).

Intermediate and high polymerization stages are composed of reactors known as the intermediate polymerizer and the high polymerizer. It is preferable to use devices where highly viscous molten mass can be continuously generated in the form of thin films by suitable mechanical action. Such devices may be classified as rotating disc contactors, wiped film devices, partially filled screw extruders, etc. Two main devices that are used in industry are wiped film reactors and disc-ring contactors (Ravindranath and Mashelkar, 1986).
These reactors operate at increasingly higher temperatures up to 290 °C, to avoid polymer degradation, and lower pressure often as low as one Torr. These operating conditions enhance the devolatilization of excess glycol and reaction by products such as water, so that the polymerization is driven more in the forward direction to form PET of high molecular weight (Polymer Plus Manual, 1999).

The Intermediate and high polymerization reactors are selected to be disk-ring reactors, which contain a number of annular disks attached to a rotating shaft. Polymer flows through holes cut into the discs. As the discs rotate they generate a surface film, which enhances the evaporation rate. Due to the viscosity of the polymer, the performance of the finishing reactors is limited by the liquid-vapor mass-transfer rate. Therefore, the design criteria of these reactors are to maximize surface area generation while minimizing back mixing. Reactor residence times range from thirty minutes to four hours depending on the number and type of reactors in the polymerization section (Polymer Plus Manual, 1999).

Aspen and Polymer Plus simulation do not take into account mass-transfer limitations encountered in the last two stages. The Polymer Group at Aspen Tech has put together a “Polyester technology Package”. This package contains process models, with literature based fitted kinetics, and also includes some added features, such as accounting for mass transfer in esterification and finisher reactors. This package is just sold to industrial customers for a rather large amount of money (John Franjione, Ph.D., Polymers IBU, Aspen Tech). The finishing reactors are simulated as plug flow reactor connected to a flash drum with vapor and liquid as valid phases. This is because the finishing reactor contains a series of disks and every disk is considered as a CSTR, so that the series can be simulated as a plug flow reactor.

The esterification section operates below the melting point of the polymer. Under this condition, the process can be considered solution polymerization. The polymerization reactors operate above the melting point of the polymer in a true melt-phase polymerization. The step growth model is used for both modes of operation (Polymer Plus Manual, 1999).

5.4.5 Condensation section (S-500)

The goal of this section is to recover the vapor, which consists mainly of EG and water from the polymerization section. The vapor can be recovered using distillation or condensation. Condensation is selected due to its lower fixed and operating cost. Spray condensers are selected to recover the vapor generated by the polymerization section since they are inexpensive,
cannot be fouled and they have very high heat transfer rates per unit volume (Kakaç and Liu, 1997).

The spray condenser is the most common direct contact condenser in which sub cooled liquid is sprayed into the vapor (Ullmann’s Encyclopedia, 2000). The spray condenser loop is composed of a contacting vessel, accumulation tank, pump, and heat exchanger. In most plants, vacuum is generated through venturi jets operated by steam or vaporized glycol.

The condensed vapor mixture is then sent to a pervaporation membrane where water is separated from EG and the later is recycled to the mixing tank in the feed preparation section.

5.4.6 Product storage section (S-600)

The goal of this section is to store the produced PET polymer. The produced polymer from the polymerization stage has an average intrinsic viscosity of 0.6 dl/g, which corresponds to a number-average degree of polymerization near 100. This product may be directly spun as clothing fiber, partially oriented yarn (POY), film, or it may be cooled and chipped for on- or off-site use.

5.5 Conclusions

- The first-order economic potential EP1 equals to 37.6 MUSS/yr. It can be concluded that the design is still feasible and the process design will be continued.

- Adding a pervaporation membrane section remove the co-product water, which is important for maximizing yield, throughput and product purity.

- The degree of polymerization in the esterification section is in the range 1-10.

- The pervaporation membrane is simulated as a separation unit (SEP2).

- The Intermediate and high polymerization reactors are selected to be disk-ring reactors.

- The finishing reactors are simulated as plug flow reactor connected to a flash drum with vapor and liquid as valid phases.

- In the low polymerization stage the degree of polymerization increases up to 30 (Ravindranath and Mashelkar, 1986).
• The produced polymer from the polymerization stage has an average intrinsic viscosity of 0.6 dl/g, which corresponds to a number-average degree of polymerization near 100.

• The equipment and the operating conditions of the PET process are selected.

• The index flowsheet for the proposed design of the PET process has been developed.

References


7. Sulzer Chemtech GmbH, Membranetechnik, Nick Wynn, Friedrichsthaler Straase 19, DE-66540 Neunkirchen, Germany, E-mail: nick.wynn@sulzermembranes.com


Chapter Six

Process Flowsheet

6.1 Introduction

This chapter discusses the development of the process flowsheet of the PET process. It starts with the tree and working diagram that represent the organization tools used in this project. The process flowsheet is synthesized from the index flowsheet simulation. The mass and energy balance results from the simulation are used for the sizing of the equipment. The heat integration and main process control are discussed. Finally, the chapter will be summarized by the conclusions at the end of the chapter.

6.2 Work Organization

The goal of this chapter is the development of the process flowsheet. This flowsheet shows the following information

- All process equipment and their interconnectivities,
- Sizes and material of construction of the equipment,
- Main process control, and
- Mass and energy balances.

The tree and working diagram summarize and organize the activities needed to develop the process flowsheet.

6.2.1 Tree diagram

The tree diagram of the development of the process flowsheet is shown in Figure (6.1). The selected equipment in the index flowsheet (see chapter 5) is simulated using the flowsheet simulators: ASPEN PLUS (version 10.1) and POLYMER PLUS. For accurate estimation of the physical and thermodynamic properties of the pure components of the mixtures, an appropriate property set is selected. The mass and energy balances are used to determine the sizes of the main equipment and unit ratios of the utilities.
For the optimization of the process the sensitivity analysis is done to determine the design variables of the process. Finally, the main process control is set up to stabilize the process and reduce off-spec products by determining the manipulated and controlled variables.

Figure (6.1) Tree diagram of the Process Flowsheet

6.2.2 Work diagram

This diagram organizes the sequence of activities indicated in the tree diagram. The working diagram of the process flowsheet is shown in Figure (6.2).
Figure (6.2) Work diagram of the Process Flowsheet
6.3 Flowsheet Simulation

This section discusses the flowsheet simulation in ASPEN PLUS and POLYMER PLUS. The discussion includes:
- Property set selection,
- Simulation strategy,
- Design variables and preliminary process optimization, and
- Mass and energy balances.

6.3.1 Property set selection

All physical and thermodynamic properties of pure components and mixtures are calculated using the selected global property set. Consequently, the accuracy of the mass and energy balances depends on the accuracy of the selected property set.

The property set is selected using Polymer Plus Guidelines, 1999. The process contains polar (non-ideal) components such as water and ethylene glycol and it contains polymeric components such as PET and its segments. Consequently, the Polymer Non-Random Two Liquid activity coefficient model (POLYNRTL) is selected.

6.3.2 Simulation strategy

The PET process is a polymerization process. This process can not be simulated using ASPEN PLUS alone. The polymer plus package is needed for two reasons. First, to estimate physical and thermodynamic properties of the monomers and the polymer produced. Second, to define the step growth polymerization reactions occur in the reactors.

The components and segments of the step growth polymerization reactions given in chapter two are defined. Then, the step growth polymerization reactions are generated and their rate constants given in chapter two are assigned. Both, components definition and reactions generation are done using the Guidelines of Polymer Plus, 1999. More details are given in Appendix J.

The process is built and simulated step by step. It is started with raw materials mixer and primary esterification reactor. Then, the pervaporation membrane, which is simulated as a separation unit (SEP2), is added. Because the conversion did not reach the required value (99 %) in residence time of two hours as recommended by literature, a secondary esterification reactor is
added. This strategy is followed till the flowsheet is totally developed without recycle. When the total flowsheet is converged, the recycle stream is closed.

Our major concern was in the esterification section where we want to investigate new ideas, whereas nothing new is added to the polymerization section. The investigated two approaches in the esterification section, which are mentioned in chapter four; are the pervaporation membrane reactors and the pervaporation membranes. The idea of the first approach is investigated through the simulation and the second approach is considered in the project.

- **Pervaporation membrane reactors**

  The idea of using process intensification is investigated. A pervaporation membrane reactor is used as a secondary esterification reactor. This reactor acts as a plug flow reactor for carrying out the esterification reaction and a membrane for separating the by-product water simultaneously. This approach is not favored since the reaction time is much higher than the separation time, i.e.; the reaction time is the limiting step. Consequently, very high membrane volume is needed to carry out the reaction, which make this approach very expensive. Coupling the membrane with a steel pipe may solve this problem, so that the separation occurs in the membrane, whereas the reaction occurs in the steel pipe.

- **Pervaporation membranes**

  This approach is considered in the simulation as discussed in chapter four. Silica membrane system is used for separating the by-product water from the reaction mixture. The operating temperature in the esterification section is limited to 240 °C, which is the maximum temperature that the membrane can withstand.

**6.3.2.1 Simulation of esterification reactors**

The esterification reactors are simulated as CSTR’s with vapor and liquid as valid phases. The temperature in these reactors is limited to 240 °C, which is the maximum temperature that the pervaporation silica membranes can withstand. The optimum pressures are selected after making a sensitivity analysis on the conversion and degree of polymerization on every reactor as discussed in section 6.3.3.
6.3.2.2 Simulation of polymerization reactors

The low polymerizer is simulated as a CSTR whereas the intermediate (LP) and high (HP) polymerization reactors are simulated as PFR’s connected to a flash drum with vapor and liquid as valid phases. The operating conditions in the low polymerizer are selected after making a sensitivity analysis whereas the operating conditions in the LP and HP are selected from literature. No sensitivity analysis is done for the LP and HP since the reactors in ASPEN PLUS package does not account for mass-transfer limitations for water and EG from liquid phase to vapor phase. This limitation is represented in our simulation by making the pressure slightly higher in the PFR than the flash drum.

6.3.2.3 Simulation of pervaporation membranes

In ASPEN PLUS package there is no item called membrane. Consequently, the function of the membrane is simulated using the unit operation model of SEP2. In this unit operation the water is removed completely from the reaction mixture. The cooling duty for condensing the separated water and the vacuum needed for the membrane to perform this separation are estimated in the membrane sizing.

6.3.2.3 Simulation of spray condensers

The three spray condensers are simulated as one heat exchanger. The detailed specifications of these condensers are specified in the spray condensers sizing.

6.3.3 Design variables and preliminary process optimization

The objective of this section is to determine the optimum operating conditions in the PET process. The optimization task is reduced by dividing the process into more manageable sections. Then, identifying the key variables and concentrating work, where the effort involved will give the greatest benefit. The key variables in this process are the molar feed ratio and the operating conditions in the esterification section. Consequently, our optimization is concentrated on these variables. However, it is difficult to optimize the polymerization section since more specialized packages like polyester package is needed.
6.3.3.1 Feed preparation section

For this section the molar feed ratio of EG to TPA is the most important design variable. It is found that as this ratio is increased, the conversion of TPA in the esterification section is increased. On the other hand, the degree of polymerization in the polymerization section is decreased. This is because EG is a by-product of the reversible polymerization reaction and higher ratio of EG to TPA will increase the rate of the reversible reaction and decrease the degree of polymerization. Consequently, it is important to optimize this ratio. The optimum value of this ratio is found to be 1.07.

6.3.3.2 Esterification section

The main design variables in this section are the reactor temperature and reactor pressure. Due to the use of pervaporation membranes, which their stability is limited to 240 °C, the temperature in the reactors of this section is set to 240 °C. A sensitivity analysis is carried out for the esterification reactors to show the effect of the operating pressure on the TPA conversion and the degree of polymerization.

The selected pressure in these reactors is chosen based on TPA conversion and degree of polymerization. For high degree of polymerizations, the viscosity of the mixture increases which affects the performance of the membranes. The intersection between the two curves; the one of TPA in the output stream (which indicates the conversion) and that of the degree of polymerization is selected to be the operating pressure. This may not give the optimum but it gives a reasonable operating pressure far from the extreme conditions (low conversion or high degree of polymerization).

The residence time is selected in the three reactors so that the total conversion of TPA in the whole process is 99 %, since esterification reactions continues in the low polymerizer in the polymerization section.

The pressure in the primary esterifier is found to be 4.5 bar. This pressure corresponds to a TPA conversion of 86 % and a degree of polymerization of 5.7. Figure (6.3) shows the sensitivity analysis done on the primary esterification reactor.
The pressure in the secondary esterifier is found to be 2.9 bar. This pressure corresponds to a TPA conversion of 95% and a degree of polymerization of 7.7. Figure (6.4) shows the sensitivity analysis done on the secondary esterification reactor.

The pressure in the tertiary esterifier is found to be 1.4 bar. This pressure corresponds to a TPA conversion of 97% and a degree of polymerization of 10.7. Figure (6.5) shows the sensitivity analysis done on the tertiary esterification reactor.
6.3.3.3 Polymerization section

Sensitivity analysis is done only on the low polymerizer as explained earlier. The pressure in the low polymerizer is found to be 137 Torr. This pressure corresponds to a TPA conversion of 99.2 % and a degree of polymerization of 23.5. Figure (6.6) shows the sensitivity analysis done on the low polymerizer.

6.3.4 Mass and energy balances

The mass and energy balances can be used to identify critical units and variables, and provide basis for many control and instrumentation decisions. Temperature and heat flow information contained in the mass and the energy balances can be used to target specific areas.
for energy conservation. Utility demands are estimated depicted in the index flowsheet. Heat integration is defined from this data so that the final plant design can be as energy efficient as possible. The mass and energy balances are taken from the ASPEN PLUS simulation. The results are depicted for the main process streams in the process flowsheets. The process flowsheets are the folded pages on the end of this chapter.

6.4 Selection of Material of Construction

Materials of construction should be selected based on economical considerations to satisfy both process and mechanical requirements; this will be the material that gives the lowest cost over the working life of the plant, allowing for maintenance and replacement. Other factors such as product contamination and process safety must be considered.

Carbon steel is the most commonly used engineering material, as it is cheap, available in a wide range of standard forms and sizes, and can be easily worked and welded. It will be used for all columns and paraphernalia unless conditions dictate otherwise. When carbon steel is not available, the next cheapest material that can withstand the conditions will be selected. Table (6.1) discusses the selection of materials of construction for PET plant.


<table>
<thead>
<tr>
<th>Rating</th>
<th>Material of construction</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>++</td>
<td>Carbon steel</td>
<td>It is relatively cheap, and its corrosion resistance is less than 20 Mil Penetration per year at operating temperature less than 30 °C. It is not efficient at high temperatures like 240 °C. It is recommended to be used as a material of construction for the TPA bin.</td>
</tr>
<tr>
<td>++</td>
<td>Stainless steel 316</td>
<td>It is more expensive than carbon steel. Its corrosion resistance is less than 20 Mil Penetration per year at temperatures up to our operating range, 240 °C. It is recommended to be used as a material of construction for the esterification reactors, polymerization reactors, spray condensers, and the agitators of the agitated vessel and the reactors.</td>
</tr>
<tr>
<td>++</td>
<td>Aluminum</td>
<td>It is more expensive than carbon steel. Its corrosion resistance is the highest; less than 2 Mil Penetration per year at temperature below 45 °C. It is recommended to be used as a material of construction for the EG storage tank and the agitated vessel and the pumps.</td>
</tr>
<tr>
<td>+</td>
<td>Copper</td>
<td>It is more expensive than carbon steel with similar corrosion resistance at a temperature below 32 °C</td>
</tr>
<tr>
<td>+</td>
<td>Nickel</td>
<td>It is little bit less expensive than stainless steel 316 with the same corrosion resistance up to 100 °C</td>
</tr>
<tr>
<td>++</td>
<td>Ceramic-silica</td>
<td>It is acid resistant, and can withstand high temperature up to 240 °C. It is recommended to be used as a material of construction for the pervaporation membranes.</td>
</tr>
</tbody>
</table>

Y. Banat & Z. Abu El-rub
The major factors influencing the materials of construction selection in this process are high temperature ranges and pH (corrosion). The temperatures in this process range from 25 °C in the storage tanks of the raw materials to 290 °C in the high polymerizer.

### 6.5 Selection of Equipment Type and Sizing

In the following section, the specific pieces of equipment as identified in the index flowsheet will be selected. This will allow for their sizing, which will be used for capital cost estimation. The equipment sizes will also indicate practical issues. The detailed sizing is shown Appendix E.

#### 6.5.1 Mixing tank sizing (M-100)

The detailed sizing of the vessel is shown in Appendix E. The summary of the agitated vessel sizing is shown in Table (6.2).

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Formula</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>H_t</td>
<td>D_t</td>
<td>1.02</td>
</tr>
<tr>
<td>D_a = 0.4 D_t</td>
<td></td>
<td>0.41</td>
</tr>
<tr>
<td>C = D_t / 3</td>
<td></td>
<td>0.39</td>
</tr>
<tr>
<td>W = D_a / 5</td>
<td></td>
<td>0.08</td>
</tr>
<tr>
<td>D_s = 2D_a / 3</td>
<td></td>
<td>0.27</td>
</tr>
<tr>
<td>L = D_s / 4</td>
<td></td>
<td>0.10</td>
</tr>
<tr>
<td>J = D_t / 12</td>
<td></td>
<td>0.09</td>
</tr>
<tr>
<td>Mixer type</td>
<td>Six blade turbine with disk</td>
<td></td>
</tr>
<tr>
<td>Power consumption (kW)</td>
<td>3.18</td>
<td></td>
</tr>
<tr>
<td>Material of construction</td>
<td>Aluminum</td>
<td></td>
</tr>
</tbody>
</table>

#### 6.5.2 Storage tanks sizing

To assure uninterrupted operation, a storage capacity is usually provided for raw materials. A storage tank for EG large enough to accommodate one or several loads discharged from the transporters is needed. A 15 to 30 days storage is recommended by Bassel, 1990 and Ulrich, 1984. The sizing of the EG storage tanks is shown in Appendix E and its sizing results are shown in Table (6.3)
Table (6.3): EG storage tank sizing results

<p>| | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Storage tank volume</td>
<td>m³</td>
<td>1,625</td>
</tr>
<tr>
<td>Tank diameter</td>
<td>m</td>
<td>13.7</td>
</tr>
<tr>
<td>Tank height</td>
<td>m</td>
<td>11</td>
</tr>
<tr>
<td>Approximate capacity</td>
<td>m³/m</td>
<td>148</td>
</tr>
<tr>
<td>Material of Construction</td>
<td>-</td>
<td>Aluminum</td>
</tr>
</tbody>
</table>

For TPA, the bags of this material are stored in specially provided areas, which must be dry and free from dust. In addition to this area, a bin is used for the solid TPA as an in process with capacity of 8 hours throughput as recommended Ulrich, 1984. The sizing of the TPA bin is shown in Appendix E and its sizing results are shown in Table (6.4)

Table (6.4): TPA bin sizing results

<p>| | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Bin volume</td>
<td>m³</td>
<td>46</td>
</tr>
<tr>
<td>Height</td>
<td>m</td>
<td>5.09</td>
</tr>
<tr>
<td>Diameter</td>
<td>m</td>
<td>3.39</td>
</tr>
<tr>
<td>Cone angle</td>
<td>-</td>
<td>30°</td>
</tr>
<tr>
<td>Material of construction</td>
<td>-</td>
<td>Carbon steel</td>
</tr>
</tbody>
</table>

6.5.3 Esterification reactors

Several types of reactors are commonly used for carrying out esterification reactions, each have their own advantages and characteristics. The following table summarizes their advantages and disadvantages (Gupta and Kumar, 1987)

Table (6.5): Characteristics of common reactors used in the esterification section

<table>
<thead>
<tr>
<th></th>
<th>Plug Flow Reactor (PFR)</th>
<th>Continuous Stirred Tank reactor (CSTR)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Advantages</td>
<td>Disadvantages</td>
<td>Advantages</td>
</tr>
<tr>
<td>- High Reynolds numbers</td>
<td>- lack of agitation</td>
<td>- Overcomes mixing problem</td>
</tr>
<tr>
<td>(turbulent flow)</td>
<td></td>
<td>- Wide residence time distribution</td>
</tr>
<tr>
<td>- Uniform velocity across the reactor</td>
<td>-Problems with high viscous products</td>
<td>- good heat transfer characteristics</td>
</tr>
<tr>
<td></td>
<td></td>
<td>- can not attain high conversions</td>
</tr>
<tr>
<td></td>
<td></td>
<td>- controlled wall deposit using appropriate stirrers</td>
</tr>
</tbody>
</table>
Detailed sizing including reactor volume, reactor dimensions, mixer sizing, heating jacket, power requirement, and reactor vessel thickness is made for the primary esterification reactor (R-200) and for the secondary esterification reactors (R-210) and (R-220). The data required for the reactor sizing are obtained from the simulation results including the average volumetric flow rate and the reactor residence time. The obtained results are summarized in the tables below.

Table (6.6): Summary of the dimensions of the esterification reactors.

<table>
<thead>
<tr>
<th></th>
<th>R-200</th>
<th>R-210</th>
<th>R-220</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total Reactor volume, m³</td>
<td>22.0</td>
<td>9.51</td>
<td>9.51</td>
</tr>
<tr>
<td>Volume liquid in the reactor, m³</td>
<td>19.8</td>
<td>8.6</td>
<td>8.6</td>
</tr>
<tr>
<td>Diameter, m</td>
<td>2.33</td>
<td>1.76</td>
<td>1.76</td>
</tr>
<tr>
<td>Liquid height, m</td>
<td>4.66</td>
<td>3.52</td>
<td>3.52</td>
</tr>
<tr>
<td>Reactor height, m</td>
<td>5.17</td>
<td>3.91</td>
<td>3.91</td>
</tr>
<tr>
<td>Vessel calculated thickness, mm</td>
<td>2.2</td>
<td>1.1</td>
<td>0.5</td>
</tr>
<tr>
<td>Vessel practical thickness, mm</td>
<td>9</td>
<td>7</td>
<td>7</td>
</tr>
</tbody>
</table>

Table (6.7): Summary of agitator geometric proportions in the esterification reactors

<table>
<thead>
<tr>
<th>Standard Geometric Proportion</th>
<th>R-200</th>
<th>R-210</th>
<th>R-220</th>
</tr>
</thead>
<tbody>
<tr>
<td>( H_s = 2 , D_t )</td>
<td>4.66</td>
<td>3.52</td>
<td>3.52</td>
</tr>
<tr>
<td>( D_s = 0.4 , D_t )</td>
<td>0.93</td>
<td>0.70</td>
<td>0.70</td>
</tr>
<tr>
<td>( C = D_t / 3 )</td>
<td>0.78</td>
<td>0.59</td>
<td>0.59</td>
</tr>
<tr>
<td>( W = D_s / 5 )</td>
<td>0.19</td>
<td>0.14</td>
<td>0.14</td>
</tr>
<tr>
<td>( D_s = 2D_o / 3 )</td>
<td>0.62</td>
<td>0.47</td>
<td>0.47</td>
</tr>
<tr>
<td>( L = D_o / 4 )</td>
<td>0.23</td>
<td>0.18</td>
<td>0.18</td>
</tr>
<tr>
<td>( J = D_t / 12 )</td>
<td>0.19</td>
<td>0.15</td>
<td>0.15</td>
</tr>
</tbody>
</table>

Table (6.8): Summary of Power consumption in the esterification reactors

<table>
<thead>
<tr>
<th></th>
<th>R-200</th>
<th>R-210</th>
<th>R-220</th>
</tr>
</thead>
<tbody>
<tr>
<td>Agitator speed, rpm</td>
<td>50</td>
<td>50</td>
<td>50</td>
</tr>
<tr>
<td>Reynold’s number</td>
<td>1000,000</td>
<td>435,000</td>
<td>426,000</td>
</tr>
<tr>
<td>Power consumption, kW</td>
<td>4.17</td>
<td>2.40</td>
<td>1.88</td>
</tr>
</tbody>
</table>

Table (6.9): Summary of material of construction of esterification reactors

<table>
<thead>
<tr>
<th>Component</th>
<th>R-200</th>
<th>R-210</th>
<th>R-220</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vessel</td>
<td>Stainless steel 316</td>
<td>Stainless steel 316</td>
<td>Stainless steel 316</td>
</tr>
<tr>
<td>Agitator</td>
<td>Stainless steel 316</td>
<td>Stainless steel 316</td>
<td>Stainless steel 316</td>
</tr>
</tbody>
</table>
6.5.4 Pervaporation membranes sizing

Several types of membranes are used for separating water from EG. Table (6.10) summarises their characteristics:

Table (6.10): Pervaporation membrane selection

<table>
<thead>
<tr>
<th>Rating</th>
<th>Membrane type</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>-</td>
<td>Organic membranes</td>
<td>Good operating records as long as they are operated within their limitations. The polymer is degraded at high temperatures such as 240 °C.</td>
</tr>
<tr>
<td>-</td>
<td>Composite membranes</td>
<td>Acid-resistant, fluxes are modest and operation temperature is restricted below 110 °C.</td>
</tr>
<tr>
<td>-</td>
<td>Zeolite-A membrane</td>
<td>It has pores small enough to pass water molecules, but it is very sensitive to even the slight acidity</td>
</tr>
<tr>
<td>+</td>
<td>Ceramic membrane</td>
<td>Ceramic membranes externally coated with amorphous silica are water selective, withstand high temperatures up to 240 °C, and high pressures up to 35 bar and wide range of acidity.</td>
</tr>
</tbody>
</table>

The pervaporation model of Wijmans and Baker (Seader and Henly, 1998) is used in sizing the pervaporation membranes of the process. Vacuum pumps are used to generate vacuum in the permeate side of the membrane. The maximum vacuum that can be produced by these pumps is 13 mbar (Coulson and Richardson, 1999). The permeability of these membranes is 2 kg/m² bar hr with water to EG selectivity of 1000 (Cot. et al., 2000 and others). The detailed sizing of the membrane is shown in Appendix E, and Table (6.11) shows the summary of the membrane sizing.

Table (6.11): Summary of membrane sizing results

<table>
<thead>
<tr>
<th>Unit</th>
<th>Area (m²)</th>
<th>Number of tubes</th>
</tr>
</thead>
<tbody>
<tr>
<td>PV-400</td>
<td>675</td>
<td>107,484</td>
</tr>
<tr>
<td>PV-410</td>
<td>105</td>
<td>16,720</td>
</tr>
<tr>
<td>PV-420</td>
<td>128</td>
<td>20,382</td>
</tr>
<tr>
<td>PV-430</td>
<td>187</td>
<td>29,777</td>
</tr>
</tbody>
</table>

From Table (6.11) it is concluded that high number of pervaporation tubes is needed, which means very high cost of the membrane units. A combination of the pervaporation technology with other technologies may decrease the cost. More details about the other alternatives are given in chapter four.

6.5.5 Polymerization reactors

Manufacture of condensation polymers like PET in a melt phase process often requires continuous removal of the condensation product from the reaction mass to drive the reaction to
high conversion. At high conversion, the high viscosity of the melt decreases the rate of transport of the condensation product (EG) through the reaction mass and thereby reduces the overall reaction rate. Primary reactor design problems are to generate large amounts of surface area within the polymerization reactor and to insure adequate mixing between the bulk of the reaction mass and the surface [1].

6.5.5.1 Low polymerizer (R-300)

Since the studied process is continuous, there are two possibilities regarding the type of the low polymerizer: the continuous tubular reactor and the continuous stirred tank reactor. In the continuous tubular reactor the high viscosity of polymer melts would lead to abroad distribution of residence times in the reactor because of the flow rate profile, with low flow rates at the wall and maximum flow rates in the center of the tube. As a consequence broad molar mass distributions and even insoluble or unmeltable sediments may arise, which may clog the reactor and are not acceptable in the final product [22].

The continuous stirred tank reactor is most often used and offers, as a consequence of stirring, a narrower distribution of residence times than the continuous tubular reactor [22]. Since the degree of polymerization of the output stream of this reactor is 24.6, which is less than 30, there is no mass transfer limitations of the by-product through the polymer, based on which, there is no need for special type of polymerization reactor at this stage of polymerization.

The required data for the sizing of the low polymerizer are taken from Aspen and Polymer Plus simulation results including the volumetric flow rate of the feed which is 11.5131 m$^3$/hr and the residence time which is 0.75 hr. The obtained results are summarized in Table (6.12).

<table>
<thead>
<tr>
<th>Table (6.12): Summary of low polymerizer dimensions</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>R-300</strong></td>
</tr>
<tr>
<td>Total Reactor volume, m$^3$</td>
</tr>
<tr>
<td>Volume liquid in the reactor, m$^3$</td>
</tr>
<tr>
<td>Diameter, m</td>
</tr>
<tr>
<td>Liquid height, m</td>
</tr>
<tr>
<td>Reactor height, m</td>
</tr>
<tr>
<td>Vessel calculated thickness, mm</td>
</tr>
<tr>
<td>Vessel practical thickness, mm</td>
</tr>
</tbody>
</table>

A preliminary selection of the agitator type is done based on the liquid viscosity and reactor volume [Coulson, Fig. 10.57]. A paddle agitator is selected to enhance mixing in the reactor. For viscosities greater than about 2.5 to 5.0 Pa.s (5000 cp), baffles are not required since
little swirling is present above these viscosities [Geankoplis]. The results of the mixer sizing are summarized in Table (6.13).

Table (6.13): Agitator dimensions, speed, power requirement, and material of construction.

<table>
<thead>
<tr>
<th>Property</th>
<th>Agitator of R-300</th>
</tr>
</thead>
<tbody>
<tr>
<td>Length of paddle impeller</td>
<td>1.24 m</td>
</tr>
<tr>
<td>Width of the blade</td>
<td>0.155 m</td>
</tr>
<tr>
<td>Agitator speed</td>
<td>50 rpm</td>
</tr>
<tr>
<td>Power requirements</td>
<td>5.65 kW</td>
</tr>
<tr>
<td>Material of construction of the reactor</td>
<td>Stainless steel 316</td>
</tr>
<tr>
<td>Material of construction of the agitator</td>
<td>Stainless steel 316</td>
</tr>
<tr>
<td>Material of construction of the heating jacket</td>
<td>Carbon steel</td>
</tr>
</tbody>
</table>

6.5.5.2 Intermediate polymerizer (R-310)

In a continuous PET process, low molecular weight prepolymers (degree of polymerization up to 30) are first produced in a stirred tank reactor at about 260-280 °C [2] and low pressure up to 30 torr. As the melt viscosity increases with an increase in polymer molecular weight, prepolymers are transferred to a specially designed finishing polymerization reactors from which EG, the main condensation by product, is removed at much lower pressure (0.1-1.0 torr) [2] until a high molecular weight is obtained. Since the main polymerization is reversible, the forward reaction should be promoted to obtain high molecular weight polymers. Thus the design and operation of a finishing reactor is usually focused on how EG can be removed from a highly viscous polymer melt while the formation of unwanted side products is minimized.

The finishing polymerization reactors that are used in industry include rotating disk reactors or similar type (e.g., twin-shaft disk reactor), wiped film reactors, screw reactors, and cage reactors [3]. Although there are many published data on the theoretical modeling of melt polycondensation processes, very few experimental studies have been published.

Secor [5], Hoftyzer and van Krevelen [6], and Hoftyzer [7] developed simple models for the final stages of polycondensation using the so called ‘penetration theory approximation’. Whereas, Ault and Mellichamp [8] developed a film model which took into account periodic mixing of the film. A generalized model for condensation polymerization occurring in wiped film reactor was developed by Amon and Denson [9].

Gupta et al [10] developed models for polycondensation reactions assuming that the functional groups are not equally reactive. Ravindranath and Mashelkar [4] developed a film model for the final stages of polycondensation assuming that polycondensation is occurring in a
film of finite thickness. Yokoyama et al [11] analyzed the polycondensation data obtained in a pilot plant scale horizontal disk ring reactor. They studied the effect of various process and operation conditions using the tanks-in-series model. Recently, experimental studies were done by Seong et al [2] followed by proposing a dynamic multicompartment model for a continuous flow rotating disk reactor for the finishing stages of melt polycondensation of PET.

Based on this survey, it is found that disk ring reactor is recommended for the melt polycondensation reaction. The rotating disk reactor is a horizontal rotating shaft on which disks are mounted as explained in Figure (6.7). These disks are immersed partially in the bulk liquid. Low molecular weight prepolyimers are continuously supplied to the reactor. As the shaft rotates at a relatively low speed, polymer melt is partially dragged upward onto the disks and thin layers or films of polymer melt are formed on the disk surfaces. High vacuum is applied to remove volatile species (most importantly, EG) from these film polymer [3].

The knowledge of various parameters influencing the performance of the reactor is critical for analyzing the polycondensation data. The mean residence time is a function of the container length, number of disk rings, chamber width, partition wall shape, height and size of partition wall openings, throughput, viscosity of the reacting mass, rotational speed of the agitator and the melt volume. The ratio of back mixing between two successive stages depends on the shape of the blades, number of partition walls and the viscosity if the reaction mixture [4].

Figure (6.7) Rotating disk reactor.
As it is mentioned before, developing a model of a reactor design with complex geometry, such as a finishing polycondensation reactor, is a challenging task; therefore, data from literature is considered in sizing the final stages polymerization reactors.

The residence time that we got from Polymer and Aspen Plus simulation can’t be used in sizing this reactor because it does not consider the mass transfer limitations of EG from the reaction melt, so, published data are taken for the sizing purposes.

It is found that the residence time in the intermediate polymerizer is 25 min to increase the degree of polymerization from 24.6 to 59.4 (from Polymer Plus simulation) using 0.09 wt% of antimony trioxide as catalyst as published by Ravindranath [13] under 1.0 torr. It is published by Seong et al [2] that only 33 vol% of the rotating disk reactor is occupied by the reaction melt. Based on this and the flow rate that we got from Polymer Plus simulation, it is found that the reactor volume is 14.7 m$^3$.

According to the wide range of L/D ratio published in literature (1.1 [2,12], 3.34 [3], 1.85, 3.07, 1.26 [13]), length to diameter ratio is taken to be 2.0 based on which, the reactor dimensions are 2.11 m diameter and 4.22 m length.

The distance between the disks is quite important. To estimate the number and the dimensions of the rings, the ratio between the disks (length of the compartment) and the vessel diameter is taken as published by Seong et al [12] to be 0.0917. Based on which the length of a compartment is found to be 0.1935 m, then the number of disks is found to be 22 disks. The disk diameter to the vessel diameter is taken to be 0.907 as published by Seong et al [12], based on which the diameter of each disk is found to be 1.9 m.

The rotation speed is function of the viscosity, for intermediate polymerizer it is found to be 10-40rpm of viscosity between 50-5000 poise as published by Ravindranath et al [4]. For the intermediate polymerizer (DP of 59.4) the viscosity is about 250 poise, which means that 10 rpm is quite sufficient. According to literature, there are no correlations to estimate the power requirement for this type of stirrer; it is assumed that the power requirement is as that for the low polymerizer which is 5.65 kW. The material of construction is selected to be stainless steel.
6.5.5.3 High polymerizer (R-310)

Same procedure is followed in sizing this reactor as that of intermediate polymerizer. The residence time that we got from Polymer and Aspen Plus simulation can’t be used in sizing this reactor because it does not consider the mass transfer limitations of EG from the reaction melt, so, published data are taken for the sizing purposes.

It is found that the residence time in the high polymerizer is 34 min to increase the degree of polymerization from 59.4 to 99 (from Polymer Plus simulation) using 0.09 wt% of antimony trioxide as catalyst as published by Ravindranath [13] under 0.5 torr. It is published by Seong et al [2] that only 33 vol% of the rotating disk reactor is occupied by the reaction melt. Based on this and the flow rate that we got from Polymer Plus simulation, it is found that the reactor volume is 19.6 m$^3$.

According to the wide range of L/D ratio published in literature (1.1 [2,12], 3.34 [3], 1.85, 3.07, 1.26 [13]), length to diameter ratio is taken to be 2.0 based on which, the reactor dimensions are 2.32 m diameter and 4.64 m length.

The distance between the disks is quite important. To estimate the number and dimensions of the rings, the ratio between the disks (length of the compartment) and the vessel diameter is taken as published by Seong et al [12] to be 0.0917. Based on which the length of a compartment is found to be 0.2127 m, then the number of disks is found to be 22 disks. The disk diameter to the vessel diameter is taken to be 0.907 as published by Seong et al [12], based on which the diameter of each disk is found to be 2.1 m.

The rotation speed is function of the viscosity, for high polymerizer it is found to be 10-40rpm of viscosity between 50-5000 poise as published by Ravindranath et al [4]. For the high polymerizer (DP of 99) the viscosity is higher than 5000 poise, which means that 40 rpm is quite sufficient. According to literature, there are no correlations to estimate the power requirement for this type of stirrer, it is assumed that the power requirement is as that for the low polymerizer which is 5.65 kW. The material of construction is selected to be stainless steel.

The sizing results of both intermediate and high polymerizers including the liquid phase volume in the reactor, reactor volume, reactor length and diameter, disc diameter and number of disks, and material of construction are explained in Table (6.14).
Table (6.14): Sizing results of intermediate and high polymerizer

<table>
<thead>
<tr>
<th></th>
<th>R-310</th>
<th>R-320</th>
</tr>
</thead>
<tbody>
<tr>
<td>Liquid volume in the reactor</td>
<td>4.9</td>
<td>6.53</td>
</tr>
<tr>
<td>Reactor volume</td>
<td>14.7</td>
<td>19.6</td>
</tr>
<tr>
<td>Length of the reactor</td>
<td>4.22</td>
<td>4.64</td>
</tr>
<tr>
<td>Diameter of the reactor</td>
<td>2.11</td>
<td>2.32</td>
</tr>
<tr>
<td>Number of discs</td>
<td>22</td>
<td>22</td>
</tr>
<tr>
<td>Disc diameter</td>
<td>1.9</td>
<td>2.1</td>
</tr>
<tr>
<td>Material of construction of reactor vessel and discs</td>
<td>Stainless steel 316</td>
<td>Stainless steel 316</td>
</tr>
</tbody>
</table>

6.5.6 Spray condensers

Since the pressures of the output vapor streams from the polymerization section are very low and their temperature is high. In addition to that, vacuum device is required for the reactor, spray condenser is found to satisfy all of these requirements in addition to that, it is proven technology in conventional processes of PET.

Spray condenser is one of the direct-contact condensers in which the coolant is brought into contact with the vapor [14]. Spray condensers are inexpensive, low-pressure-drop devices that are moderately efficient for heat and mass transfer, and they have simple mechanical design.

The coolant is sprayed, using nozzles, into a vessel to which the vapor is supplied. This is shown schematically in Figure (6.8). It is important that the spray nozzles are designed to produce a fine spray of liquid to give a large interfacial area for heat transfer and a long enough residence time of liquid droplets in the vessel.

![Figure (6.8) Schematic diagram of a spray condenser](image-url)
The sizing and design results including the dimensions, the material of construction, the required recycle flow rate, its temperature, and the required cooling using shell and tube heat exchanger are explained in Table (6.15, 16 and 17) [for more details see Appendix G]

Table (6.15): Design results of the spray condenser that follows the low polymerizer (D-500)

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Diameter of the column</td>
<td>0.425</td>
</tr>
<tr>
<td>Height of the column</td>
<td>3.8</td>
</tr>
<tr>
<td>Inlet temperature of the recycled EG (°C)</td>
<td>25</td>
</tr>
<tr>
<td>Flow rate of the recycled EG-W (kg/hr)</td>
<td>1895</td>
</tr>
<tr>
<td>The required heat of cooling (kW)</td>
<td>153.6</td>
</tr>
<tr>
<td>Type of nozzle</td>
<td>Solid-cone spray nozzle</td>
</tr>
<tr>
<td>Material of construction</td>
<td>Stainless steel type 316</td>
</tr>
</tbody>
</table>

Table (6.16): Design results of spray condenser following the intermediate polymerizer (D-510)

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Diameter of the column</td>
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</tr>
<tr>
<td>Height of the column</td>
<td>6.9</td>
</tr>
<tr>
<td>Inlet temperature of the recycled EG (°C)</td>
<td>25</td>
</tr>
<tr>
<td>Flow rate of the recycled EG-W (kg/hr)</td>
<td>6544.5</td>
</tr>
<tr>
<td>The required heat of cooling (kW)</td>
<td>76</td>
</tr>
<tr>
<td>Type of nozzle</td>
<td>Solid-cone spray nozzle</td>
</tr>
<tr>
<td>Material of construction</td>
<td>Stainless steel type 316</td>
</tr>
</tbody>
</table>

Table (6.17): Design results of the spray condenser that follows the high polymerizer (D-520)

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Diameter of the column</td>
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</tr>
<tr>
<td>Height of the column</td>
<td>10</td>
</tr>
<tr>
<td>Inlet temperature of the recycled EG (°C)</td>
<td>10</td>
</tr>
<tr>
<td>Flow rate of the recycled EG-W (kg/hr)</td>
<td>1242</td>
</tr>
<tr>
<td>The required heat of cooling (kW)</td>
<td>18.4</td>
</tr>
<tr>
<td>Type of nozzle</td>
<td>Solid-cone spray nozzle</td>
</tr>
<tr>
<td>Material of construction</td>
<td>Stainless steel type 316</td>
</tr>
</tbody>
</table>

6.5.7 Heat exchangers (E-500, 510, 520)

All the heat exchangers used in spray condensers will be selected here in addition to that used for the membrane units. General selection criteria will be discussed first, followed by selection arguments for each exchanger. In selecting heat exchangers, a number of alternatives can be chosen for a single application. Factors such as operating temperatures, pressure and pressure drop, fouling, process stream and utility stream characteristics, and of course capital cost, all play a major role in choosing the most suitable heat exchanger.

Table (6.18) gives a general summary of the applicability of the different types of heat exchangers [Van Den Berg, 2000].
Table (6.18): Exchanger characteristics

<table>
<thead>
<tr>
<th>Type</th>
<th>Advantage</th>
<th>Disadvantage</th>
<th>Operating range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Shell and tube</td>
<td>Flexible operation and robust, easy to maintain</td>
<td>Often not economic for pressures below 16 bar or 200°C; requires high ∆T</td>
<td>Tube-side 1400 bar, Shell-side 300 bar</td>
</tr>
<tr>
<td>Air cooler</td>
<td>Large heat loads possible, utility (air) free</td>
<td>Economic for process fluid T &gt; 65°C, Acceptable &gt; 45°C</td>
<td>470 bar; process fluid up to 500°C</td>
</tr>
<tr>
<td>Double pipe</td>
<td>High pressures possible, cheap construction, easy to maintain</td>
<td>Poor heat transfer coefficient – expensive for large duties</td>
<td>Tube-side 1400 bar</td>
</tr>
<tr>
<td>Printed circuit</td>
<td>High effectiveness factor, low ∆T possible</td>
<td>Fluids must not be fouling, expensive construction</td>
<td>1000 bar, -200-800°C</td>
</tr>
<tr>
<td>Plate and frame</td>
<td>High effectiveness factor, lower areas needed, compact</td>
<td>Not suitable for carbon steel, limited to below 30 bar</td>
<td>30 bar; -40 - 170 °C,(200 °C with special materials)</td>
</tr>
<tr>
<td>Welded plate</td>
<td>High effectiveness factor, high pressures</td>
<td>Expensive construction method and materials of construction</td>
<td>300 bar, max. temp. 700 °C</td>
</tr>
<tr>
<td>Plate fin</td>
<td>High effectiveness factor (up to .98), common in cryogenic applications.</td>
<td>Limited to lower temperature ranges, expensive construction</td>
<td>90 bar; -200- 150 °C (Alumina), 600 °C (steel)</td>
</tr>
</tbody>
</table>

As it is clear in the above table, the shell and tube heat exchanger is the most suitable one for the three spray condensers that follow the polymerization reactors and for the membrane units.

Where shell and tube heat exchangers are selected, the decision must be made to determine which fluid is on the shell or tube side. The fluid allocation heuristics are taken from Chemical Engineering, Vol.6 [Sinnot,1993]. Table (6.19) gives some heuristics for the fluid allocation.

Table (6.19) Fluid allocation heuristics

<table>
<thead>
<tr>
<th>Consideration</th>
<th>Solution</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fouling</td>
<td>Fouling fluid on tube side – higher allowable velocities reduce fouling</td>
</tr>
<tr>
<td>Temperature</td>
<td>Place the hottest liquid on the tube side – more expensive materials limited to tube construction</td>
</tr>
<tr>
<td>Operating pressures</td>
<td>Place high-pressure fluid on tube side – high pressure tubing cheaper than high pressure shell</td>
</tr>
<tr>
<td>Pressure drop</td>
<td>Fluid with lowest allowable ∆T should be allocated to tube side – obtains the best heat transfer coefficient.</td>
</tr>
</tbody>
</table>
Based on the previous table, it is clear that to obtain the best heat transfer coefficient, cooling water has to be in the tube side. Based on the fouling considerations, cooling water could cause some fouling whereas the process medium is non-fouling, therefore the cooling water will be supplied in the more easily cleaned tube side. The shell and tube heat exchangers will therefore be horizontal exchangers with the process fluid cooling inside the shell.

6.5.8 Pumps

Pumps can be classified into two general types;
1. Dynamic pumps, such as centrifugal pumps.
2. Positive displacement pumps, such as reciprocating and diaphragm pumps.

The single-stage, horizontal, overhung, centrifugal pump is by far the most commonly used type in the chemical process industry. Other types are used where a high head or other special process considerations are specified (Coulson and Richardson, 1999).

- They are simple in construction and cheap
- They can handle liquid with large amount of solids
- Maintenance costs are lower than for other types of pumps

Detailed pumps sizing is shown in Appendix G. Table (6.20) shows a summary of the pumps sizing.

Table (6.20): Summary of pumps sizing

<table>
<thead>
<tr>
<th>Pump No.</th>
<th>Type</th>
<th>Capacity (m³/s)</th>
<th>Power (kW)</th>
<th>Material of construction</th>
</tr>
</thead>
<tbody>
<tr>
<td>P-100</td>
<td>Horizontal centrifuge</td>
<td>1.075E-3</td>
<td>0.11</td>
<td>Aluminum</td>
</tr>
<tr>
<td>P-110</td>
<td>Horizontal centrifuge</td>
<td>2.75E-3</td>
<td>2.00</td>
<td>Aluminum</td>
</tr>
<tr>
<td>P-500</td>
<td>Horizontal centrifuge</td>
<td>6.19E-3</td>
<td>12.78</td>
<td>Aluminum</td>
</tr>
<tr>
<td>P-510</td>
<td>Horizontal centrifuge</td>
<td>1.73E-3</td>
<td>7.78</td>
<td>Aluminum</td>
</tr>
<tr>
<td>P-520</td>
<td>Horizontal centrifuge</td>
<td>3.31E-4</td>
<td>3.67</td>
<td>Aluminum</td>
</tr>
</tbody>
</table>

6.6 Main Process Control

In recent years the performance requirements for process plants have become increasingly difficult to satisfy. Stronger competition, tougher environmental and safety regulations, are rapidly changing economic conditions have been key factors in the tightening of
plant product quality specifications. A further complication is that modern processes have become more difficult to operate because of the trend toward larger, highly integrated plants with smaller surge capacities between the various processing units [Fogler, 1989].

A method for the identification, selection, and implementation of the control loops is required. Luyben (1997) advocates the following methodology for controller selection:

- Define the objectives of the control system and the nature of the disturbance.
- Understand the principles of the process in terms of its dynamic behaviour and understand the environment in which the control program operates.
- Propose a control structure consistent with the objectives and the process characteristics.
- Assign controllers and evaluate through simulation the proposed control structure with the anticipated disturbance.

Only main control loops, needed for steady plant operation, are emphasised in process index flowsheet and discussed in following text. Other control loops are subject of detailed analysis of process controls. Modelling of the actual control loops is considered to be outside the scope of the current project, but as mentioned earlier that the major control loops will be discussed.

The choice of the system parameter that should be controlled is based on whether it influences operation of downstream purification processes or operation of plant in general, i.e. if it is identified as a critical parameter.

6.6.1 Control of feed ratio

The ratio of EG/TPA has to be controlled since it is required to maintain the two flows at a constant ratio; therefore a ratio control is required to maintain the reactor feeds at a constant ratio.

6.6.2 Control of esterification and polymerization reactors

All the reactors have to be operated at constant temperature and pressure. Hence the control actions are critical. Generally, the schemes used for reactor control depend on the process and the type of the reactor. If a reliable on-line analyzer is available, and the reactor
dynamics are suitable, the product composition can be monitored continuously and the reactor conditions and feed flows controlled automatically, to maintain the desired product composition and yield.

More often, the operation is the final link in the control loop; adjusting the controller set points to maintain the product within specifications, based on periodic laboratory analysis.

- Reactor temperature is controlled by regulating the flow of the heating medium, the temperature of the first, the second and the third esterification reactor is to be controlled at a value of 240 °C. Furthermore, the temperatures of the polymerization reactors are controlled at values of 270 °C, 280 °C, and 290 °C for the low, the intermediate, and the high polymerizer respectively.

- The pressure of the esterification reactors is controlled by regulating the pressure of the pumps that pump the fluid to these reactors. In such away, the pressure in the first esterification reactor is held constant at a value of 4.44 atm, that for the second esterification reactor is held constant at a value of 2.86 atm, and that of the third esterification reactor is held constant at a value of 1.38 atm.

- The pressure of the polymerization reactor is controlled by controlling the spray condensers, which follow the polymerization reactors. This can be done through regulating the steam ejectors that are connected to the spray condensers. The pressures of the polymerizers are held constants at 105 torr, 1 torr, and 0.5 torr for the low, the intermediate, and the high polymerizer.

A control scheme for a jacketed reactor is shown in Figure (6.9).

Figure (6.9) A control scheme for a jacketed reactor.
6.6.3 Control of pumps

To ensure a definite amount and pressure of stream entering and exiting the reactors, the flowrates of the pumped streams have to be regulated. For this purpose, pumps have to be controlled.

Pumps are usually designed to run at constant speed, since variable speed pumps are more expensive. The flow control is then achieved by a by-pass control as represented in Figure (6.10) [Sinnot, (1996)]

![Figure (6.10) A control scheme for a pump.]

6.6.4 Control of heat exchangers

The heat exchangers discussed here are those exchangers that directly coupled to the spray condensers.

A number of equipment configurations are used in heat exchangers using utilities, but the most common control is given in Figure (6.11.a). The product outlet stream temperature is controlled by manipulating the utility stream flowrate to the exchanger [Perry]. Feedforward control can be applied using the product flow to the exchanger in cascade with the outlet temperature as given in Figure (6.11.b).
6.6.5 Control of steam ejector

Steam ejectors are required for working under vacuum pressure. A method of steam ejector control is illustrated in Fig. 6.11.

![Control schemes for a heat exchanger](image)

Figure (6.11) Control schemes for a heat exchanger.

The basic method for controlling vacuum system is by using a load gas. A load gas is a gas admitted to the vacuum system between the process and the steam ejector. The feed rate of the load gas is controlled with a simple feedback loop to maintain constant system pressure. The load gas can be air, nitrogen, or other inert gases, but the ideal load gas is the air [Minton, 1986].

![Control of steam ejector by atmospheric air load](image)

Figure (6.12) Control of steam ejector by atmospheric air load
6.7 Conclusions

- The polyethylene terephthalate process has been simulated using POLYMER and ASPEN PLUS to obtain mass and energy balances for the process flowsheet.

- The POLYMER PLUS package has been required for two reasons, to estimate physical and thermodynamic properties of the monomer and the produced polymer, and to define the step growth reaction kinetics of this process.

- The Polymer Non-Random Two Liquid activity coefficient model (POLYNRTL) has been selected as a property set for ASPEN and POLYMER PLUS simulation.

- The process has been built and simulated step by step. It is started with raw materials mixing and ended by high polymerization equipment.

- The operating temperature in the esterification section is limited to 240 °C, which is the maximum temperature that the used silica membrane can withstand.

- The low polymerizer is simulated as a CSTR whereas the intermediate and the high polymerization reactors are simulated as PFR. Each of these reactors is connected to a flash drum with vapor and liquid as valid phases.

- In ASPEN PLUS package there is no item called membrane. Consequently, the function of the membrane has been simulated using the unit operation model of SEP2. In this unit operation the water is considered to be removed completely from the reaction mixture due to the high permeability through the membrane.

- Sensitivity analysis has been carried out for the esterification reactors to obtain the optimum operating conditions. The main design variables are reactor temperature, and reactor pressure.

- The optimum pressure in the primary, the secondary, and the tertiary esterifier has been found to be 4.5, 2.9, and 1.4 bar respectively.

- The materials of construction have been selected based on economical considerations to satisfy both process and mechanical requirements taking into account other factors such as product contamination and process safety.
The types of equipment have been selected and their sizes have been estimated. Their cost will be determined later on during the economic evaluation.

A main process control scheme has been set up. The methodology of Luyben for identification, selection, and implementation of the control loops has been followed.

The results of mass and energy balances that were got from Aspen and Polymer Plus have some differences than that of hand calculations based on the general chemical reaction equations specially that of water, this is due to the side reactions of EG to form DEG and its segments which also produce water (see Table 2.6).

6.8 Recommendations

Developing a model of a reactor design with complex geometry, such as a finishing polycondensation reactor, is a challenging task; therefore, studying of the sizing of the final stages polymerization reactors is recommended.

The performance of the finishing reactors is limited by the liquid-vapour mass transfer rate. This makes the reactor performance a function of the shaft rotation rate, as well as the temperature, pressure, and throughput. Modification of Polymer Plus package is recommended by introducing certain subroutines that consider the mass transfer limitations.

Side reactions other than the DEG formation shall be involved in this process, such as that of acetaldehyde. Hopefully that kinetic data will be published on this topic. Since acetaldehyde formation reduce the polymer yield (this reaction lead to the loss of EG in the form of acetaldehyde). We recommend studying of the effects of acetaldehyde formation on the polymer yield.

Our simulation has the objective of the lowest EG/TPA ratio and the recommended DP. We recommend studying and optimizing this process based on the process economy and the product quality.
References


Chapter Seven

Detailed Primary Esterification Reactor Design

7.1 Introduction

A continuous stirred tank reactor has been designed to work as the primary Esterification reactor (R-100). The reaction mixture is heated using steam that transfers the heat from the reactor jacket through the shell side of the reactor. The chemical engineering design is based on the results of ASPEN PLUS and POLYMER PLUS simulation that simulates the operation of the primary esterification reactor over its operating conditions. The F.O.B reactor cost is estimated to be US$ 280,000 excluding the cost of heat charges, the control system and inventory of spares.

7.2 Design Strategy

The primary esterification reactor is equipment; which must satisfy both mass and heat transfer requirements. A combination of knowledge from related processes and the application of chemical engineering ‘first principles’ are used to satisfactorily complete the design. This report considers the design strategy of Rey and Sneesby, 1998. This strategy has the following stages:
- Design basis (what must the design be capable of?),
- Design parameters (what design decisions must be made?),
- Design criteria (how are these decisions to be made?),
- Design methods (what is the physical, chemical or mechanical basis for these decisions?), and
- Detailed design specifications (what are the results of these decisions?)

7.3 Design Basis

A jacketed continuous stirred tank reactor is preferred as discussed in chapter five. The reactor must be capable of producing 93.7 kT/year of PET with a degree of polymerization of 6.0. The conversion of TPA should be 86.0 wt %.
The feed is available at 28 °C from the mixing tank and should leave the reactor at not more than 240 °C. The reactor vessel should be able to withstand a temperature of 240 °C and a pressure of 4.5 bar.

7.4 Design Parameters

The final design must specify all dimensions to enable reactor to be constructed. The design parameters which require evaluation at this stage are;
- Composition of reaction mixture,
- Heat transfer area, and
- Method of controlling heating steam flow rate.

7.5 Design Criteria

Several types of reactors are used for carrying out the esterification reactions. The continuous stirred tank reactor has been generally selected. This process is capable of operating at higher TPA conversion in the esterification reaction section; up to 99.0 wt %. The final design was selected from the results of many simulations, which were performed using different operating conditions and parameters.

7.6 Chemical Engineering Design Methods

7.6.1 Kinetics

The set of esterification reactions considered in the simulation of the primary esterification reactor are shown in Table 2.6. The values of the rate constants and equilibrium rate constants are shown in Table 2.8. The rate of esterification reactions increases as the reactor temperature increases. Two factors limit increasing the reactor temperature. The increased rate of by-products formation and the instability of the pervaporation membrane above 240 °C, which follows the reactor.

7.6.2 Reactor simulation

ASPEN PLUS and POLYMER PLUS simulation programs are used to simulate the reactor. The TPA conversion and degree of polymerization of PET are studied at different operating conditions. The heat duty of the steam is also determined. The temperature and conversion profiles are not studied as determined by the supervisors.
7.7 Reactor Configuration

A jacketed continuous stirred tank reactor will be used. It will be operated continuously for 8150 hours per year. This reactor is used to carry out the esterification reactions and to suspend the finely suspended solids, which are held in suspension by agitation. The height of liquid in the reactor is selected to be twice its diameter and it is generally 90 % full as recommended by Bassel, 1990. The heating jacket is welded into the heating tubes running from bottom to top. Any electrical heating device must be protected against explosion. In order to attain short heating and reaction times, the heating efficiency must be adjusted accordingly.

7.8 Chemical Engineering Design Specifications

<table>
<thead>
<tr>
<th>General</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Type of reactor</td>
<td>Stirred tank reactor</td>
</tr>
<tr>
<td>Orientation</td>
<td>Vertical</td>
</tr>
<tr>
<td>Operation</td>
<td>Continuous</td>
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</table>

<table>
<thead>
<tr>
<th>Feed</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Reactants</td>
<td>99.9 wt % EG, 99.99 wt % TPA</td>
</tr>
<tr>
<td>Total Flow</td>
<td>15 T/hr</td>
</tr>
<tr>
<td>Temperature</td>
<td>28 °C</td>
</tr>
<tr>
<td>Pressure</td>
<td>4.5 bar</td>
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</table>

<table>
<thead>
<tr>
<th>Vessel</th>
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<tbody>
<tr>
<td>Temperature</td>
<td>240 °C</td>
</tr>
<tr>
<td>Pressure</td>
<td>4.5 bar</td>
</tr>
<tr>
<td>Inside Diameter</td>
<td>2.33 m</td>
</tr>
<tr>
<td>Height of Liquid</td>
<td>4.66 m</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Jacket</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Fluid</td>
<td>Steam</td>
</tr>
<tr>
<td>Inlet temperature</td>
<td>240.9 °C</td>
</tr>
<tr>
<td>Outlet temperature (condensate)</td>
<td>240.9 °C</td>
</tr>
<tr>
<td>Pressure</td>
<td>34 bar</td>
</tr>
<tr>
<td>Mass flow</td>
<td>13,500 kg/hr</td>
</tr>
<tr>
<td>Heat duty</td>
<td>6.6 MW</td>
</tr>
<tr>
<td>Heat transfer area</td>
<td>36.6 m²</td>
</tr>
<tr>
<td>Overall heat transfer coefficient</td>
<td>850 W/m².K</td>
</tr>
<tr>
<td>Available heat transfer area</td>
<td>39.5 m²</td>
</tr>
</tbody>
</table>
7.9 Mechanical Engineering Design

7.9.1 Vessel design

The data required for the reactor sizing are obtained from the simulation results. The average volumetric flow rate is (9.9 m$^3$/hr), whereas the reactor residence time is (2 hr).

\[ V = \Theta \times v \]  

(7.1)

The volume is estimated to be (19.8 m$^3$). The reactor is generally 90 % full and the height of the reactor is generally twice the diameter (Bassel, 1990).

\[ V = \frac{\pi}{4} D^2 H_L \]  

(7.2)

\[ V = \frac{\pi}{4} D^2 H \]  

(7.2')

\[ H_L = 0.9H \]  

(7.3)

Using the previous equations, the dimensions of the reactor vessel are estimated

7.9.2 Head design

The ends of cylindrical vessels are closed by heads of various types. The principal types used and their characteristics are shown in Table 7.1, Coulson and Richardson, 1999. This Table shows that Torispherical heads are the most suitable. The design equations of the Torispherical heads are taken from Coulson and Richardson, 1999.

<table>
<thead>
<tr>
<th>Rating</th>
<th>Type</th>
<th>Remarks</th>
</tr>
</thead>
</table>
| +      | Flat plates and formed flat head | - The cheapest head  
|        |                              | - Limited to low pressure and small diameter vessels |
| -      | Hemispherical heads         | - The strongest head  
|        |                              | - The highest cost of formation                    |
| +      | Ellipsoidal heads           | - Most economical above 15 bar                     |
| ++     | Torispherical heads         | - Most commonly used for vessels up to operating pressures above 15 bar |

The design equations:
Production of Polyethylene Terephthalate by Direct Esterification Using Pervaporation

\[ e = \frac{P_i \times R_c \times C_s}{2 \times J \times f + P_i (C_s - 0.2)} \]  
(7.4)

\[ C_s = \frac{1}{4} \left( 3 + \sqrt{\frac{R_c}{R_k}} \right) \]  
(7.5)

\[ R_c = D_i \]  
(7.6)

\[ R_k = 0.06 R_c \]  
(7.7)

Where,

<table>
<thead>
<tr>
<th>( e )</th>
<th>Head thickness</th>
</tr>
</thead>
<tbody>
<tr>
<td>( C_s )</td>
<td>Stress concentration factor for Torispherical heads</td>
</tr>
<tr>
<td>( R_c )</td>
<td>Crown radius</td>
</tr>
<tr>
<td>( R_k )</td>
<td>Knuckle radius</td>
</tr>
</tbody>
</table>

7.9.3 Vessel support design

The method used to support a vessel depends on several parameters:

- Size, shape and weight of the vessel,
- Design temperature and pressure,
- Vessel location and arrangement, and
- Internal and external fittings and attachments.

Table 7.2 shows types of supports and their characteristics, Coulson and Richardson, 1999.

Table (7.2) Types of supports and their characteristics, Coulson and Richardson, 1999.

<table>
<thead>
<tr>
<th>Rating</th>
<th>Type of support</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>-</td>
<td>Saddle</td>
<td>- Used for horizontal vessels</td>
</tr>
<tr>
<td>+</td>
<td>Skirt</td>
<td>- Used for tall, vertical columns and vertical vessels</td>
</tr>
</tbody>
</table>

A straight cylindrical skirt of plain carbon steel is selected to support the reactor. The max dead weight load on the skirt will occur when the vessel is full of water. The following design equations taken from Coulson and Richardson, 1999 are used:

\[ W_w = \left( \frac{\pi}{4} D_i^2 H_v \right) \rho_w g \]  
(7.8)

\[ W_v = C_s \pi \rho_w D_m g (H_v + 0.8D_m) \times 10^{-3} \]  
(7.9)

\[ W_{tot} = W_w + W_v \]  
(7.10)

\[ D_m = D_i + e \]  
(7.11)
Production of Polyethylene Terephthalate by Direct Esterification Using Pervaporation

\[ F_w = P_w D_{eff} \quad (7.12) \]
\[ D_{eff} \approx D_i + 2e \quad (7.13) \]
\[ M = \frac{F_w}{2} H_v^2 \quad (7.14) \]
\[ \delta_{bs} = \frac{4M_s}{\pi(D_s + t_s)D_s} \quad (7.15) \]
\[ \delta_{ws} = \frac{W_{Tot}}{\pi(D_s + t_s)D_s} \quad (7.16) \]
\[ \delta_s (\text{tensile}) = \delta_{bs} - \delta_{ws} \quad (7.17) \]
\[ \delta_s (\text{compressive}) = \delta_{bs} + \delta_{ws} \quad (7.18) \]

The criteria of the design that to find a skirt thickness that achieves the following criteria,
\[ \delta_s (\text{tensile}) \geq f_s J \sin \Theta \quad (7.19) \]
\[ \delta_s (\text{compressive}) \geq 0.125E \left( \frac{t_s}{D_s} \right) \sin \Theta \quad (7.20) \]
\[ t_{design} = t_s + 2 \quad (7.21) \]

Where,

| \( W_w \) | Weight of water in the vessel, N |
| \( H_v \) | Height of the vessel (cylindrical section only) m |
| \( \rho_w \) | Density of water Kg/m³ |
| \( g \) | Acceleration of gravity M/s² |
| \( W_v \) | Weight of the vessel excluding internal fittings N |
| \( C_v \) | A factor to account for the weight of nozzles, manways, internal supports, etc. Equal 1.15 for vessels with many internal fittings - |
| \( D_m \) | Mean diameter of the vessel m |
| \( t_s \) | Wall thickness mm |
| \( W_{Tot} \) | Total weight of the vessel and its contents N |
| \( D_i \) | Inside diameter of the vessel m |
| \( e \) | Wall thickness m |
| \( F_w \) | Wind pressure N/m |
### Table 7.3 Types of jackets and their characteristics, Coulson and Richardson, 1999.

<table>
<thead>
<tr>
<th>Rating</th>
<th>Type</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>+</td>
<td>Simple, not baffled</td>
<td>Lowest cost, and used up to 10 bar</td>
</tr>
<tr>
<td>+</td>
<td>Spirally, baffled jackets</td>
<td>High heat transfer rate</td>
</tr>
<tr>
<td>+</td>
<td>Dimple jacket</td>
<td>Used up to 20 bar</td>
</tr>
<tr>
<td>++</td>
<td>Half pipe jacket</td>
<td>High heat transfer rate, and used for high pressures up to 70 bar</td>
</tr>
</tbody>
</table>

Since the steam used for heating the vessel is at about 70 bar, the half pipe jacket is selected. This jacket is formed by welding sections of pipe, cut in half along the longitudinal axis, to the vessel wall. The pipe is usually weld round the vessel in a helix; Figure 7.1, Trampbouze, 1988.
7.9.5 Mixer design

The type of mixer is selected to be an axial turbine (six blade turbine with agitator disk) based on the guidelines of Ulrich, 1984. The geometric proportions of the agitation system are taken to be as the standard geometric proportions described by Geankoplis, 1993, pp. 144.

7.9.6 Materials of construction

The choice of construction material is based on chemical resistance, mechanical properties at the operating temperatures and overall cost of construction. The preferred construction material of the reactor vessel and jacket is stainless steel 316 and plain carbon steel for the skirt.

7.9.7 Summary of engineering specifications

<table>
<thead>
<tr>
<th>Mechanical Design of Reactor Vessel</th>
</tr>
</thead>
<tbody>
<tr>
<td>Overall Height</td>
</tr>
<tr>
<td>Outside Diameter</td>
</tr>
<tr>
<td>Weight (Empty)</td>
</tr>
<tr>
<td>Design Pressure</td>
</tr>
<tr>
<td>Wall Thickness</td>
</tr>
</tbody>
</table>
Production of Polyethylene Terephthalate by Direct Esterification Using Pervaporation

Mechanical Design of Vessel Head

<table>
<thead>
<tr>
<th>Type</th>
<th>Torispherical</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thickness</td>
<td>8 mm</td>
</tr>
<tr>
<td>Crown Radius</td>
<td>2.33 m</td>
</tr>
<tr>
<td>Knuckle radius</td>
<td>0.14 m</td>
</tr>
</tbody>
</table>

Mechanical Design of the Mixer

<table>
<thead>
<tr>
<th>Type</th>
<th>Six blade turbine with agitator disk</th>
</tr>
</thead>
<tbody>
<tr>
<td>Power Consumption</td>
<td>4.17 kW</td>
</tr>
</tbody>
</table>

Jacket Selection

<table>
<thead>
<tr>
<th>Type</th>
<th>Half Pipe Jacket</th>
</tr>
</thead>
</table>

Mechanical Design of Support

<table>
<thead>
<tr>
<th>Type</th>
<th>Straight skirt</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thickness</td>
<td>11 mm</td>
</tr>
</tbody>
</table>

Material of Construction

<table>
<thead>
<tr>
<th>Component</th>
<th>Material</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vessel</td>
<td>Stainless Steel 316</td>
</tr>
<tr>
<td>Head</td>
<td>Stainless Steel 316</td>
</tr>
<tr>
<td>Jacket</td>
<td>Stainless Steel 316</td>
</tr>
<tr>
<td>Mixer</td>
<td>Stainless Steel 316</td>
</tr>
<tr>
<td>Skirt</td>
<td>Plain Carbon Steel</td>
</tr>
</tbody>
</table>

7.10 Costing

The F.O.B estimated cost of the reactor is US$ 280,000 (year 2000 prices). This cost estimate is made using the following web site which gives good estimates for equipment in the early developments of projects: [http://www.matche.com/EquipCost/Reactor.htm](http://www.matche.com/EquipCost/Reactor.htm).
7.11 P&I Diagram

Piping and instrumentation diagrams are schematic diagrams showing the interconnection of every component in the process plant as process equipment, all piping and piping items, and all instrumentation. They show how they are interrelated and all special instructions regarding design, installation and operation.

The P&I diagram for the primary esterification reactor has been drawn according to the guidelines given by Eckmann (2000) [8]. This P&I diagram is shown at the end of this chapter and includes:

- All process equipment identified by an equipment number: the primary esterification reactor R-200.
- All pipes, identified by a line number, pipe size, and material specification.
- All valves, the control and block valves with identification number.
- Ancillary fittings that are part of the piping system, such as flow meter and steam traps, with an identification number.
- All hardwired control loops and instruments, with identification number. Computerized control loops, where the connections are done by software, are not shown.

7.11.1 Equipment nozzles

A letter and size identify all equipment nozzles. If pipes are connected to the equipment, the size of the nozzle is identical to the line size. Otherwise, a reducer is installed. The sizes of the nozzles for the instrumentation are 1 or 2 inch. These sizes are chosen arbitrarily because the size of the instrumentation is not known. The nozzles for drainage and venting are of 1 or 2 inch.

7.11.2 Piping

7.11.2.1 line sizing

The pipe diameter is calculated using tow methods; that based on the recommended design velocities, and that based on the economic (optimum) pipe diameter correlations [6]. It is found that the diameters based on the two methods are too closed to each other. All pipes that are connected to R-200 are sized as explained in Appendix I. the results of the calculations are given in Table (7.4).
Table (7.4) Pipes sizing results based on the recommended fluid velocities and the optimum diameter based on economic considerations.

<table>
<thead>
<tr>
<th>Pipe number</th>
<th>Description</th>
<th>øv (m³/hr)</th>
<th>V (m/s)</th>
<th>d, based on velocities (mm)</th>
<th>d,opt (mm)</th>
<th>Pipe size (inch)</th>
</tr>
</thead>
<tbody>
<tr>
<td>102</td>
<td>Reactor input stream</td>
<td>9.904</td>
<td>2.4</td>
<td>38</td>
<td>35.7</td>
<td>1.5</td>
</tr>
<tr>
<td>200</td>
<td>Reactor output stream</td>
<td>900.74</td>
<td>9.4</td>
<td>184</td>
<td>173</td>
<td>7</td>
</tr>
<tr>
<td>2000</td>
<td>Input heating steam to the jacket</td>
<td>792.45</td>
<td>40</td>
<td>84</td>
<td>--</td>
<td>3.5</td>
</tr>
<tr>
<td>2001</td>
<td>Output heating condensate</td>
<td>16.62</td>
<td>3.0</td>
<td>44</td>
<td>47</td>
<td>2</td>
</tr>
</tbody>
</table>

7.11.2.2 Pipe material

For the selection of pipe material, piping material specifications given by Eckmann [8] are used for this purpose. These specifications include the pipe base material and the pressure class. For high-pressure steam (34 bar), the most suitable raw material is carbon steel that have the abbreviation of BAC. For the process material (input and output fluid of the reactor), stainless steel is selected as a raw material for the pipes and the valves of that pipes for the same reasons that have been discussed in the previous chapter.

7.11.2.3 Insulation

The major purpose of insulating pipes 200, 2000, and 2001 is for energy conservation, maintaining a particular temperature, and protection against heat supply from the environment. Because the temperatures exceed 240 °C, the additional purpose is the personal protection. Additional heat tracing is not necessary to prevent liquids from freezing or becoming too viscous.

Mineral wool is selected as insulation material, since it has a low price and can be used in the temperature range of 30 to 500 °C, and very often-used insulation material.

7.11.3 Instrumentation and control

The preliminary scheme of instrumentation and control shown on the P&I diagram is set up according to the process flowsheet (Chapter Six) including temperature, pressure, and level controllers. The control system that is indicated on the P&I diagram is computerized control system indicated with diamonds. The diamonds represent input to or output from a process computer system.
7.11.4 Safety devices

A safety trip is incorporated in the control loop for regulating the steam flow rate. Pressure safety relief valve with pressure rupture disc is installed on the top of the reactor because of high temperature of the reactor, so no leakage can be tolerated. The space between the rupture disc and the safety valve should be enough, otherwise the parts of ruptured disc will plug the safety valve.

7.12 Conclusions

- A jacketed continuous stirred tank reactor has been designed to work as the primary esterification reactor.
- This report considered the design strategy of Ray and Sneesby, 1998 in designing the reactor.
- The F.O.B cost of the reactor is estimated to be US$ 280,000.
- The vessel head is selected to be torispherica head.
- The reactor support is selected to be a straight skirt.
- The reactor jacket is selected to be half pipe jacket.
- The agitator is selected to be a six-blade turbine with agitator disk.
- P&ID is established including equipment nozzles, pipes sizes, pipes materials, insulation materials, control loops, and safety devices.
References


Chapter Eight

Safety Analysis

8.1 Introduction

This chapter is to give an overall view of the safety aspects for one of the process equipment. This process equipment is selected to be the primary esterification reactor that is the same equipment for which the detailed design is done. Detailed analysis is performed which includes determination of fire and explosion index (F&EI) and a hazard and operability study (HAZOP). R-200 is a reactor in which esterification reaction takes place between ethylene glycol and terephthalic acid using diantimony trioxide as a catalyst.

8.2 Tree and Work Diagram

The tree and work diagram as a work organisation tool are shown in Figure 8.1 and Figure 8.2, respectively.

![Tree diagram of safety analysis](image-url)
Figure 8.2 Work diagram of safety analysis
8.3 Fire and Explosion Index

The fire and explosion risk analysis system is a step-by-step objective evaluation of the realistic fire, explosion and reactivity potential of process equipment and its contents. The purpose of the fire and explosion index is to:

1. Quantify the expected damage of the potential fire, explosion and reactivity incidents in realistic terms.
2. Identify equipment that would be likely to contribute to the creation or escalation of an incident.
3. Communicate the fire and explosion index risk potential to the management.

The Dow F&EI system attempts to determine the realistic maximum loss that can occur to a process plant or process unit or related facility. Although the F&EI system is primarily designed for any operation in which flammable, combustible or reactive material is stored, handled or processed, it may also be used in analyzing the loss potential of sewage treating facilities, distribution systems, pipelines, rectifiers, transformers, boilers, thermal oxidizers and certain elements of power plants.

The first step in making the F&EI calculation requires using an efficient and logical procedure to determine which process units should be studied. A process unit is defined as any major item of process equipment. It is quite clear that the manufacturing unit of PET has many process units. To calculate the F&EI, however, only one process unit could have an impact from a loss prevention standpoint should be evaluated.

There are no hard and fast rules governing the choice of process units for evaluation. Usually, the F&EI is calculated for the unit with directly fired heating and for unit with highest pressure (first esterification reactor), as these are considered to be the units contributing most to the risk of fire and explosion.

For calculating the F&EI, three major subsections should be defined and calculated which can be summarized as follows:

- Material Factor (MF)

The material factor is the basic starting value in the calculations of the F&EI. The material factor is a measure of the intrinsic rate of potential energy release from fire or explosion produced by combustion or chemical reaction. As it is known
that if the temperature of the material on which the material factor is based is over 60 °C, a certain adjustment may be required. For EG which has a MF of 4 and a flashing point of 111.1 °C, no adjustment is required because the material is above its flash point at ambient temperature [Dow Index]. EG is considered since the main hazard is from unreacted material in the first esterification reactor.

- Process Unit Hazards Factor (F₃)

After the appropriate Material Factor has been determined, the next step is to calculate the Process Unit Hazards Factor, which is the term that is multiplied by the Material Factor to obtain the F&EI.

The numerical value of the Process Unit Hazards Factor is determined by first determining the General Process Hazards Factor and Special Process Hazards Factor listed on the F&EI form.

The General Process Hazard (F₁) includes some items to be studied, these items can be summarized as follows:

1. Exothermic chemical reactions
   This penalty is taken into account if the process unit under study is a reactor in which a chemical reaction takes place. Since esterification reactions are classified as moderate exotherms, they require a penalty of 0.5

2. Endothermic processes
   This penalty is taken for any endothermic process-taking place in a reactor. Since the reaction that we deal with is esterification reaction (moderate exotherm) there is no penalty for this point.

3. Material handling and transfer
   This item is evaluated with regard to the potential fire involving the pertinent process unit during the handling, transfer and warehousing of materials. Since there is no storage or loading operations, the penalty is 0.0

4. Enclosed or indoor process units
   An enclosed area is identified as any roofed area with three or more sides or an area enclosed by a roofless structure with walls on all sides. Since it is outdoor operation, the penalty is 0.0
5. Access
   Emergency equipment must have ready access to the area housing the pertinent process unit. Access from at least two sides is considered the minimum requirement. An access can be ensured during the design, so the penalty is 0.0

6. Drainage and spill control
   This includes the penalties for design conditions that could cause large spills of flammable or combustible liquids to be retained around or near process equipment. The penalty factor is taken to be the minimum value, which is 0.25

This gives a general process hazards factor \( K_1 = 1.75 \)

The special process hazards are factors that contribute primarily to the probability of a loss incident. They consist of specific process conditions that have themselves to be major cause of fire and explosion incidents. They are twelve items listed and discussed as follows:

I. Toxic material
   Since the health factor \( N_H \) of EG is 1, then the penalty is 0.2

II. Sub-atmosphere pressure
   This is applied to a process condition where air leakage in a system could create a hazard. Since sub-atmosphere pressure never occurs, the penalty is 0.0

III. Operation in or near flammable range
   None of the conditions for the operation in or near flammable range are met; penalty is 0.0

IV. Dust explosion
   No dust is found, the penalty is 0.0

V. Relief pressure
   Where operating pressure is above atmospheric, a penalty is applied for the higher release rates caused by higher pressure in the event of a leak. The
operating pressure in the first esterification reactor is 4.5 bar, the penalty is 0.25

VI. Low temperature
   The operating temperature is high, so the penalty is 0.0

VII. Quantity of flammable/unstable material
   The reactivity number ($N_R$) for $EG = 1$, the penalty is 0.0

VIII. Corrosion and erosion
   A penalty of 0.1 is taken for corrosion and erosion.

IX. Leakage-joints and packing
   For leakage-joints and packing, a penalty of 0.1 is taken.

X. Use of fired equipment
   Through normal operations, no necessity of fire equipment, penalty is 0.0

XI. Hot oil heat exchange system
   No oil heat exchange systems are present, so penalty is 0.0

XII. Rotating equipment
   Because of the agitator (mixer), a penalty of 0.5 is taken.

This gives a special process hazards factor ($F_2$) of 2.15
The process unit hazards factor ($F_1 \times F_2$) = $(1.75 \times 2.15)$ = 3.7625
The $F & EI = (F_1 \times F_2) \times MF = (1.75 \times 2.15) \times 4 = 15.05$ , Since the F&EI is less than 60, so the unit can be considered has light degree of hazard [DOW]

8.4 Hazard and Operability Studies (HAZOP)

A HAZOP study is a structural analysis of a system, process or operation. It is based on line-by-line or stage-by-stage examination of a firm design for the process or operation. Whilst being systematic and rigorous, the analysis also aims to be open and creative. This is done by using a set of guidewords in combination with the system parameters to seek meaningful deviations from the design intention. A meaningful deviation is that is physically possible – for example, no flow or high pressure. Deviations such as no temperature or reverse viscosity have
no sensible, physical meaning and are not considered. Deviations that could lead to potential hazards to safety, health or environment are considered.

A HAZOP study is normally performed when the F&EI is higher than 110 for new plants and higher than 130 for existing plants (Berg, 2000). Even though the F&EI is much less than that (15.05), it is performed as a part of the detailed equipment design for the primary esterification reactor (R-200). The HAZOP tables are included in Appendix --.

8.5 Conclusions

- The fire and explosion index and HAZOP study were studied in this chapter.
- The F&IE has indicated that the primary esterification reaction system is of light risk (the F&IE is 15.05).
- HAZOP study was performed on the primary esterification reaction system even that the F&IE has indicated a light risk. The purpose of this is to indicate the procedure required to evaluate the entire plant.
- No serious intrinsic risk factors were found that would require a change in the design or more drastically shelf the project.
References


Chapter Nine

Economic Evaluation

9.1 Introduction

This chapter deals with the economic evaluation of the production of PET by direct esterification using pervaporation. This process was designed in the previous chapters with a capacity of 100,000 ton PET per year. The goal of the economic evaluation is to assess the profitability of the process. Due to the limited design details and cost data, the accuracy will not be high, probably larger than 30% (Asselberg, 1999). To perform the evaluation the capital and the operating costs are estimated. Then, together with depreciation and tax schedules, cash flows are computed that lead to profitability measures such as the discounted cash flow rate of return. Finally, a sensitivity analysis of some parameters is made to assess possible weaknesses and strengths.

9.2 Work Organization

The work organization of the economic evaluation is represented by the tree and the work diagrams shown in Figure (9.1) and Figure (9.2), respectively. The economic evaluation consists of discount cash flow analysis and sensitivity analysis. The total capital investment and the manufacturing costs are estimated to do the discount cash flow analysis. The second part of the economic evaluation is the sensitivity analysis to examine the influence of price /cost fluctuations on the economic profitability of the process.

Figure (9.1): Tree diagram of economic evaluation
9.3 Total Capital Investment

The total capital investment consists of three components, (Asselberg, 1999):

- Fixed capital for process equipment, piping, instrumentation and buildings
- Working capital for inventories, salaries/wages and cash
- Start-up costs for modifications, start-up labor and loss in production

Capital cost estimates for chemical process plants are often based on an estimate of the purchase cost of the major equipment items required for the process, the other costs being estimated as factors of the equipment cost. The purchase cost of equipment is estimated using different references, including:

- Internet web site, such as: http://www.matche.com
- Vendor quotes, the price of the pervaporation membranes is gotten from Sulzer
- DACE ‘prijzenboekje’.

The purchased cost of equipment is shown in Table (9.1). Appendix K gives detailed purchased cost of equipment.
Table (9.1) Purchased cost of major equipment items

<table>
<thead>
<tr>
<th>Equipment</th>
<th>Purchased cost F.O.B in USD, (2001)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S-100</td>
<td>441,000</td>
</tr>
<tr>
<td>S-110</td>
<td>130,000</td>
</tr>
<tr>
<td>M-100</td>
<td>12,000</td>
</tr>
<tr>
<td>R-200</td>
<td>280,000</td>
</tr>
<tr>
<td>R-210</td>
<td>179,000</td>
</tr>
<tr>
<td>R-220</td>
<td>179,000</td>
</tr>
<tr>
<td>R-300</td>
<td>292,000</td>
</tr>
<tr>
<td>R-310</td>
<td>339,000</td>
</tr>
<tr>
<td>R-320</td>
<td>395,000</td>
</tr>
<tr>
<td>PV-400</td>
<td>1,276,000</td>
</tr>
<tr>
<td>PV-410</td>
<td>198,000</td>
</tr>
<tr>
<td>PV-420</td>
<td>242,000</td>
</tr>
<tr>
<td>PV-430</td>
<td>353,000</td>
</tr>
<tr>
<td>E(400-430, 500-520)</td>
<td>37,000</td>
</tr>
<tr>
<td>D(500-520)</td>
<td>46,000</td>
</tr>
</tbody>
</table>

Subtotal

Miscellaneous (15% of the equipment cost)

Total cost (USD)

The detailed estimation of the total capital investment is shown in Table (9.2). The method presented by Peter and Timmerhaus (1991) will be used in this evaluation. This table shows that the estimated total capital investment is --- million USD. The purchased cost of equipment accounts for ---% of the total investment. From Chapter four, the sales revenue is --- million USD with ----million USD as a total capital investment gives a turnover ratio of --.

9.4 Manufacturing Cost

An estimate of the manufacturing cost, the cost of manufacturing the product, is needed to judge the viability of the project. These costs can be estimated from the index and process flowsheets, which give the raw materials and service requirements, and capital cost estimate.

The total manufacturing cost consists of, (Asselberg, 1999)

- production cost, which covers: direct production costs, fixed charges and plant overhead
- general expenses.

The amount of raw materials needed to produce 100,000 ton per annum of PET were calculated in chapter four. Whereas the amount of utilities was calculated using the Aspen Plus simulation as discussed in chapter five.
The method presented by Asselberg, 1999 is used to estimate the total manufacturing cost. Table (9.3) shows the breakdown of the manufacturing cost for the PET process.

9.5 Discount Cash Flow Analysis

Two principal profitability measures that involve discounted cash flow are:

- Net present value (NPV), and
- Internal rate of return (IRR) or the discounted cash flow rate of return (DCFRR)

To evaluate the net present value (NPV) of the PET plant, its cash flows are computed for each year of the proposed life of the plant, which is proposed as 10 years. Then, a typical value of 15% of the interest rate is used (Seider et. al., 1999). Each cash flow is discounted to its present worth, assuming that the fixed capital is depreciated linearly in 10 years and the tax rate is 35% (the Netherlands tax rate). The sum of all the discounted cash flows is the net present value. It provides a quantitative measure for comparing the capital required for competing processes in current terms. However, the results are quite sensitive to the interest rate, with proposed processes changing favor as the interest rate varies. In the last year of operation, it is common to take credit for the working capital investment. Some companies take credit for the salvage values of the plant, assuming that it is dismantled and sold for salvage at the end of its useful life. Because salvage values are difficult to estimate, and in some cases, distort the NPV and IRR, it is preferred in the economic evaluation of the PET plant to be conservative and assume a zero salvage value.

The internal rate of return (IRR) also called the discounted cash-flow rate of return (DCFRR), is the interest rate at which the net present value is zero. Since the net present value is a complex nonlinear function of the interest rate, an iterative procedure accomplished easily using an excel spreadsheet is made to solve the root of its residual.

\[ NPV(r) = 0 \]

When comparing proposed processes, the largest internal rate of return is the most desirable. However, often the processes having the largest internal rate of return have the smaller net present value (Seider et. al., 1999). The DCFRR was found to be ---, which is ---. The DCF and NPV for the PET project are shown in Figure (9.#)

Figure (9.#): Cumulative cash flow and NPV of the PET process

9.6 Sensitivity Analysis
A sensitivity analysis is performed to see the influence of price fluctuations on the project profitability. The effect of the cost variation of the following variables was studied:

- Prices of raw materials
- Selling price of PET
- Purchased cost of equipment

For the sensitivity analysis, the values of the NPV at a discounted rate of 15% and IRR after 10 years (end lifetime of the project) are calculated by multiplying the cost for the base case with a factor. The results are shown in Table (9.4).

Table (9.4): Sensitivity analysis results on profitability of PET process.

<table>
<thead>
<tr>
<th>Case</th>
<th>Factor</th>
<th>NPV (MUS$)</th>
<th>IRR (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Base</td>
<td>1</td>
<td>4.2</td>
<td>18.9</td>
</tr>
<tr>
<td>EG Price</td>
<td>0.5</td>
<td>50.47</td>
<td>57.1</td>
</tr>
<tr>
<td></td>
<td>0.75</td>
<td>38.8</td>
<td>27.33</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>4.17</td>
<td>18.9</td>
</tr>
<tr>
<td></td>
<td>1.25</td>
<td>-18.94</td>
<td>-7.0</td>
</tr>
<tr>
<td>TPA Price</td>
<td>0.5</td>
<td>148.08</td>
<td>131.8</td>
</tr>
<tr>
<td></td>
<td>0.75</td>
<td>76.14</td>
<td>76.9</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>4.2</td>
<td>18.9</td>
</tr>
<tr>
<td></td>
<td>1.1</td>
<td>-5.28</td>
<td>-17.1</td>
</tr>
<tr>
<td>PET Price</td>
<td>0.95</td>
<td>-16.66</td>
<td>-3.7</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>4.2</td>
<td>18.9</td>
</tr>
<tr>
<td></td>
<td>1.25</td>
<td>108.49</td>
<td>101.7</td>
</tr>
<tr>
<td></td>
<td>1.5</td>
<td>212.78</td>
<td>180.9</td>
</tr>
<tr>
<td>Purchased Cost of Equipment</td>
<td>0.5</td>
<td>15.08</td>
<td>41.05</td>
</tr>
<tr>
<td></td>
<td>0.75</td>
<td>9.64</td>
<td>26.7</td>
</tr>
<tr>
<td></td>
<td>1.0</td>
<td>4.2</td>
<td>18.9</td>
</tr>
<tr>
<td></td>
<td>1.5</td>
<td>-6.69</td>
<td>10.6</td>
</tr>
<tr>
<td></td>
<td>2</td>
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<td>6</td>
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<tr>
<td></td>
<td>4</td>
<td>-61.11</td>
<td>-1.8</td>
</tr>
</tbody>
</table>

9.7 Conclusions
Reference

Contents

1. Appendix A: Original Assignment
2. Appendix B: Physical and Chemical Properties of Raw Materials
3. Appendix C: Black Box Calculations
4. Appendix D: Mole and Mass Balance for the Recycle Structure
5. Appendix E: Equipment Sizing
6. Appendix F: Safety and Environmental Aspects
7. Appendix G: Fire and Explosion Index
8. Appendix H: HAZOP Study Tables
9. Appendix I: Piping and Instrumentation
Appendix A

The Original Assignment
Design an esterification process based on pervaporation with inorganic membranes

The function of the membrane is to complete the esterification reaction by selectively removing the water byproduct. The reaction system, capacity, etc. is not selected yet but should be that harsh that an inorganic membrane should be used. Please come with suggestions based on literature.

We found and based on literature survey that a lot of data were published on the direct esterification of ethylene glycol and terephthalic acid in polyethylene terephthalate production. This project represents studying the production of polyethylene terephthalate (PET) by direct esterification using pervaporation as a separation technology.
Appendix B

Physical and Chemical Properties of Raw Materials*

- B1. EG Physical and Chemical Properties
- B2. TPA Physical and Chemical Properties

*The data are taken from NIST Chemistry WebBook
NIST Standard Reference Database Number 69 - February 2000 Release
http://webbook.nist.gov/chemistry/
B1. Ethylene Glycol

1. Material Identification

- **Formula:** \( \text{C}_2\text{H}_6\text{O}_2 \)
- **Molecular Weight:** 62.07
- **CAS Registry Number:** 107-21-1

- **Chemical Structure:**

  \[ \text{HO} - \text{CH}_2 - \text{CH}_2 - \text{OH} \]

- **Other Names:** Ethylene glycol; Ethylene alcohol; Ethylene dihydrate; Glycol; Glycol alcohol; Lutrol 9; Macrogol 400 BPC; Monoethylene glycol; Ramp; Tescol; 1,2-Di hydroxyethane; 2-Hydroxyethanol; HOCH\text{H}_2\text{OH}; Dihydroxyethane; Ethanediol; Ethylene glycol; Glygen; Athylenglykol; Ethane-1,2-diol; Fridex; M.e.g.; 1,2-Ethandiol; Ucar 17; Dowtherm SR 1; Norkool; Zerex

- **Gas phase thermochemistry data**
- **Condensed phase thermochemistry data**
- **Phase change data**
- **Reaction thermochemistry data**
- **Henry's Law data**
- **References**
2. Gas phase thermochemistry data

Data compiled as indicated in comments:

ALS - H.Y. Afeefy, J.F. Liebman, and S.E. Stein

GT - Glushko Thermocenter, Russian Academy of Sciences, V.S. Yungman, director

<table>
<thead>
<tr>
<th>Quantity</th>
<th>Value</th>
<th>Units</th>
<th>Method</th>
<th>Reference</th>
<th>Comment</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Delta H^\circ_{\text{gas}}$</td>
<td>-394.4 ± 2.8</td>
<td>kJ/mol</td>
<td>Ccr</td>
<td>Knauth and Sabbah, 1990</td>
<td>see Knauth and Sabbah, 1989; ALS</td>
</tr>
<tr>
<td>$\Delta H^\circ_{\text{gas}}$</td>
<td>-388. ± 2.</td>
<td>kJ/mol</td>
<td>Ccb</td>
<td>Gardner and Hussain, 1972</td>
<td>ALS</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Quantity</th>
<th>Value</th>
<th>Units</th>
<th>Method</th>
<th>Reference</th>
<th>Comment</th>
</tr>
</thead>
<tbody>
<tr>
<td>$S^\circ_{\text{gas}}$</td>
<td>311.84</td>
<td>J/mol*K</td>
<td>N/A</td>
<td>Chao J., 1986</td>
<td>Other third-law entropy values at 298.15 K known from literature are 284.5 [Buckley P., 1967], 312.5 [Stull D.R., 1969], and 315.47(5.36) J/mol*K [Yeh T.-S., 1994]; GT</td>
</tr>
</tbody>
</table>

Constant pressure heat capacity of gas.

<table>
<thead>
<tr>
<th>$C_{p,\text{gas}}$ (J/mol*K)</th>
<th>Temperature (K)</th>
<th>Reference</th>
<th>Comment</th>
</tr>
</thead>
<tbody>
<tr>
<td>59.79</td>
<td>200.</td>
<td>Yeh T.-S., 1994</td>
<td>Other statistically calculated values of entropy at 298.15 K (274.76 [Buckley P., 1967], 293.76 [Frei H., 1977], 303.8 [Chao J., 1986], and 323.55 J/mol*K [Dyatkina M.E., 1954]) are in worse agreement with third-law entropy value.; GT</td>
</tr>
<tr>
<td>77.99</td>
<td>298.15</td>
<td></td>
<td></td>
</tr>
<tr>
<td>78.41</td>
<td>300.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>97.99</td>
<td>400.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>113.64</td>
<td>500.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>125.65</td>
<td>600.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>135.23</td>
<td>700.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>143.26</td>
<td>800.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>150.25</td>
<td>900.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>156.40</td>
<td>1000.</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
3. Condensed phase thermochemistry data

Data compiled as indicated in comments:

ALS - H.Y. Afeefy, J.F. Liebman, and S.E. Stein

DH - E.S. Domalski and E.D. Hearing

| Quantity     | Value         | Units     | Method | Reference                  | Comment                                               |
|--------------|---------------|-----------|--------|----------------------------|                                                      |
| $\Delta H^\circ_{\text{liquid}}$ | $-460.0 \pm 2.8$ | kJ/mol    | Ccr    | Knauth and Sabbah, 1990    | see Knauth and Sabbah, 1989; ALS                    |
| $\Delta H^\circ_{\text{liquid}}$ | $-455.6 \pm 0.8$ | kJ/mol    | Ccb    | Gardner and Hussain, 1972  | ALS                                                  |
| $\Delta H^\circ_{\text{liquid}}$ | $-455.85$     | kJ/mol    | Ccb    | McClaine, 1947            | ALS                                                  |
| $\Delta H^\circ_{\text{liquid}}$ | $-454.93 \pm 0.29$ | kJ/mol    | Ccb    | Parks, West, et al., 1946  | ALS                                                  |
| $\Delta H^\circ_{\text{liquid}}$ | $-453.13 \pm 1.21$ | kJ/mol    | Ccb    | Moureu and Dode, 1937      | Reanalyzed by Cox and Pilcher, 1970, Original value = $-452.3$ kJ/mol; ALS |

| Quantity     | Value         | Units     | Method | Reference                  | Comment                                               |
|--------------|---------------|-----------|--------|----------------------------|                                                      |
| $S^\circ_{\text{liquid}}$ | 166.9         | J/mol*K   | N/A    | Parks, Kelley, et al., 1929 | Extrapolation below 90 K, 8.2 cal/mol*K.             |
| $S^\circ_{\text{liquid}}$ | 179.5         | J/mol*K   | N/A    | Parks and Kelley, 1925     | Extrapolation below 90 K, 11.46 cal/mol*K.; DH       |
## Constant pressure heat capacity of liquid.

<table>
<thead>
<tr>
<th>( C_{p,\text{liquid}} ) (J/mol*K)</th>
<th>Temperature (K)</th>
<th>Reference</th>
<th>Comment</th>
</tr>
</thead>
<tbody>
<tr>
<td>149.8</td>
<td>298.</td>
<td>Zaripov, 1982</td>
<td>T = 298, 323, 363 K.; DH</td>
</tr>
<tr>
<td>149.3</td>
<td>298.</td>
<td>Stephens and Tamlpin, 1979</td>
<td>T = 273 to 493 K.; DH</td>
</tr>
<tr>
<td>149.6</td>
<td>298.15</td>
<td>Murthy and Subrahmanyam, 1977</td>
<td></td>
</tr>
<tr>
<td>145.2</td>
<td>303.</td>
<td>Kawaizumi, Otake, et al., 1972</td>
<td>DH</td>
</tr>
<tr>
<td>150.6</td>
<td>301.2</td>
<td>Paz Andrade, Paz, et al., 1970</td>
<td>T = 28, 40°C.; DH</td>
</tr>
<tr>
<td>150.33</td>
<td>298.15</td>
<td>Nikolaev and Rabinovich, 1967</td>
<td>T = 80 to 300 K.; DH</td>
</tr>
<tr>
<td>147.3</td>
<td>298.</td>
<td>Tungusov and Mishchenko, 1965</td>
<td>DH</td>
</tr>
<tr>
<td>148.87</td>
<td>298.</td>
<td>Rabinovich and Nikolaev, 1962</td>
<td>T = 10 to 55°C.; DH</td>
</tr>
<tr>
<td>145.6</td>
<td>293.4</td>
<td>Neiman and Kurlyankin, 1932</td>
<td>T = 20.2 to 78.4°C. Value is unsmoothed experimental datum.; DH</td>
</tr>
<tr>
<td>149.4</td>
<td>293.0</td>
<td>Parks and Kelley, 1925</td>
<td>T = 88 to 293 K. Value is unsmoothed experimental datum.; DH</td>
</tr>
</tbody>
</table>

### 4. Phase change data

**Data compiled as indicated in comments:**

- **BS** - R.L. Brown and S.E. Stein
- **DH** - E.S. Domalski and E.D. Hearing

<table>
<thead>
<tr>
<th>Quantity</th>
<th>Value</th>
<th>Units</th>
<th>Method</th>
<th>Reference</th>
<th>Comment</th>
</tr>
</thead>
<tbody>
<tr>
<td>( T_{\text{boil}} )</td>
<td>471.2</td>
<td>K</td>
<td>N/A</td>
<td>Weast and Grasselli, 1989</td>
<td>BS</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Quantity</th>
<th>Value</th>
<th>Units</th>
<th>Method</th>
<th>Reference</th>
<th>Comment</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \Delta_{\text{vap}}H^* )</td>
<td>65.6 ± 0.3</td>
<td>kJ/mol</td>
<td>C</td>
<td>Kauth and Sabbah, 1988</td>
<td>ALS</td>
</tr>
</tbody>
</table>
Enthalpy of vaporization

<table>
<thead>
<tr>
<th>$\Delta_{\text{vap}}H$ (kJ/mol)</th>
<th>Temperature (K)</th>
<th>Method</th>
<th>Reference</th>
<th>Comment</th>
</tr>
</thead>
<tbody>
<tr>
<td>67.8 ± 1.7</td>
<td>409. - 469.</td>
<td>V</td>
<td>Gardner and Hussain, 1972</td>
<td>ALS</td>
</tr>
<tr>
<td>61.92 ± 6.28</td>
<td>273.</td>
<td>V</td>
<td>Gallaugher and Hibbert, 1937</td>
<td>Reanalyzed by Pedley, Naylor, et al., 1986, Original value = 57.07 kJ/mol; ALS</td>
</tr>
</tbody>
</table>

Enthalpy of fusion

<table>
<thead>
<tr>
<th>$\Delta_{\text{fus}}H$ (kJ/mol)</th>
<th>Temperature (K)</th>
<th>Reference</th>
<th>Comment</th>
</tr>
</thead>
<tbody>
<tr>
<td>9.958</td>
<td>260.6</td>
<td>Nikolaev and Rabinovich, 1967</td>
<td>DH</td>
</tr>
<tr>
<td>11.623</td>
<td>260.8</td>
<td>Parks and Kelley, 1925</td>
<td>DH</td>
</tr>
</tbody>
</table>

Entropy of fusion

<table>
<thead>
<tr>
<th>$\Delta_{\text{fus}}S$ (J/mol*K)</th>
<th>Temperature (K)</th>
<th>Reference</th>
<th>Comment</th>
</tr>
</thead>
<tbody>
<tr>
<td>38.21</td>
<td>260.6</td>
<td>Nikolaev and Rabinovich, 1967</td>
<td>DH</td>
</tr>
<tr>
<td>44.57</td>
<td>260.8</td>
<td>Parks and Kelley, 1925</td>
<td>DH</td>
</tr>
</tbody>
</table>

5. Reaction thermochemistry data

Data compiled as indicated in comments:
- B - J.E. Bartmess
Production of Polyethylene Terephthalate by Direct Esterification Using Pervaporation

<table>
<thead>
<tr>
<th>Quantity</th>
<th>Value</th>
<th>Units</th>
<th>Method</th>
<th>Reference</th>
<th>Comment</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Delta_{c}H^{\circ}$</td>
<td>-1184.6 ± 2.8 kJ/mol</td>
<td>Ccr</td>
<td>Knauth and Sabbah, 1990</td>
<td>liquid phase; see Knauth and Sabbah, 1989; ALS</td>
<td></td>
</tr>
<tr>
<td>$\Delta_{c}H^{\circ}$</td>
<td>-1188.8 ± 0.67 kJ/mol</td>
<td>Ccb</td>
<td>Gardner and Hussain, 1972</td>
<td>liquid phase; ALS</td>
<td></td>
</tr>
<tr>
<td>$\Delta_{c}H^{\circ}$</td>
<td>-1190.2 kJ/mol</td>
<td>Cm</td>
<td>Parks and Manchester, 1952</td>
<td>liquid phase; From heat of solution; ALS</td>
<td></td>
</tr>
<tr>
<td>$\Delta_{c}H^{\circ}$</td>
<td>-1189. ± 0.8 kJ/mol</td>
<td>Ccb</td>
<td>McClaine, 1947</td>
<td>liquid phase; ALS</td>
<td></td>
</tr>
<tr>
<td>$\Delta_{c}H^{\circ}$</td>
<td>-1189.6 ± 0.71 kJ/mol</td>
<td>Ccb</td>
<td>Parks, West, et al., 1946</td>
<td>liquid phase; ALS</td>
<td></td>
</tr>
<tr>
<td>$\Delta_{c}H^{\circ}$</td>
<td>-1202.6 ± 1.2 kJ/mol</td>
<td>Ccb</td>
<td>Jung and Dahmlos, 1942</td>
<td>liquid phase; Reanalyzed by Cox and Pilcher, 1970, Original value = -1201. kJ/mol; ALS</td>
<td></td>
</tr>
<tr>
<td>$\Delta_{c}H^{\circ}$</td>
<td>-1191.4 ± 1.2 kJ/mol</td>
<td>Ccb</td>
<td>Moureu and Dode, 1937</td>
<td>liquid phase; Reanalyzed by Cox and Pilcher, 1970, Original value = -1192. kJ/mol; ALS</td>
<td></td>
</tr>
</tbody>
</table>

6. Henry’s Law data

Data compiled by: R. Sander

Henry’s Law constant (water solution)

$k_{H}^{\circ}$ = Henry’s law constant for solubility in water at 298.15 K (mol/kg*bar)

<table>
<thead>
<tr>
<th>$k_{H}^{\circ}$ (mol/kg*bar)</th>
<th>d(ln($k_{H}^{\circ}$))/d(1/T) (K)</th>
<th>Method</th>
<th>Reference</th>
<th>Comment</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.0×10^-4</td>
<td>M</td>
<td>Bone, Cullis, et al., 1983</td>
<td>Value at T = 293. K.</td>
<td></td>
</tr>
<tr>
<td>17000</td>
<td>M</td>
<td>Butler and Ramchandani, 1935</td>
<td>Saxena and Hildemann, 1996 say that this value is unreliable.</td>
<td></td>
</tr>
</tbody>
</table>
References


B2. Terephthalic acid

1. Material Identification

- **Formula:** C₈H₆O₄
- **Molecular Weight:** 166.13
- **CAS Registry Number:** 100-21-0

![Chemical Structure of Terephthalic Acid]

- **Chemical Structure:**
- **Other Names:** Terephthalic acid; p-Benzenedicarboxylic acid; p-Dicarboxybenzene; p-Phthalic acid; WR 16262; Benzene, 1,4-Dicarboxylic acid; Acide terephthalique; Benzene-p-dicarboxylic acid; Kyselina terftalova; TPA; Kyselina teretftalova; TA 12; Ta-33mp
- **Condensed phase thermochemistry data**
- **Phase change data**
- **Reaction thermochemistry data**
- **References**

2. Condensed phase thermochemistry data

Data compiled as indicated in comments:

*ALS* - H.Y. Afeefy, J.F. Liebman, and S.E. Stein

*DH* - E.S. Domalski and E.D. Hearing

<table>
<thead>
<tr>
<th>Quantity</th>
<th>Value</th>
<th>Units</th>
<th>Method</th>
<th>Reference</th>
<th>Comment</th>
</tr>
</thead>
<tbody>
<tr>
<td>ΔH°solid</td>
<td>-816.3±1.5</td>
<td>kJ/mol</td>
<td>Ccb</td>
<td>Karyakin, Rabinovich, et al., 1978</td>
<td>ALS</td>
</tr>
<tr>
<td>ΔH°solid</td>
<td>-816.17</td>
<td>kJ/mol</td>
<td>Ccb</td>
<td>Schwabe and Wagner, 1961</td>
<td>ALS</td>
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</table>
Constant pressure heat capacity of solid.

<table>
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<tr>
<th>$C_{p,\text{solid}}$ (J/mol*K)</th>
<th>Temperature (K)</th>
<th>Reference</th>
<th>Comment</th>
</tr>
</thead>
<tbody>
<tr>
<td>199.6</td>
<td>323</td>
<td>Satoh and Sogabe, 1941</td>
<td>$T = 0 \text{ to } 100 \text{ C. Mean value;}$ $DH$</td>
</tr>
</tbody>
</table>

3. Phase change data

Data compiled as indicated in comments:

ALS - H.Y. Afeefy, J.F. Liebman, and S.E. Stein
C - J.S. Chickos

<table>
<thead>
<tr>
<th>Quantity</th>
<th>Value</th>
<th>Units</th>
<th>Method</th>
<th>Reference</th>
<th>Comment</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Delta_{\text{sub}H^\circ}$</td>
<td>98.115</td>
<td>kJ/mol</td>
<td>V</td>
<td>Hirshbrunner, 1934</td>
<td>ALS</td>
</tr>
</tbody>
</table>

Enthalpy of sublimation

<table>
<thead>
<tr>
<th>$\Delta_{\text{sub}H}$ (kJ/mol)</th>
<th>Temperature (K)</th>
<th>Method</th>
<th>Reference</th>
<th>Comment</th>
</tr>
</thead>
<tbody>
<tr>
<td>139.2</td>
<td>523. - 633.</td>
<td>N/A</td>
<td>Stephenson and Malanowski, 1987</td>
<td>C</td>
</tr>
<tr>
<td>131.</td>
<td>523. - 633.</td>
<td>GS</td>
<td>Kraus, Beranek, et al., 1962</td>
<td>C</td>
</tr>
<tr>
<td>98.24 ± 2.50</td>
<td>392. - 425.</td>
<td>N/A</td>
<td>Hirshbrunner, 1934, 2</td>
<td>C</td>
</tr>
</tbody>
</table>

Reaction thermochemistry data

Data compiled by: H.Y. Afeefy, J.F. Liebman, and S.E. Stein

<table>
<thead>
<tr>
<th>Quantity</th>
<th>Value</th>
<th>Units</th>
<th>Method</th>
<th>Reference</th>
<th>Comment</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Delta_H^\circ$</td>
<td>-3189.3 ± 1.5</td>
<td>kJ/mol</td>
<td>Ccb</td>
<td>Karyakin, Rabinovich, et al., 1978</td>
<td>solid phase</td>
</tr>
<tr>
<td>$\Delta_H^\circ$</td>
<td>-3189.5 ± 0.42</td>
<td>kJ/mol</td>
<td>Ccb</td>
<td>Schwabe and Wagner, 1961</td>
<td>solid phase</td>
</tr>
<tr>
<td>$\Delta_H^\circ$</td>
<td>-3227.96</td>
<td>kJ/mol</td>
<td>Ccb</td>
<td>Hirshbrunner, 1934</td>
<td>solid phase</td>
</tr>
</tbody>
</table>
References

Appendix E

Equipment Sizing

- E1. Storage Tanks Sizing
- E2. Pumps Sizing
- E3. Mixing Tank Sizing
- E4. Esterification Reactors Sizing
- E5. Pervaporation Membranes Sizing
- E6. Low Polymerizer Sizing
- E7. Intermediate Polymerizer Sizing
- E8. High Polymerizer Sizing
- E9. Spray Condensers Sizing
- E10. Heat Exchangers Sizing
E1. Storage Tanks Sizing

To assure uninterrupted operation, a storage capacity is usually provided for raw materials and manufactured products.

E1.1 Storage Tank (S-100)

This tank is used to store the raw material ethylene glycol. This tank should be large enough to accommodate one or several loads discharged from the transporters. Since ethylene glycol is very hygroscopic, the tank must be protected from atmospheric moisture. In addition to that, it must be heated enough to prevent freezing.

The plant is producing 103 million kg of product polyethylene terephthalate. From the scope and unit ratio material balance, the following information is obtained: 0.338 kg of ethylene glycol is required for each kg of product. A 15-30-days storage is recommended in literature (Bassel, 1990 and Ulrich, 1984). A capacity of 20-days is specified for ethylene glycol; and plant will operate 8150 hr/yr.

Kilograms of ethylene glycol used per year

\[(0.338 \text{ kg EG/kg product}) \times (103 \text{ million kg product / yr}) \times (1 \text{ yr / 8150 hr}) \times (24 \text{ hr / day}) = 102,500\]

Kilograms of EG that must be stored:

\[(96,016 \text{ kg / day}) \times (20 \text{ days}) = 2.05 \text{ million kg}\]

The specific gravity of EG (at 25 °C, see chapter two) is 1.11. Meter cubes of EG that must be stored:

\[(2,05,000 \text{ kg}) \times (1 \text{ m}^3 / 1110 \text{ kg}) = 1865 \text{ m}^3\]

Bassel, 1990, pp. 113, states that when the quantities to be stored above 25,000 gal (94.7 m³), the tanks should be constructed according to the dimensions given by the American Petroleum Institute standards.

The closest volume to estimated value from the API standards is 1,625 m³, which corresponds to 17.4-days storage period. From this table the following sizing results are obtained:
**E1.1.1 Material of construction**

Aluminum is recommended by Ulrich, 1984 and Schweitzer, 1991, due to its low corrosion rate for ethylene glycol (less than 2 Mills penetration per year).

**E1.2 Storage Tank (S-110)**

The bags of terephthalic acid (TPA) are stored in specially provided areas, which must be, dry, and free from dust. They are moved by means of fork-lift trucks or other mechanical transportation or stacking devices.

In addition to this area, a bin is used for the solid TPA as an in process with capacity equal to 8 hours throughput. (Ulrich, 1984). Kilograms of TPA used per 8 hours:

\[
(0.850 \text{ kg TPA / kg product}) \times (103 \text{ million kg product / yr}) \times (\text{yr / 8150 hr}) \times (8 \text{ hr}) = 86,000 \text{ kg}
\]

The specific gravity of TPA (at 25 °C, see chapter two) is 1.871. Meter cubes of TPA that must be stored:

\[
(86,000 \text{ kg}) \times (1 \text{ m}^3 / 1871\text{kg}) = 46 \text{ m}^3
\]

For easy flowing material, Bassel, 1990, recommends to use the height of the vessel 1.5 times the diameter and 30° as angle for the cone of the bin. The bin sizing results are as follows:

<table>
<thead>
<tr>
<th>Bin volume</th>
<th>m³</th>
<th>46</th>
</tr>
</thead>
<tbody>
<tr>
<td>Height</td>
<td>m</td>
<td>5.09</td>
</tr>
<tr>
<td>Diameter</td>
<td>m</td>
<td>3.39</td>
</tr>
<tr>
<td>Cone angle</td>
<td>°</td>
<td>30°</td>
</tr>
</tbody>
</table>

The material of construction is selected to carbon steel.

**E2.1 Pumps Sizing**

The pumps are sized using the following relations, and Table (E.1) summarizes the results of pumps sizing.
\[ \Delta P = \rho \times g \times h \]
\[ W_s = q \times P / E_i \]
\[ P = W_s / E_d \]

Where,

- \( \rho \) = Density \( \text{kg} / \text{m}^3 \)
- \( g \) = Acceleration of gravity \( \text{m/s}^2 \)
- \( h \) = Height of liquid \( \text{m} \)
- \( W_s \) = Shaft power, \( \text{kW} \)
- \( q \) = Volumetric flow rate, \( \text{m}^3/\text{s} \)
- \( \Delta P \) = Pressure drop, \( \text{Pa} \)
- \( E_i \) = Intrinsic pump efficiency [1], -
- \( E_d \) = Drive efficiency [1], -

**Table (E.1) summary of pumps sizing**

<table>
<thead>
<tr>
<th>Pump No.</th>
<th>Type [2]</th>
<th>( q ) (m³/s)</th>
<th>( \Delta P ) (Pa)</th>
<th>Power consumption</th>
<th>Material of Construction [2]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>( E_i ) Ws (kW)</td>
<td>( E_d ) P (kW)</td>
</tr>
<tr>
<td>P-100</td>
<td>Horizontal centrifuge</td>
<td>1.075E-3</td>
<td>50,000</td>
<td>0.5</td>
<td>0.11</td>
</tr>
<tr>
<td>P-110</td>
<td>Horizontal centrifuge</td>
<td>2.75E-3</td>
<td>343,000</td>
<td>0.5</td>
<td>1.89</td>
</tr>
<tr>
<td>P-500</td>
<td>Horizontal centrifuge</td>
<td>6.19E-3</td>
<td>39,400</td>
<td>0.5</td>
<td>0.49</td>
</tr>
<tr>
<td>P-510</td>
<td>Horizontal centrifuge</td>
<td>1.73E-3</td>
<td>73,200</td>
<td>0.5</td>
<td>0.25</td>
</tr>
<tr>
<td>P-520</td>
<td>Horizontal centrifuge</td>
<td>3.31E-4</td>
<td>105,000</td>
<td>0.5</td>
<td>0.07</td>
</tr>
</tbody>
</table>

**E2.2 Vacuum Pumps Sizing**

Vacuum pumps are sized based on the amount of gases and vapors that must be removed per hour under operating conditions and desired vacuum. The air leakage may be calculated from the following equation, Bassel, 1990:

\[ W = 0.064 P^{0.26} V^{0.6} \]

\( 10 \leq P \leq 100 \, \text{torr} \)
Where,

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>P</td>
<td>System operating pressure</td>
<td>Torr</td>
</tr>
<tr>
<td>V</td>
<td>Volume</td>
<td>Ft³</td>
</tr>
<tr>
<td>w</td>
<td>Air leakage resulting from metal porosities and cracks along weld lines</td>
<td>lb/hr</td>
</tr>
</tbody>
</table>

The type of vacuum pump is selected using Figure (E.1), which shows the vacuum level of various types of equipment. Rotary oil vacuum pump is selected.

![Figure (E.1) Vacuum levels attainable with various types of equipment, Perry's, 1984](image)

Figure (E.1) Vacuum levels attainable with various types of equipment, Perry's, 1984

Figure (E.2) is used to convert the air flow rate from kg/hr into dm³/s. This value is then used in Figure (E.3) to find the power consumption. A summary of these calculations CAN BE found in Table (E.2).
Figure (E.2) Relationship between inlet vacuum pressure, mass, and volume flow rates (for air at 20 °C), Woods, 1995.
Figure (E.3) Air exhausted from the system, actual volume, dm³/hr, Woods, 1995

Table (E.2) Summary of vacuum pump sizing calculations

<table>
<thead>
<tr>
<th>Pump NO</th>
<th>Capacity (Kg air/hr)</th>
<th>V (dm³/s)</th>
<th>Power (kW)</th>
</tr>
</thead>
<tbody>
<tr>
<td>400</td>
<td>0.29</td>
<td>3.7</td>
<td>0.4</td>
</tr>
<tr>
<td>410</td>
<td>0.17</td>
<td>2.5</td>
<td>0.2</td>
</tr>
<tr>
<td>420</td>
<td>0.15</td>
<td>2.3</td>
<td>0.15</td>
</tr>
<tr>
<td>430</td>
<td>0.13</td>
<td>1.7</td>
<td>0.10</td>
</tr>
</tbody>
</table>

The material of construction of these pumps is selected to be carbon steel, due to its low cost and ability to withstand the operating conditions of these pumps, Ulrich, 1984.
E3. Mixing Tank Sizing

E3.1 Mixing tank mass balance

Figure (E.4) shows the mixer (M-100) mass balance.

![Mixer (M-100) mass balance](image)

Figure (E.4): Mixer (M-100) mass balance.

E3.2 Mixing tank (M-100) sizing

The data required for sizing is
- Average volumetric flow rate
- Residence time
The average volumetric flow rate is obtained from the simulation results (9.9 m$^3$/hr). Whereas the residence time is function of the mixing time. The mixing time is function of the fluid characteristics such as
- solid and liquid density
- solid liquid of the slurry
- settling velocity of particles

These properties need experimental data. Due to the non-availability of these data a sufficient mixing time of (5 minutes) is assumed.

$$\Theta = \frac{V}{\nu}$$  
\text{(E.1)}

Where,
\(\Theta\) Residence time, min
\(V\) Mixing tank volume, m$^3$
\(\nu\) Average volumetric flow rate, m$^3$/hr

The mixing tank volume is (0.825 m$^3$), calculated using equation (E.1).

The type of mixer is selected to be axial turbine (six blade turbine agitator with disk) based on the guide given by (Ulrich, 1984, pp.168). The geometric proportions of the agitation system are taken to be as the standard geometric proportions described by Geankoplis, 1993, pp.144.

Figure (E.5): Baffled tank with six blade turbine agitator with disk showing flow patterns: (a) side view, (b) bottom view, (c) dimensions of turbine and tank.
Standard Geometric Proportion | Estimated Value (m)
--- | ---
H = D | 1.02
Dₐ = 0.4 D | 0.41
C = D / 3 | 0.39
W = D / 5 | 0.08
Dₜ = 2D / 3 | 0.27
L = D / 4 | 0.10
J = D / 12 | 0.09

The height of the vessel is taken to be 1.5 the diameter (H = 1.53 m) as recommended by Ulrich, 1984, pp. 432.

**E3.3 Power requirement**

In order to calculate the power consumption, the following equations are used

\[
Re = D_a^2 N \frac{\rho}{\mu} \tag{E.2}
\]

\[
N_p = P \left( \frac{\rho}{\mu} \frac{1}{N^3 D_a^5} \right) \tag{E.3}
\]

- **Re** Reynolds number, -
- **Dₐ** Agitator diameter, m
- **N** Rotational speed, rev / s
- **ρ** Fluid density, kg / m³
- **μ** Fluid viscosity, Kg / m.s
- **N_p** Power number, -
- **P** Power, W

Herman Ludewig, 1971, pp. 103, states that the speed of mixer for the esterification reactor is 40 to 60 revolution per minute. A value of 60 rpm will be taken as the value for the mixing tank. Substituting the values of the parameters (Dₐ = 0.41 m, ρ = 1551 kg / m³, μ = 0.00111 Kg / m.s) in equation (E.2). Re is estimated to be 235,000.

From Coulson and Richardson, 1999, pp. 473, is used to find Nₚ. It is found to be (5). Equation (E.2) is used to estimate the power consumption P. It is estimated to be 3.18 kW.
E3.4 Material of construction

Schweitzer, 1991, part A, pp. 1029 recommends the use of aluminum for this range of temperature (42 °C) and this type of fluid (ethylene glycol). The corrosion of this material is less than (2) Mils penetration per year.

E4. Esterification Reactors Sizing

Detailed sizing will be made for the primary esterification reactor (R-200) and the results of sizing will be summarized for the secondary esterification reactors: (R-210) and (R-220).

E4.1 (R-200) Mass Balance

![Figure (E.6): Esterification reactor (R-200) mass balance](image)

\[ \text{VL} = \Theta \nu \]  

(E.4)

E4.2 (R-200) Sizing

The procedure of sizing the reactor is the same as that used for sizing the mixing tank (M-100). The data required for the reactor sizing are obtained from the simulation results. The average volumetric flow rate is \(9.9 \text{ m}^3/\text{hr}\), whereas the reactor residence time is (2 hr).
The volume is estimated to be (19.8 m$^3$). The reactor is generally 90 % full and the height of the reactor is generally twice the diameter (Bassel, 1990).

\[
V_L = \frac{\pi}{4} D^2 H_L \quad \text{(E.5)}
\]

\[
V = \frac{\pi}{4} D^2 H \quad \text{(E.6)}
\]

\[
H_L = 0.9 H \quad \text{(E.7)}
\]

Using the previous equations, the dimensions of the reactor vessel are estimated, and the results are shown in the following table:

<table>
<thead>
<tr>
<th></th>
<th>Total Reactor volume, m$^3$</th>
<th>22.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>$V_L$</td>
<td>Volume liquid in the reactor, m$^3$</td>
<td>19.8</td>
</tr>
<tr>
<td>D</td>
<td>Diameter, m</td>
<td>2.33</td>
</tr>
<tr>
<td>$H_L$</td>
<td>Liquid height, m</td>
<td>4.66</td>
</tr>
<tr>
<td>H</td>
<td>Reactor height, m</td>
<td>5.17</td>
</tr>
</tbody>
</table>

**E4.3 (R-200) Mixer Sizing**

The type of mixer is selected to be an axial turbine (six blade turbine with agitator disk) based on the guidelines of Ulrich, 1984. The geometric proportions of the agitation system are taken to be as the standard geometric proportions described by Geankoplis, 1993, pp. 144.

<table>
<thead>
<tr>
<th>Standard Geometric Proportion</th>
<th>Estimated Value (m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$H_L = 2 D_s$</td>
<td>4.66</td>
</tr>
<tr>
<td>$D_s = 0.4 D_r$</td>
<td>0.93</td>
</tr>
<tr>
<td>$C = D_i / 3$</td>
<td>0.78</td>
</tr>
<tr>
<td>$W = D_r / 5$</td>
<td>0.19</td>
</tr>
<tr>
<td>$D_y = 2D_s / 3$</td>
<td>0.62</td>
</tr>
<tr>
<td>$L = D_s / 4$</td>
<td>0.23</td>
</tr>
<tr>
<td>$J = D_r / 12$</td>
<td>0.19</td>
</tr>
</tbody>
</table>

**E4.4 (R-200) Heating Jacket**

Heating jackets are welded into the heating tubes running obliquely from bottom to top. Any electrical heating device must be protected against explosion. In order to attain short heating and reaction times, the heating efficiency must be adjusted accordingly.
E4.5 (R-200) Power Requirement

The agitator is filled in the interior of the vessel. It is driven by an a.c. motor via a reduction
gear, which transforms the revolutions of the motor to a speed of 40 to 60 rpm (Hermann Ludewig,
1971). All parts must be protected against explosion.

The power requirement is calculated using the same relations used in the power calculation
for the mixer M-100. Reynolds number is estimated to be (at a speed of 50 rpm) 1000,000. Np is
found to be (5). The power is estimated to be 4.17 kW.

E4.6 Reactor Vessel Thickness

The minimum thickness of the reactor vessel required to resist internal pressure can be
determined from the following equation (Richardson and Coulson, 1999, pp.812)

\[
e = \frac{P_i \times D_i}{2 \times f - P_i},
\]

(E.8)

Where,

<table>
<thead>
<tr>
<th>e</th>
<th>Minimum wall thickness</th>
<th>m</th>
</tr>
</thead>
<tbody>
<tr>
<td>P_i</td>
<td>Internal pressure</td>
<td>Pa</td>
</tr>
<tr>
<td>D_i</td>
<td>Internal diameter</td>
<td>m</td>
</tr>
<tr>
<td>f</td>
<td>Design stress</td>
<td>Pa</td>
</tr>
</tbody>
</table>

* double-welded butt or equivalent and 100 % degree of radioactivity (Coulson and Richardson)
** at design temperature 240 °C and stainless steel 316 as material of construction (Coulson and Richardson)

The minimum wall thickness is estimated to be 4.5 mm. Add a corrosion allowance of 2 mm, then the
thickness is 6.5 mm. Coulson and Richardson, 1999, pp. 811 gives the minimum practical wall
thickness including corrosion allowance as shown in Table (E.3):

Table (E.3) Minimum Practical wall thickness including corrosion allowance

<table>
<thead>
<tr>
<th>Vessel diameter (m)</th>
<th>Minimum thickness (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>5</td>
</tr>
<tr>
<td>1 to 2</td>
<td>7</td>
</tr>
<tr>
<td>2 to 2.5</td>
<td>9</td>
</tr>
<tr>
<td>2.5 to 3.0</td>
<td>10</td>
</tr>
<tr>
<td>3.0 to 3.5</td>
<td>12</td>
</tr>
</tbody>
</table>
Since the estimated wall thickness is less than the practical one, the practical value is considered, i.e., 9 mm.

**E4.7 Material of Construction**

**E4.7.1 Reactor vessel**

The reactor vessel is subjected to high temperature and moderate pressure and the esterification reaction medium. Schweitzer, 1991, part A, pp. 1029 and Hermann Ludewig, 1971, pp. 103 recommends the use of stainless steel 316 as a material of construction.

**E4.7.2 Reactor jacket**

Hermann Ludewig, 1971, pp. 103 recommends the use of mild steel when steam heating is used.

**E4.7.3 Reactor agitator**

Hermann Ludewig, 1971, pp. 103 recommends the use of high-grade steel. Stainless steel 316 is selected.

**E4.8 Summary of Esterification Reactors Sizing**

Table (E.4) Summary of esterification reactors dimensions

<table>
<thead>
<tr>
<th></th>
<th>R-200</th>
<th>R-210</th>
<th>R-220</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total Reactor volume, m³</td>
<td>22.0</td>
<td>9.51</td>
<td>9.51</td>
</tr>
<tr>
<td>Volume liquid in the reactor, m³</td>
<td>19.8</td>
<td>8.6</td>
<td>8.6</td>
</tr>
<tr>
<td>Diameter, m</td>
<td>2.33</td>
<td>1.76</td>
<td>1.76</td>
</tr>
<tr>
<td>Liquid height, m</td>
<td>4.66</td>
<td>3.52</td>
<td>3.52</td>
</tr>
<tr>
<td>Reactor height, m</td>
<td>5.17</td>
<td>3.91</td>
<td>3.91</td>
</tr>
<tr>
<td>Vessel calculated thickness, mm</td>
<td>6.5</td>
<td>4.9</td>
<td>3.4</td>
</tr>
<tr>
<td>Vessel practical thickness, mm</td>
<td>9</td>
<td>7</td>
<td>7</td>
</tr>
</tbody>
</table>
Table (E.5) Summary of agitator geometric proportions in the esterification reactors

<table>
<thead>
<tr>
<th>Standard Geometric Proportion</th>
<th>R-200</th>
<th>R-210</th>
<th>R-220</th>
</tr>
</thead>
<tbody>
<tr>
<td>$H_l = 2 D_t$</td>
<td>4.66</td>
<td>3.52</td>
<td>3.52</td>
</tr>
<tr>
<td>$D_u = 0.4 D_t$</td>
<td>0.93</td>
<td>0.70</td>
<td>0.70</td>
</tr>
<tr>
<td>$C = D_t / 3$</td>
<td>0.78</td>
<td>0.59</td>
<td>0.59</td>
</tr>
<tr>
<td>$W = D_u / 5$</td>
<td>0.19</td>
<td>0.14</td>
<td>0.14</td>
</tr>
<tr>
<td>$D_d = 2 D_u / 3$</td>
<td>0.62</td>
<td>0.47</td>
<td>0.47</td>
</tr>
<tr>
<td>$L = D_u / 4$</td>
<td>0.23</td>
<td>0.18</td>
<td>0.18</td>
</tr>
<tr>
<td>$J = D_t / 12$</td>
<td>0.19</td>
<td>0.15</td>
<td>0.15</td>
</tr>
</tbody>
</table>

Table (E.6) Summary of Power consumption in the esterification reactors

<table>
<thead>
<tr>
<th></th>
<th>R-200</th>
<th>R-210</th>
<th>R-220</th>
</tr>
</thead>
<tbody>
<tr>
<td>Agitator speed rpm</td>
<td>50</td>
<td>50</td>
<td>50</td>
</tr>
<tr>
<td>Reynolds number</td>
<td>-</td>
<td>1000000</td>
<td>435000</td>
</tr>
<tr>
<td>Power consumption kW</td>
<td>4.17</td>
<td>2.40</td>
<td>1.88</td>
</tr>
</tbody>
</table>

Table (E.7) Summary of material of construction of esterification reactors

<table>
<thead>
<tr>
<th>Component</th>
<th>R-200</th>
<th>R-210</th>
<th>R-220</th>
</tr>
</thead>
<tbody>
<tr>
<td>vessel</td>
<td>Stainless steel 316</td>
<td>Stainless steel 316</td>
<td>Stainless steel 316</td>
</tr>
<tr>
<td>agitator</td>
<td>Stainless steel 316</td>
<td>Stainless steel 316</td>
<td>Stainless steel 316</td>
</tr>
</tbody>
</table>

E5. Pervaporation membrane Sizing

Detailed sizing will be made for the pervaporation membrane PV-400, and the results of sizing of the other membranes will be summarized.

E5.1 (PV-400) Mass Balance

![Figure (E.7) Pervaporation membrane (PV-400) mass balance](image-url)
E5.2 pervaporation Membranes Sizing

A particularly convenient PV model is that of Wijmans and Baker (Seader and Henly, 1998, pp. 769). They express the driving force in terms of a partial pressure difference. Because pressures on both sides of the membrane are low, the gas phase follows the ideal gas low. Therefore, at the upstream membrane surface (1), permeant activity for the water component is expressed as

\[ a_{w}^{(1)} = \frac{f_{w}^{(1)}}{f_{w}^{(0)}} = \frac{p_{w}^{(1)}}{P_{w}^{s(1)}} \]  \hspace{1cm} (E.9)

the liquid on the upstream side of the membrane is generally nonideal, Thus:

\[ a_{w}^{(1)} = \gamma_{w}^{(1)} x_{w}^{(1)} \]  \hspace{1cm} (E.10)

Combining (E.9) and (E.10):

\[ p_{w}^{(1)} = \gamma_{w}^{(1)} x_{w}^{(1)} P_{w}^{s(1)} \]  \hspace{1cm} (E.11)

On the downstream vapor side of the membrane (2), the partial pressure is

\[ p_{w}^{(2)} = y_{w}^{(2)} P_{P}^{(2)} \]  \hspace{1cm} (E.12)

Thus the driving force can be expressed as \((\gamma_{w}^{(1)} x_{w}^{(1)} P_{w}^{s(1)} - y_{w}^{(2)} P_{P}^{(2)})\)

The corresponding permeant flux, after dropping unnecessary superscripts, is

\[ N_{w} = (P_{Mw}/M_{w}) (\gamma_{w} x_{w} P_{w}^{s} - y_{w} P_{P}^{(2)}) \]  \hspace{1cm} (E.13)

Or

\[ N_{w} = P'_{Mw} (\gamma_{w} x_{w} P_{w}^{s} - y_{w} P_{P}^{(2)}) \]  \hspace{1cm} (E.14)

The membrane is estimated

\[ A = \text{Permeate} / N_{w,ave} \]  \hspace{1cm} (E.15)

Where,

\[ A \quad \text{Membrane surface area} \]

\[ a_{w}^{(1)} \quad \text{Permeant activity coefficient for water at the upstream membrane surface} \]
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Y. Banat & Z. Abu El-rub

The activity coefficient of water and EG is found using Figure (E.8), which is based on Wilson equation of state. This figure is established using ASPEN PLUS simulation. The silica membrane system has the following data for water-EG system at 240 °C:

- Water permeability ($P'_Mw$) = 2 kg/m² bar hr
- Water selectivity = 1000

Due to the use of vacuum pumps for generating vacuum, the maximum vacuum that can be produced is (10 mm Hg = 13 mbar) (Coulson and Richardson, pp. 477, 1999). Consequently, a 10 mm Hg total pressure is applied on the permeate side. Because of the high selectivity to the water, its mole fraction in the permeate side is ca. 1.0. The water vapor pressure at 240 °C is constant and it is estimated using Antoine equation to be 33.2 bar.

![Gamma for WATER/EG](image)

Figure (E.8) Activity coefficient of water and EG at 240 °C. (ASPEN PLUS)
As shown in the mass balance tables, the feed to the membrane contains appreciable amount of vapor. The actual liquid water mole fraction \( (x_w) \) is found by trial and error using equation (5.8).

\[
P_{tot} = x_w p_w \gamma_w + x_{EG} p_{EG} \gamma_{EG}
\]  
(E.16)

In this equation it is assumed that the total pressure in the feed side equals the summation of water and EG partial pressures, neglecting those of TPA and PET since they have relatively low vapor pressures.

The calculated inlet liquid water mole fraction decreases along the membrane. This leads to a decrease in the permeation driving force. Figure (E.9a) shows the linear relation between the permeation flux \( (N_w) \) and \( (x_w) \) for the membrane PV-400. To compensate for this decrease an average value of the inlet and outlet liquid water mole fraction will be considered. Since the exit liquid water mole fraction is relatively very low, the average value of \( X_w \) is considered to be half the inlet mole fraction.

![Figure (E.9a) Permeation flux as function of liquid water mole fraction](image)

The following two tables summarize the calculations.

<table>
<thead>
<tr>
<th>Unit</th>
<th>T (°C)</th>
<th>P (bar)</th>
<th>( X_w )</th>
<th>( X_{w,av} )</th>
<th>( \gamma_{w,av} )</th>
<th>( \gamma_{EG,av} )</th>
<th>( P_{w,av} ) (bar)</th>
<th>( P_{EG,av} ) (bar)</th>
<th>( P_{w}^{(1)} ) (bar)</th>
<th>( P_{w}^{(2)} ) (bar)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PV-400</td>
<td>240</td>
<td>4.4</td>
<td>0.081</td>
<td>0.040</td>
<td>1.022</td>
<td>1.00</td>
<td>33.2</td>
<td>3.113</td>
<td>1.357</td>
<td>0.013</td>
</tr>
<tr>
<td>PV-410</td>
<td>240</td>
<td>2.86</td>
<td>0.0725</td>
<td>0.0363</td>
<td>1.022</td>
<td>1.00</td>
<td>33.2</td>
<td>3.113</td>
<td>1.232</td>
<td>0.013</td>
</tr>
<tr>
<td>PV-420</td>
<td>240</td>
<td>1.38</td>
<td>0.0325</td>
<td>0.0162</td>
<td>1.022</td>
<td>1.00</td>
<td>33.2</td>
<td>3.113</td>
<td>0.549</td>
<td>0.013</td>
</tr>
<tr>
<td>PV-430</td>
<td>110</td>
<td>1.01</td>
<td>0.71</td>
<td>0.3548</td>
<td>1.004</td>
<td>1.41</td>
<td>0.035</td>
<td>0.502</td>
<td>0.013</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Unit</th>
<th>( N ) (Kg/m²hr)</th>
<th>Permeate (kg/hr)</th>
<th>Area (m²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PV-400</td>
<td>2.69</td>
<td>1815</td>
<td>675</td>
</tr>
<tr>
<td>PV-410</td>
<td>2.44</td>
<td>256</td>
<td>105</td>
</tr>
<tr>
<td>PV-420</td>
<td>1.07</td>
<td>137</td>
<td>128</td>
</tr>
<tr>
<td>PV-430</td>
<td>0.98</td>
<td>183</td>
<td>187</td>
</tr>
</tbody>
</table>
The dimensions of the ceramic silica membrane offered by Sulzer Chemtech Membrane Systems are 8 mm inner diameter, 14 mm maximum outer diameter as shown in Figure (E.9b).

![Membrane Dimensions](image)

Figure (E.9b) Membrane dimensions of the silica membrane tube.

From Figure (E.9) every tube has 62.8 cm$^2$. The number of tubes needed in every unit is shown in the following table:

<table>
<thead>
<tr>
<th>Unit</th>
<th>Area (m$^2$)</th>
<th>Number of tubes</th>
</tr>
</thead>
<tbody>
<tr>
<td>PV-400</td>
<td>675</td>
<td>107,484</td>
</tr>
<tr>
<td>PV-410</td>
<td>105</td>
<td>16,720</td>
</tr>
<tr>
<td>PV-420</td>
<td>128</td>
<td>20,382</td>
</tr>
<tr>
<td>PV-430</td>
<td>187</td>
<td>29,777</td>
</tr>
</tbody>
</table>

**E5.3 Material of Construction**

Sulzer Chemtech Membrane Systems has developed tubular ceramic membranes externally coated with amorphous silica and these membranes will be used.

**E6. Low Polymerizer (R-300) Sizing**

The required data for the sizing of the low polymerizer are taken from Aspen and Polymer Plus simulation results.

- The volumetric flow rate of the feed (404) is 11.5131 m$^3$/hr.
- The residence time is 0.75 hr.

The volume of the reactor can be estimated using this relation [8]

$$ V = \tau \times F_{v,i} \tag{E.16} $$

where,

- $V$ is the volume of the reaction medium.
- $\tau$ is the residence time.
- $F_{v,i}$ is the volumetric flow rate.
By applying this equation, the volume of the reactor is 8.635 m$^3$. Take the height to diameter ratio (H/D) to be 2.0 [9], then the diameter is 1.77 m$^3$, and the height of the reaction medium is 3.55 m. Take 20% of the height to be for vapor, then H, is 0.7 m, based on which, the total height is 4.25 m.

E6.1 Sizing of the low polymerizer mixer

The degree of polymerization (DP) in the low polymerizer is 24.7. The viscosity of the reaction mixture in the low polymerizer rises to about 5.0 Pa.s (DP is from 20-30) [10].

A preliminary selection of the agitator type is done based on the liquid viscosity and reactor volume [6]. A paddle agitator is selected to enhance mixing in the reactor. For viscosities greater than about 2.5 to 5.0 Pa.s (5000 cp), baffles are not required since little swirling is present above these viscosities [3].

Various types of paddle agitators are often used at low speeds between about 20 and 200 rpm [3]. For the low polymerizer, it is found that the speed of the agitator is 40-60 rpm for the low polymerizer [11], that insure the applicability of a paddle agitator for this case.

The four-bladed flat paddles are often used. The total length of the paddle impeller is usually 60 to 80% of the tank diameter and the width of the blade 1/6 to 1/10 of its length. Take the length of the paddle impeller to be 70% of the tank diameter, and the width of the blade to be 1/8 of its length. Using these relations, the total length of the paddle impeller and the width of the blade to be 1.24 and 0.155 m respectively.

E6.2 Power requirements

The impeller Reynolds number can be calculated using this equation [3],

$$N_{Re} \equiv \frac{D_a \times N \times \rho}{\mu}$$  \hspace{1cm} (E.17)

where $D_a$ is the impeller (agitator) diameter in m, $N$ is the rotational speed in rev/s, $\rho$ is the fluid density in kg/m$^3$, and $\mu$ is the viscosity in kg/m.s. $N_{Re}$ is found to be 284.2 at which the flow is transitional.

The power number $N_P$ can be estimated using Figure (3.4-4) from Geankoplis [3] which is found to be 3. Then, the power consumption can be estimated to be 5.65 kW, using this correlation [3] $P$ is in J/s,
E6.3 Heating jacket

To increase the temperature from 240 to 270 °C and to supply the heat of the reaction, a heating jacket surrounds the cylindrical and the bottom parts of the reactor.

E6.3.1 Material of construction

- Reactor vessel

The low polymerizer is subjected to a high temperature (270 °C), low pressure (105 torr), and polymer, TPA, W and EG mixture. Schweitzer [12], and Herman [11] recommend the use of stainless steel as a material of construction.

- Reactor agitator

Due to the same reasons, stainless steel as a material of construction is recommended to be used.

- Heating jacket

Steam as a heating medium is used for heating, so, carbon steel can be used as a material of construction.

E6.4 Reactor vessel thickness

For a cylindrical shell the minimum thickness required to resist the internal pressure can be determined from this equation [6]:

\[
P = N_p \times \rho \times N^3 \times D_u^5
\]

(E.18)

where,

\[
f = \text{design stress, N/mm}^2
\]

\[
e = \frac{P_i D_i}{2 f - P_i}
\]

(E.19)
The finishing polymerization reactors that are used in industry include rotating disk reactors or similar type (e.g., twin-shaft disk reactor), wiped film reactors, screw reactors, and cage reactors [14]. Although there are many published data on the theoretical modeling of melt polycondensation processes, very few experimental studies have been published.

Secor [15], Hoftyzer and van Krevelen [16], and Hoftyzer [17] developed simple models for the final stages of polycondensation using the so called ‘penetration theory approximation’. Whereas, Ault and Mellichamp [18] developed a film model which took into account periodic mixing of the film. A generalized model for condensation polymerization occurring in wiped film reactor was developed by Amon and Denson [19].

Gupta et al [20] developed models for polycondensation reactions assuming that the functional groups are not equally reactive. Ravindranath and Mashelkar [10] developed a film model for the final stages of polycondensation assuming that polycondensation is occurring in a film of finite
thickness. Yokoyama et al [21] analyzed the polycondensation data obtained in a pilot plant scale horizontal disk ring reactor. They studied the effect of various process and operation conditions using the tanks-in-series model. Recently, experimental studies were done by Seong et al [13] followed by proposing a dynamic multicompartment model for a continuous flow rotating disk reactor for the finishing stages of melt polycondensation of PET.

Based on this survey, it is found that disk ring reactor is recommended for the melt polycondensation reaction. The rotating disk reactor is a horizontal rotating shaft on which disks are mounted as explained in Figure (E.10). These disks are immersed partially in the bulk liquid. Low molecular weight prepolymers are continuously supplied to the reactor. As the shaft rotates at a relatively low speed, polymer melt is partially dragged upward onto the disks and thin layers or films of polymer melt are formed on the disk surfaces. High vacuum is applied to remove volatile species (most importantly, EG) from these film polymers [14].

The knowledge of various parameters influencing the performance of the reactor is critical for analyzing the polycondensation data. The mean residence time is a function of the container length, number of disk rings, chamber width, partition wall shape, height and size of partition wall openings, throughput, viscosity of the reacting mass, rotational speed of the agitator and the melt volume. The ratio of back mixing between two successive stages depends on the shape of the blades, number of partition walls and the viscosity if the reaction mixture [10].

![Figure (E.10) Rotating disk reactor.](image-url)
As it is mentioned before, developing a model of a reactor design with complex geometry, such as a finishing polycondensation reactor, is a challenging task; therefore, data from literature is considered in sizing the final stages polymerization reactors.

The residence time that we got from Polymer and Aspen Plus simulation can't be used in sizing this reactor because it does not consider the mass transfer limitations of EG from the reaction melt, so, published data are taken for the sizing purposes.

It is found that the residence time in the intermediate polymerizer is 25 min to increase the degree of polymerization from 24.6 to 59.4 (from Polymer Plus simulation) using 0.09 wt% of antimony trioxide as catalyst as published by Ravindranath [23] under 1.0 torr. It is published by Seong et al [13] that only 33 vol% of the rotating disk reactor is occupied by the reaction melt. Based on this and the flow rate that we got from Polymer Plus simulation, it is found that the reactor volume is 14.7 m³.

According to the wide range of L/D ratio published in literature (1.1 [13,22], 3.34 [14], 1.85, 3.07, 1.26 [23]), length to diameter ratio is taken to be 2.0 based on which, the reactor dimensions are 2.11 m diameter and 4.22 m length.

The distance between the disks is quite important. To estimate the number and the dimensions of the rings, the ratio between the disks (length of the compartment) and the vessel diameter is taken as published by Seong et al [22] to be 0.0917. Based on which the length of a compartment is found to be 0.1935 m, then the number of disks is found to be 22 disks. The disk diameter to the vessel diameter is taken to be 0.907 as published by Seong et al [22], based on which the diameter of each disk is found to be 1.9 m.

The rotation speed is function of the viscosity, for intermediate polymerizer it is found to be 10-40rpm of viscosity between 50 - 5000 poise as published by Ravindranath et al [10]. For the intermediate polymerizer (DP of 59.4) the viscosity is about 250 poise, which means that 10 rpm is quite sufficient. The material of construction is selected to be stainless steel.

E8. High Polymerizer (R-320) Sizing

Same procedure is followed in sizing this reactor as that of intermediate polymerizer. The residence time that we got from Polymer and Aspen Plus simulation can't be used in sizing this reactor because it does not consider the mass transfer limitations of EG from the reaction melt, so, published data are taken for the sizing purposes.
It is found that the residence time in the high polymerizer is 34 min to increase the degree of polymerization from 59.4 to 99 (from Polymer Plus simulation) using 0.09 wt% of antimony trioxide as catalyst as published by Ravindranath [23] under 0.5 torr. It is published by Seong et al [13] that only 33 vol% of the rotating disk reactor is occupied by the reaction melt. Based on this and the flow rate that we got from Polymer Plus simulation, it is found that the reactor volume is 19.6 m$^3$.

According to the wide range of L/D ratio published in literature (1.1 [13,22], 3.34 [14], 1.85, 3.07, 1.26 [23]), length to diameter ratio is taken to be 2.0 based on which, the reactor dimensions are 2.32 m diameter and 4.64 m length.

The distance between the disks is quite important. To estimate the number and dimensions of the rings, the ratio between the disks (length of the compartment) and the vessel diameter is taken as published by Seong et al [22] to be 0.0917. Based on which the length of a compartment is found to be 0.1935 m, then the number of disks I found to be 22 disks. The disk diameter to the vessel diameter is taken to be 0.907 as published by Seong et al [22], based on which the diameter of each disk is found to be 2.1 m.

The rotation speed is function of the viscosity, for high polymerizer it is found to be 10-40 rpm of viscosity between 50-5000 poise as published by Ravindranath et al [10]. For the high polymerizer (DP of 99) the viscosity is higher than 5000 poise, which means that 40 rpm is quite sufficient. The material of construction is selected to be stainless steel.

The sizing results of both intermediate and high polymerizers including the liquid phase volume in the reactor, reactor volume, reactor length and diameter, disc diameter and number of disks, and material of construction are explained in Table (E.8).

<table>
<thead>
<tr>
<th>Table (E.8): Sizing results of intermediate and high polymerizer</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>R-310</strong></td>
</tr>
<tr>
<td>Liquid volume in the reactor $m^3$</td>
</tr>
<tr>
<td>Reactor volume $m^3$</td>
</tr>
<tr>
<td>Length of the reactor m</td>
</tr>
<tr>
<td>Diameter of the reactor m</td>
</tr>
<tr>
<td>Number of discs --</td>
</tr>
<tr>
<td>Disc diameter m</td>
</tr>
<tr>
<td>Material of construction of reactor vessel and discs</td>
</tr>
</tbody>
</table>
E.9 Spray Condensers Sizing

E9.1 Sizing of the spray condenser that follows the high polymerizer (D-520)

Thermodynamic data including heat of vaporization, specific heat of liquid and vapor EG and water are taken from Daubert [24].

For EG:
\[ \Delta H_v = 31049.52 \text{ J/mol} \]
\[ C_{PL} = 6.148 \text{ J/mol.}^\circ\text{K} \]
\[ C_{PV} = 286.140 \text{ J/mol.}^\circ\text{K} \]

For water:
\[ \Delta H_v = 31067.40 \text{ J/mol} \]
\[ C_{PL} = 41.75 \text{ J/mol.}^\circ\text{K} \]
\[ C_{PV} = 096.67 \text{ J/mol.}^\circ\text{K} \]

1. Determination of the temperature and the flow rate of the recycled stream

- It is found from Aspen Plus that the condensation temperature of the vapor mixture that leaves the high polymerizer is 32 °C at 0.5 torr.
- Assume the temperature of the recycled mixture is 28 °C to prevent flashing that might occur in the pump that follows the column.
- Assume that the recycled mixture temperature is 10 °C. To reduce its temperature from 28 to 10 °C, chilled water is used of 10 °C [6] inlet temperature
- Assume that the mixture is only EG and water by ignoring the effects of the traces of TPA and DEG. The mole fractions of EG and water (from Aspen) are 0.37 and 0.63 respectively.
- Based on the mole fractions, the thermodynamic properties of the mixture will be:

\[ \Delta H_v = 3100434.45 \text{ J/mol} \]
\[ C_{PL} = 5.102 \text{ J/mol.}^\circ\text{K} \]
\[ C_{PV} = 18.94 \text{ J/mol.}^\circ\text{K} \]

- The total heat duty of cooling is the summation of the sensible heat duty in the vapor phase, the latent heat duty of condensation, and the sensible heat duty in the liquid phase.
\[ Q_T = Q_1 + Q_2 + Q_3 \]  
\[ Q_1 = F \cdot C_{PV} \cdot (T_1 - T_C) \]  
\[ Q_2 = F \cdot \Delta H_v \]  
\[ Q_3 = F \cdot C_{PL} \cdot (T_C - T_2) \]

where,

- \( Q_T \) is the total heat duty (kJ/hr)
- \( Q_1 \) is the sensible heat duty in the vapor phase (kJ/hr)
- \( Q_2 \) is the latent heat duty (kJ/hr)
- \( Q_3 \) is the sensible heat duty in the liquid phase (kJ/hr)
- \( T_1 \) is the inlet vapor temperature °C, which is 290 °C
- \( T_C \) is the condensation temperature °C, which is 32 °C
- \( T_2 \) is the outlet liquid temperature °C, which is 28 °C

Using these equations and the values of inlet and outlet temperature, molar flow rate of the vapor mixture (as explained in Fig (E.11)), and the mentioned thermodynamics data:

\[ Q_1 = 23,100 \text{ kJ/hr} \]
\[ Q_2 = 42,820 \text{ kJ/hr} \]
\[ Q_3 = 390 \text{ kJ/hr} \]
\[ Q_T = 66,310 \text{ kJ/hr} \]

Based on the total heat duty, the flow rate of the cooling media (EG-W mixture) can be calculated based on:

\[ Q_T = m \cdot C_{PL} \cdot (T_{out} - T_{in})_{cooling} \]  
\[ T_{in} = 10 \text{ °C} \]
\[ T_{out} = 28 \text{ °C} \]

\( m \) is the molar flow rate of recycled EG-W (kmol/hr)

\( m \) is found to be 35.94 kmol mixture/hr which is 1,242 kg mixture/hr

These results can be summarized as follows:

The inlet temperature of recycled EG-W mixture is 10 °C
The output temperature of recycled EG-W mixture is 28 °C
The required EG-W mixture to be recycled is 1,242 kg/hr.

Figure (E.11) The spray condenser (D-520) that follows the high polymerizer.

2. Sizing of the spray condenser (D-520)

- Mean temperature difference.

The logarithmic mean temperature is given by [6]:

\[
\Delta T_{lm} = \frac{(T_1 - t_2) - (T_2 - t_1)}{\ln\left(\frac{T_1 - t_2}{T_2 - t_1}\right)}
\]  

(E.25)

where,

- \(\Delta T_{lm}\) = log mean temperature difference.
- \(T_1\) = inlet fluid temperature 290 °C (554 °F).
- \(T_2\) = outlet fluid temperature 28 °C (82.4 °F).
- \(t_1\) = inlet temperature of the coolant 10 °C (50 °F).
- \(t_2\) = outlet temperature of the coolant 28 °C (82.4 °F).

Based on these values, \(\Delta T_{lm} = 164 \text{ °F}\).
For maximum allowable vapor capacity, the Souders-Brown coefficient may be applied [25]:

\[
\nu_{t,\text{max}} = 0.2 \left( \frac{\rho_t - \rho_g}{\rho_g} \right)^{0.5} \tag{E.26}
\]

\[
\rho_t = 1071 \text{ kg/m}^3
\]

\[
\rho_g = 4.92 \times 10^{-4} \text{ kg/m}^3
\]

\[
\Rightarrow \nu_{t,\text{max}} = 295 \text{ ft/sec}
\]

Assume the inside diameter to be 1.75 ft (Area of 2.405 ft\(^2\)), and take the vapor volumetric rate of 66,766.7 m\(^3\)/hr (655 ft\(^3\)/sec). This gives a design velocity of 272.35 ft/sec, which is less than the maximum velocity and therefore is acceptable.

- Heat transfer

For solid-cone nozzle used in commercial applications (0.33 in), this equation can be used [D25] for estimating heat transfer coefficient:

\[
h_ga = 0.0146 \times G^{0.82} \times L^{0.47} \frac{Z_T^{0.38}}{Z_T^{0.38}} \tag{E.27}
\]

where,

- \(h_ga\) = volumetric heat transfer coefficient in the gas phase, Btu/(hr.ft\(^3\).°F)
- \(G\) = gas mass velocity, lb/hr.ft\(^2\)
- \(L\) = liquid mass velocity, lb/hr.ft\(^2\)
- \(Z_T\) = height of contacting zone, ft.

Based on this equation and after substituting the values of \(G = 30.05\) lb/hr.ft\(^2\) and \(L = 1136.13\) lb/hr.ft\(^2\), we can get:

\[
(h_ga)Z_T^{0.38} = 6.5 \text{ Btu/(hr.ft}^3.°\text{F})
\]

The overall volumetric heat transfer coefficient (\(U_a\)) can be estimated for total condensation by this equation [25]

\[
U_a = \frac{1}{\frac{1}{h_ga} + \left( \frac{1}{h_ga} \right) \left( \frac{Q_g}{Q_T} \right)} \tag{E.28}
\]

where,
Production of Polyethylene Terephthalate by Direct Esterification Using Pervaporation

\[ h_a \] = volumetric heat transfer coefficient in the liquid phase, Btu/(hr*ft^3*°F)

\[ Q_g \] = sensible heat transfer rate for gas stream, Btu/hr

\[ Q_T \] = total heat transfer rate, Btu/hr

Assuming negligible liquid-side resistance to heat transfer, then:

\[
Ua = \frac{h_a a}{823.2} \\
\Rightarrow Ua(Z_T)^{0.38} = 18.35
\]

The required volume can be calculated from [25]:

\[
V_T = \frac{Q_T}{(Ua) T_{in}} 
\]

(E.29)

Now, using the previous equation and remembering that \( V_T = A \times Z_T \)

\[
\Rightarrow Z_T = 32.5 \text{ ft (10 m)}
\]

Based on these calculations, the dimensions of this drum are (0.55 m inside diameter and 10 m height)

3. Material of construction

This spray condenser is subjected to high temperature, low pressure, and WG-water medium. Schweitzer [12] recommends the use of stainless steel 316 as a material of construction for EG-water at this temperature.

4. The column thickness

For a cylindrical shell the minimum thickness required to resist the internal pressure can be determined from this equation [6]:

\[
e = \frac{P_i D_i}{2f - P_i} 
\]

(E.30)
where,
\[ f = \text{design stress, N/mm}^2 \]
\[ P_i = \text{internal pressure, N/mm}^2 \]
\[ D_i = \text{internal diameter, mm} \]

Design pressure; take as 10 per cent above operating pressure \([6]\), \[= 7.333 \times 10^{-5} \text{ N/mm}^2.\]

Design temperature 290 °C, for stainless steel 316 at temperature of 290 °C, the design stress is 111 N/mm².

Substituting the value of \(D_i\) of 550 mm, the minimum thickness will be very small \((2 \times 10^{-4} \text{ mm})\), taking 2 mm as corrosion allowance; this will give about 2 mm thickness. But since the column is tall, this means that 2 mm is not sufficient for wind loads, so take the thickness to be 5 mm.

5. Vacuum producing equipment:

Two types of vacuum producing devices are used; jet ejectors and mechanical pumps. Jet ejectors usually have lower initial cost, lower maintenance costs and equivalent mechanical systems. Because ejectors have no moving parts, they are almost maintenance-free. Furthermore, they operate with motive steam that is already available. On the other hand, mechanical vacuum pumps require higher initial investment and operating cost than the standard jet-ejector. The operation of a steam ejector is illustrated in Figure (E.12)

![Figure (E.12) Steam jet-ejector.](image)

A steam jet ejector consists of three parts: motive steam nozzle, a mixing chamber, and a diffuser. Ejectors operate by the action of one high-pressure steam entraining air and other vapor at a
lower pressure into the moving stream and thereby removing them from the process system at an intermediate pressure.

To produce a vacuum up to 0.2 torr of a flow rate (10-1,000,000 ft³/min), four-stage steam ejector can be used. In the case of high polymerizer and its spray condenser, the pressure is 0.5 torr that can be handled by three-stage steam ejector [26].

**E9.2 Sizing of the spray condenser that follows the intermediate polymerizer (D-510)**

1. Determination of the temperature and the flow rate of the recycled stream
   - It is found from Aspen Plus that the condensation temperature of the vapor mixture that leaves the intermediate polymerizer is 44 °C at 1 torr.
   - Assume the temperature of the recycled mixture is 40 °C to prevent flashing that might occur in the pump that follows the column.
   - Assume that the recycled mixture temperature is 25 °C. To reduce its temperature from 40 to 25 °C, chilled water is used of 10 °C [6] inlet temperature.
   - Assume that the mixture is only EG and water by ignoring the effects of the traces of TPA and DEG. The mole fractions of EG and water (from Aspen) are 0.485 and 0.515 respectively.
   - Based on the mole fractions, the thermodynamic properties of the mixture will be:

\[
\Delta H_v = 46.4 \times 10^3 \text{ J/mol}
\]
\[
C_{PL} = 110.91 \text{ J/mol.}^\circ \text{K}
\]
\[
C_{PV} = 102.6 \text{ J/mol.}^\circ \text{K}
\]

   - The total heat duty of cooling is the summation of the sensible heat duty in the vapor phase, the latent heat duty of condensation, and the sensible heat duty in the liquid phase.

Using (E.20 to E.23) equations and the values of inlet and outlet temperature, molar flow rate of the vapor mixture (as explained in Fig (E.13)) and the mentioned thermodynamics data:

\[
Q_1 = 92,310 \text{ kJ/hr}
\]
\[
Q_2 = 179,600 \text{ kJ/hr}
\]
\[
Q_3 = 1,690 \text{ kJ/hr}
\]
\[
Q_T = 273,600 \text{ kJ/hr}
\]
Based on the total heat duty, the flow rate of the cooling media (EG-W mixture) can be calculated based on:

\[
Q_T = m C_{PL} (T_{out} - T_{in})_{cooling} + m_{HP} C_{HP} (T_{out(HP)} - T_{in(HP)})
\]  

(E.31)

\[
T_{in\ cooling} = 25 \, ^\circ\text{C}
\]
\[
T_{out\ cooling} = 40 \, ^\circ\text{C}
\]
\[
T_{in\ from\ HP} = 28 \, ^\circ\text{C}
\]
\[
T_{out\ from\ IP} = 40 \, ^\circ\text{C}
\]

\(m\) is the molar flow rate of recycled EG-W (kmol/hr)

\(m_{HP}\) is the molar flow rate of EG-W from high polymerizer, which is 0.9506 kmol/hr

\(m\) is found to be 163.755 kmol mixture/hr which is 6,544.5 kg mixture/hr

These results can be summarized as follows:

The inlet temperature of recycled EG-W mixture is 25 °C

The output temperature of recycled EG-W mixture is 40 °C

The required EG-W mixture to be recycled is 6,544.5 kg/hr.

Figure (E.13) The spray condenser (D-510) that follows the intermediate polymerizer.

2. Sizing of the spray condenser (D-510)

- Mean temperature difference.

The logarithmic mean temperature is given in equation (E.25)
\( T_1 \) = inlet fluid temperature 280 °C (536 °F).
\( T_2 \) = outlet fluid temperature 40 °C (104 °F).
\( t_1 \) = inlet temperature of the coolant 25 °C (77 °F).
\( t_2 \) = outlet temperature of the coolant 40 °C (104 °F).

Based on these values, \( \Delta T_{lm} = 146 °F \).

- The vapor velocity.

Using equation (E.26) and these values of densities

\[
\rho_i = 1082.6 \text{ kg/m}^3
\]
\[
\rho_g = 1.159 \times 10^{-3} \text{ kg/m}^3
\]

\( \Rightarrow v_{t,max} = 193.3 \text{ ft/sec} \)

Assume the inside diameter to be 0.9 m (2.953 ft, area of 6.8477 ft\(^2\)), and take the vapor volumetric rate of 131,520 m\(^3\)/hr (1290.2 ft\(^3\)/sec). This gives a design velocity of 188.4 ft/sec, which is less than the maximum velocity and therefore is acceptable.

- Heat transfer

For solid-cone nozzle used in commercial applications (0.33 in), equation (E.27) can be used [15] for estimating heat transfer coefficient:

Based on this equation and after substituting the values of \( G = 48.95 \text{ lb/hr.ft}^2 \) and \( L = 2102.6 \text{ lb/hr.ft}^2 \), we can get:

\[
(h_g a) \left( \frac{Z}{T} \right)^{0.38} = 12.93 \text{ Btu/(hr.ft}^2.°F)\]

The overall volumetric heat transfer coefficient (\( U_a \)) can be estimated for total condensation from equation (E.28)

Assuming negligible liquid-side resistance to heat transfer, then:

\[
U_a = 2.91 \times h_g a
\]
The required volume can be calculated from equation (E.29), remembering that \( V_T = A \times Z_T \)

\[ \Rightarrow Z_T = 22.535 \, \text{ft (6.9 m)} \]

Based on these calculations, the dimensions of this drum are (0.9 m inside diameter and 6.9 m height)

3. Material of construction

This spray condenser is subjected to high temperature, low pressure, and WG-water medium. Schweitzer [12] recommends the use of stainless steel 316 as a material of construction for EG-water at this temperature.

4. The column thickness

For a cylindrical shell the minimum thickness required to resist the internal pressure can be determined from equation (E.30):

Design pressure; take as 10 per cent above operating pressure [6], \( = 1.6 \times 10^{-4} \, \text{N/mm}^2 \). Design temperature 280 °C, for stainless steel 316 at temperature of 280 °C, the design stress is 112 N/mm².

Substituting the value of \( D_1 \) of 900 mm, the minimum thickness will be very small (6.43\times10^{-4} \, \text{mm}) taking 2 mm as corrosion allowance, this will give about 2 mm thickness. But since the column is tall, this means that 2 mm is not sufficient for wind loads, so take the thickness to be 4 mm.

5. Vacuum producing equipment:

To produce a vacuum up to 1 torr of a flow rate (10-1,000,000 ft³/min), three-stage steam ejector can be used. In the case of high polymerizer and its spray condenser, the pressure is 1 torr that can be handled by three-stage steam ejector [26].
E9.3 Sizing of the spray condenser that follows the low polymerizer (D-500)

1. Determination of the temperature and the flow rate of the recycled stream

   - It is found from Aspen Plus that the condensation temperature of the vapor mixture that leaves the intermediate polymerizer is 114 °C at 105 torr.
   - Assume the temperature of the recycled mixture is 110 °C to prevent flashing that might occur in the pump that follows the column.
   - Assume that the recycled mixture temperature is 25 °C. To reduce its temperature from 110 to 25 °C, chilled water is used of 10 °C [6] inlet temperature.
   - Assume that the mixture is only EG and water by ignoring the effects of the traces of TPA and DEG. The mole fractions of EG and water (from Aspen) are 0.22 and 0.78 respectively.
   - Based on the mole fractions, the thermodynamic properties of the mixture will be:

     \[
     \Delta H_f = 43.27 \times 10^3 \text{ J/mol} \\
     C_{PL} = 91.51 \text{ J/mol.}^\circ \text{K} \\
     C_{PV} = 83.2 \text{ J/mol.}^\circ \text{K}
     \]

   - The total heat duty of cooling is the summation of the sensible heat duty in the vapor phase, the latent heat duty of condensation, and the sensible heat duty in the liquid phase.

     Using (E.20 to E.23) equations and the values of inlet and outlet temperature, molar flow rate of the vapor mixture (as explained in Figure (E.14) and the mentioned thermodynamics data:

     \[
     Q_1 = 129,230 \text{ kJ/hr} \\
     Q_2 = 420,070 \text{ kJ/hr} \\
     Q_3 = 3,550 \text{ kJ/hr} \\
     Q_T = 552,850 \text{ kJ/hr}
     \]

     Based on the total heat duty, the flow rate of the cooling media (EG-W mixture) can be calculated based on:

     \[
     Q_T = m.C_{PL}(T_{out} - T_{in})_{cooling} + m_{HP}.C_{PLP}(T_{out(LP)} - T_{in(LP)})
     \]

     \[
     T_{in\,cooling} = 25 \text{ °C}
     \]
\[ T_{\text{out cooling}} = 110 \, ^\circ C \]
\[ T_{\text{in from IP}} = 40 \, ^\circ C \]
\[ T_{\text{out from LP}} = 110 \, ^\circ C \]

\( m \) is the molar flow rate of recycled EG-W (kmol/hr)

\( m_{\text{IP}} \) is the molar flow rate of EG-W from intermediate polymerizer, which is 3.8125 kmol/hr

\( m \) is found to be 67.27 kmol mixture/hr which is 1895 kg mixture/hr

These results can be summarized as follows:

The inlet temperature of recycled EG-W mixture is 25 \(^\circ\)C.
The output temperature of recycled EG-W mixture is 110 \(^\circ\)C.
The required EG-W mixture to be recycled is 1895 kg/hr.

Figure (E.14) The spray condenser (D-500) that follows the low polymerizer.

2. Sizing of the spray condenser (D-500)

- Mean temperature difference.
  The logarithmic mean temperature is given in equation (E.25)

\[ T_1 \] = inlet fluid temperature 270 \(^\circ\)C (518 \(^\circ\)F).
\[ T_2 \] = outlet fluid temperature 110 \(^\circ\)C (230 \(^\circ\)F).
\[ t_1 \] = inlet temperature of the coolant 25 \(^\circ\)C (77 \(^\circ\)F).
\[ t_2 \] = outlet temperature of the coolant 110 \(^\circ\)C (518 \(^\circ\)F).
Based on these values, $\Delta T_{lm} = 213.4^\circ F$.

- The vapor velocity.

Using equation (E.26) and these values of densities

$$\rho_l = 1055 \text{ kg/m}^3$$
$$\rho_g = 0.0874 \text{ kg/m}^3$$

$$\Rightarrow v_{t,\text{max}} = 22 \text{ ft/sec}$$

Assume the inside diameter to be 0.425 m (1.394 ft, area of 1.5262 ft$^2$), and take the vapor volumetric rate of 3130 m$^3$/hr (30.7 ft$^3$/sec). This gives a design velocity of 20.115 ft/sec, which is less than the maximum velocity and therefore is acceptable.

- Heat transfer

For solid-cone nozzle used in commercial applications (0.33 in), equation (E.27) can be used [25] for estimating heat transfer coefficient:

Based on this equation and after substituting the values of $G = 394.25 \text{ lb/hr.ft}^2$ and $L = 2731.62 \text{ lb/hr.ft}^2$, we can get:

$$\left(h_g a \right)^{0.38} = 80.91 \text{ Btu/(hr.ft}^3{.^\circ F})$$

The overall volumetric heat transfer coefficient ($U_a$) can be estimated for total condensation from equation (E.28)

Assuming negligible liquid-side resistance to heat transfer, then:

$$U_a = 4.1637 \times h_g a$$

$$\Rightarrow U_a(Z_T)^{0.38} = 336.9$$

The required volume can be calculated from equation (E.29), remembering that $V_T = A \times Z_T$

$$\Rightarrow Z_T = 12.47 \text{ ft (3.8 m)}$$
Based on these calculations, the dimensions of this drum are (0.425 m inside diameter and 3.8 m height)

3. Material of construction

This spray condenser is subjected to high temperature, low pressure, and WG-water medium. Schweitzer [12] recommends the use of stainless steel 316 as a material of construction for EG-water at this temperature.

4. The column thickness

For a cylindrical shell the minimum thickness required to resist the internal pressure can be determined from equation (E.30):

\[
\text{Design pressure; take as 10 per cent above operating pressure [6], } p = 16.76 \times 10^{-3} \text{ N/mm}^2.
\]
\[
\text{Design temperature 270 } ^\circ \text{C, for stainless steel 316 at temperature of 270 } ^\circ \text{C, the design stress is 113 N/mm}^2.
\]

Substituting the value of D_{i} of 900 mm, the minimum thickness will be very small (3.2 \times 10^{-2} mm), taking 2 mm as corrosion allowance, this will give about 2 mm thickness. But since the column is tall, this means that 2 mm is not sufficient for wind loads, so take the thickness to be 3 mm.

5. Vacuum producing equipment:

To produce a vacuum up to 75 torr of a flow rate (10-1,000,000 ft^3/min), one-stage steam ejector can be used. In the case of high polymerizer and its spray condenser, the pressure is 105 torr that can be handled by three-stage steam ejector [26].

**E10. Heat Exchangers Sizing**

This section includes sizing of the condensers that follow the membrane units and the coolers that follow the spray condensers.

**E10.1 Sizing of the condensers that follow the membrane units**
E10.1.1 Sizing of E-400

As found from Aspen simulation that the net heat duty (Q) over E-400 is −1438.32 kW, and using the overall heat transfer coefficient (U) of 400 W/m² °C, U = 200 – 500 W/m² °C for the case of condensation under vacuum [6]. Then, the heat transfer area can be estimated using this equation [6].

\[ Q = U \cdot A \cdot \Delta T_m \]  \hspace{1cm} (E.33)

\( \Delta T_m \) is \( \Delta T_{lm} \), which can be estimated using equation (E.25), based on these data:

\begin{align*}
T_1 &= 240 \ ^\circ C \\
T_2 &= 25 \ ^\circ C \\
t_1 &= 10 \ ^\circ C \\
t_2 &= 25 \ ^\circ C
\end{align*}

\( \Delta T_m \) is equal to 75.1°C. Using equation (E.33) and U of 400 W/m² °C. The heat transfer area of this condenser is 48 m².

E10.1.2 Sizing of E-410

As found from Aspen simulation that the net heat duty (Q) over E-410 is −202.87 kW, and using the overall heat transfer coefficient (U) of 400 W/m² °C, U = 200 – 500 W/m² °C for the case of condensation under vacuum [6]. Then, the heat transfer area can be estimated using this equation (E.33). \( \Delta T_m \) can be estimated using equation (E.25), based on these data:

\begin{align*}
T_1 &= 240 \ ^\circ C \\
T_2 &= 25 \ ^\circ C \\
t_1 &= 10 \ ^\circ C \\
t_2 &= 25 \ ^\circ C
\end{align*}

\( \Delta T_m \) is equal to 75.1°C. Using equation (E.33) and U of 400 W/m² °C. The heat transfer area of this condenser is 6.75 m².

E10.1.3 Sizing of E-420

As found from Aspen simulation that the net heat duty (Q) over E-420 is −108.57 kW, and using the overall heat transfer coefficient (U) of 400 W/m² °C, U = 200 – 500 W/m² °C for the case of
condensation under vacuum [6]. Then, the heat transfer area can be estimated using this equation (E.33). \( \Delta T_m \) can be estimated using equation (E.25), based on theses data:

\[
\begin{align*}
T_1 &= 240 \, ^\circ C \\
T_2 &= 25 \, ^\circ C \\
\theta_1 &= 10 \, ^\circ C \\
\theta_2 &= 25 \, ^\circ C
\end{align*}
\]

\( \Delta T_m \) is equal to 75.1°C. Using equation (E.33) and \( U \) of 400 W/m²°C. The heat transfer area of this condenser is 3.6 m².

E10.1.4 Sizing of E-430

As found from Aspen simulation that the net heat duty (Q) over E-430 is –132.29 kW, and using the overall heat transfer coefficient (U) of 400 W/m²°C, \( U = 200 – 500 \) W/m²°C for the case of condensation under vacuum [6]. Then, the heat transfer area can be estimated using this equation (E.33). \( \Delta T_m \) can be estimated using equation (E.25), based on theses data:

\[
\begin{align*}
T_1 &= 110 \, ^\circ C \\
T_2 &= 25 \, ^\circ C \\
\theta_1 &= 10 \, ^\circ C \\
\theta_2 &= 25 \, ^\circ C
\end{align*}
\]

\( \Delta T_m \) is equal to 40.36°C. Using equation (E.33) and \( U \) of 400 W/m²°C. The heat transfer area of this condenser is 6.73 m².

E10.2 Sizing of the coolers that follow the spray condensers

E10.2.1 Sizing of E-500

The net heat duty (Q) over E-500 can be estimated from section E.9.3 as –134.5 kW, and using the overall heat transfer coefficient (U) of 500 W/m²°C, \( U = 200 – 700 \) W/m²°C for the case of organic compounds (EG-W mixture), and water systems [6]. Then, the heat transfer area can be estimated using this equation (E.33). \( \Delta T_m \) can be estimated using equation (E.25), based on theses data:

\[
T_1 = 110 \, ^\circ C
\]
\( T_2 = 25 \, ^\circ C \)
\( t_1 = 10 \, ^\circ C \)
\( t_2 = 25 \, ^\circ C \)

\( \Delta T_m \) is equal to 40.36 \( ^\circ C \). Using equation (E.33) and U of 500 W/m\(^2\)\(^\circ C\). The heat transfer area of this cooler is 6.7 m\(^2\).

**E10.2.2 Sizing of E-510**

The net heat duty (Q) over E-500 can be estimated from section E.9.2 as \(-75.68\) kW, and using the overall heat transfer coefficient (U) of 500 W/m\(^2\)\(^\circ C\), \( U = 200 - 700\) W/m\(^2\)\(^\circ C\) for the case of organic compounds (EG-W mixture), and water systems \([6]\). Then, the heat transfer area can be estimated using this equation (E.33). \( \Delta T_m \) can be estimated using equation (E.25), based on these data:

\( T_1 = 40 \, ^\circ C \)
\( T_2 = 25 \, ^\circ C \)
\( t_1 = 10 \, ^\circ C \)
\( t_2 = 25 \, ^\circ C \)

\( \Delta T_m \) is equal to 15 \( ^\circ C \). Using the average temperature other than using equation (E.33), since the difference at both ends of the cooler is the same, and U of 500 W/m\(^2\)\(^\circ C\). The heat transfer area of this cooler is 10 m\(^2\).

**E10.2.3 Sizing of E-520**

The net heat duty (Q) over E-520 can be estimated from section E.9.1 as \(-18.42\) kW, and using the overall heat transfer coefficient (U) of 500 W/m\(^2\)\(^\circ C\), \( U = 200 - 700\) W/m\(^2\)\(^\circ C\) for the case of organic compounds (EG-W mixture), and water systems \([6]\). Then, the heat transfer area can be estimated using this equation (E.33). \( \Delta T_m \) can be estimated using equation (E.25), based on these data:

\( T_1 = 28 \, ^\circ C \)
\( T_2 = 15 \, ^\circ C \)
\( t_1 = 10 \, ^\circ C \)
\( t_2 = 15 \, ^\circ C \)
$\Delta T_m$ is equal to 8.37 °C. Using equation (E.33) and $U$ of 500 W/m$^2$°C. The heat transfer area of this cooler is 4.4 m$^2$.

References


Appendix F

Safety and Environmental Aspects

- F1. EG Material Safety Data Sheet
- F2. TPA Material Safety Data Sheet
- F3. PET Material Safety Data Sheet
F1. Ethylene Glycol Material Safety Data Sheet

1. Product Identification

Synonyms: 1,2-Ethanediol; glycol; 1,2-Dihydroxyethane; Ethylene Alcohol; Ethylene Dihydrate
CAS No.: 107-21-1
Molecular Weight: 62.07
Chemical Formula: CH2OHCH2OH
Product Codes:
J.T. Baker: 5387, 5845, 9140, 9298, 9300, 9346, 9349, 9356, L715
Mallinckrodt: 5001, 5037

2. Composition/Information on Ingredients

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>CAS No</th>
<th>Percent</th>
<th>Hazardous</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethylene Glycol</td>
<td>107-21-1</td>
<td>99 - 100%</td>
<td>Yes</td>
</tr>
</tbody>
</table>

3. Hazards Identification

Emergency Overview

WARNING! HARMFUL OR FATAL IF SWALLOWED. HARMFUL IF INHALED OR ABSORBED THROUGH SKIN. MAY CAUSE ALLERGIC SKIN REACTION. MAY CAUSE IRRITATION TO SKIN, EYES, AND RESPIRATORY TRACT. AFFECTS CENTRAL NERVOUS SYSTEM.

J.T. Baker SAF-T-DATA (tm) Ratings (Provided here for your convenience)
Potential Health Effects

Inhalation:
Vapor inhalation is generally not a problem unless heated or misted. Exposure to vapors over an extended time period has caused throat irritation and headache. May cause nausea, vomiting, dizziness and drowsiness. Pulmonary edema and central nervous system depression may also develop. When heated or misted, has produced rapid, involuntary eye movement and coma.

Ingestion:
Initial symptoms in massive dosage parallel alcohol intoxication, progressing to CNS depression, vomiting, headache, rapid respiratory and heart rate, lowered blood pressure, stupor, collapse, and unconsciousness with convulsions. Death from respiratory arrest or cardiovascular collapse may follow. Lethal dose in humans: 100 ml (3-4 ounces).

Skin Contact:
Minor skin irritation and penetration may occur.

Eye Contact:
Splashes may cause irritation, pain, eye damage.

Chronic Exposure:
Repeated small exposures by any route can cause severe kidney problems. Brain damage may also occur. Skin allergy can develop. May damage the developing fetus.

Aggravation of Pre-existing Conditions:
Persons with pre-existing skin disorders, eye problems, or impaired liver, kidney, or respiratory function may be more susceptible to the effects of this substance.
4. First Aid Measures

**Inhalation:**
Remove to fresh air. If not breathing, give artificial respiration. If breathing is difficult, give oxygen. Call a physician.

**Ingestion:**
Induce vomiting immediately as directed by medical personnel. Never give anything by mouth to an unconscious person. Get medical attention.

**Skin Contact:**
Remove any contaminated clothing. Wash skin with soap and water for at least 15 minutes. Get medical attention if irritation develops or persists.

**Eye Contact:**
Immediately flush eyes with plenty of water for at least 15 minutes, lifting lower and upper eyelids occasionally. Get medical attention immediately.

**Note to Physician:**
Give sodium bicarbonate intravenously to treat acidosis. Urinalysis may show low specific gravity, proteinuria, pyuria, cylindruria, hematuria, calcium oxide, and hippuric acid crystals. Ethanol can be used in antidotal treatment but monitor blood glucose when administering ethanol because it can cause hypoglycemia. Consider infusion of a diuretic such as mannitol to help prevent or control brain edema and hemodialysis to remove ethylene glycol from circulation.

5. Fire Fighting Measures

**Fire:**
Flash point: 111°C (232°F) CC
Autoignition temperature: 398°C (748°F)
Flammable limits in air % by volume:
lel: 3.2; uel: 15.3
Slight to moderate fire hazard when exposed to heat or flame.

**Explosion:**
Above flash point, vapor-air mixtures are explosive within flammable limits noted above.
Containers may explode when involved in a fire.
Fire Extinguishing Media:
Dry chemical, foam or carbon dioxide. Water or foam may cause frothing. Water spray may be used to extinguish surrounding fire and cool exposed containers. Water spray will also reduce fume and irritant gases.

Special Information:
In the event of a fire, wear full protective clothing and NIOSH-approved self-contained breathing apparatus with full facepiece operated in the pressure demand or other positive pressure mode. Toxic gases and vapors may be released if involved in a fire.

6. Accidental Release Measures
Ventilate area of leak or spill. Remove all sources of ignition. Wear appropriate personal protective equipment as specified in Section 8. Isolate hazard area. Keep unnecessary and unprotected personnel from entering. Contain and recover liquid when possible. Use non-sparking tools and equipment. Collect liquid in an appropriate container or absorb with an inert material (e.g., vermiculite, dry sand, earth), and place in a chemical waste container. Do not use combustible materials, such as saw dust. Do not flush to sewer! US Regulations (CERCLA) require reporting spills and releases to soil, water and air in excess of reportable quantities. The toll free number for the US Coast Guard National Response Center is (800) 424-8802.

7. Handling and Storage
Keep in a tightly closed container, stored in a cool, dry, ventilated area. Protect against physical damage. Separate from acids and oxidizing materials. Containers of this material may be hazardous when empty since they retain product residues (vapors, liquid); observe all warnings and precautions listed for the product.

8. Exposure Controls/Personal Protection
Airborne Exposure Limits:
- OSHA Permissible Exposure Limit (PEL):
  50 ppm Ceiling

- ACGIH Threshold Limit Value (TLV):
50 ppm Ceiling (vapor)

Ventilation System:
A system of local and/or general exhaust is recommended to keep employee exposures below the Airborne Exposure Limits. Local exhaust ventilation is generally preferred because it can control the emissions of the contaminant at its source, preventing dispersion of it into the general work area. Please refer to the ACGIH document, *Industrial Ventilation, A Manual of Recommended Practices*, most recent edition, for details.

Personal Respirators (NIOSH Approved):
If the exposure limit is exceeded, a half-face respirator with an organic vapor cartridge and particulate filter (NIOSH type P95 or R95 filter) may be worn for up to ten times the exposure limit or the maximum use concentration specified by the appropriate regulatory agency or respirator supplier, whichever is lowest. A full-face piece respirator with an organic vapor cartridge and particulate filter (NIOSH P100 or R100 filter) may be worn up to 50 times the exposure limit, or the maximum use concentration specified by the appropriate regulatory agency or respirator supplier, whichever is lowest. Please note that N series filters are not recommended for this material. For emergencies or instances where the exposure levels are not known, use a full-face piece positive-pressure, air-supplied respirator. WARNING: Air-purifying respirators do not protect workers in oxygen-deficient atmospheres.

Skin Protection:
Wear protective gloves and clean body-covering clothing.

Eye Protection:
Use chemical safety goggles. Maintain eye wash fountain and quick-drench facilities in work area.

9. Physical and Chemical Properties

Appearance:
Clear oily liquid.

Odor:
Odorless.

Solubility:
Miscible in water.

Specific Gravity:
1.1 @20°C/4°C
pH:
No information found.

% Volatiles by volume @ 21C (70F):
100

Boiling Point:
197.6C (388F)

Melting Point:
-13C (9F)

Vapor Density (Air=1):
2.14

Vapor Pressure (mm Hg):
0.06 @ 20C (68F)

Evaporation Rate (BuAc=1):
No information found.

10. Stability and Reactivity

Stability:
Stable under ordinary conditions of use and storage.

Hazardous Decomposition Products:
Carbon dioxide and carbon monoxide may form when heated to decomposition. May produce acrid smoke and irritating fumes when heated to decomposition.

Hazardous Polymerization:
Will not occur.

Incompatibilities:
Strong oxidizing agents. Reacts violently with chlorosulfonic acid, oleum, sulfuric acid, perchloric acid. Causes ignition at room temperature with chromium trioxide, potassium permanganate and sodium peroxide; causes ignition at 212F(100C) with ammonium dichromate, silver chlorate, sodium chloride and uranyl nitrate.

Conditions to Avoid:
Heat, flames, ignition sources, water (absorbs readily) and incompatibles.

11. Toxicological Information
Toxicological Data:
Oral rat LD50: 4700 mg/kg; skin rabbit LD50: 9530 mg/kg.
Irritation - skin rabbit: 555mg(open), mild; eye rabbit: 500mg/24H, mild.
Investigated as a tumorigen, mutagen, reproductive effector.

Reproductive Toxicity:
Has shown teratogenic effects in laboratory animals.

Cancer Lists (NTP Carcinogen)

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>Known</th>
<th>Anticipated</th>
<th>IARS Category</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethylene Glycol (107-21-1)</td>
<td>No</td>
<td>No</td>
<td>None</td>
</tr>
</tbody>
</table>

12. Ecological Information

Environmental Fate:
When released into the soil, this material is expected to readily biodegrade. When released into the soil, this material is expected to leach into groundwater. When released into the soil, this material is not expected to evaporate significantly. When released into water, this material is expected to readily biodegrade. When released into the water, this material is expected to have a half-life between 1 and 10 days. This material is not expected to significantly bioaccumulate. This material has a log octanol-water partition coefficient of less than 3.0. When released into water, this material is not expected to evaporate significantly. When released into the air, this material is expected to be readily degraded by reaction with photochemically produced hydroxyl radicals. When released into the air, this material is expected to have a half-life between 1 and 10 days.

Environmental Toxicity:
The LC50/96-hour values for fish are over 100 mg/l.

13. Disposal Considerations
Whatever cannot be saved for recovery or recycling should be managed in an appropriate and approved waste disposal facility. Processing, use or contamination of this product may change the waste management options. State and local disposal regulations may differ from federal disposal regulations. Dispose of container and unused contents in accordance with federal, state and local requirements.

14. Transport Information

Not regulated.

15. Regulatory Information

Chemical Inventory Status - Part 1

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>TSCA</th>
<th>EC</th>
<th>Japan</th>
<th>Austria</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethylene Glycol (107-21-1)</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
</tr>
</tbody>
</table>

Chemical Inventory Status - Part 2

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>Korea</th>
<th>DSL</th>
<th>NDSL</th>
<th>Phil</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethylene Glycol (107-21-1)</td>
<td>Yes</td>
<td>Yes</td>
<td>No</td>
<td>Yes</td>
</tr>
</tbody>
</table>

**Australian Hazchem Code:** No information found.

**Poison Schedule:** No information found.

**WHMIS:**

This MSDS has been prepared according to the hazard criteria of the Controlled Products Regulations (CPR) and the MSDS contains all of the information required by the CPR.

16. Other Information
**NFPA Ratings:** Health: 1 Flammability: 1 Reactivity: 0

**Label Hazard Warning:**
WARNING! HARMFUL OR FATAL IF SWALLOWED. HARMFUL IF INHALED OR ABSORBED THROUGH SKIN. MAY CAUSE ALLERGIC SKIN REACTION. MAY CAUSE IRRITATION TO SKIN, EYES, AND RESPIRATORY TRACT. AFFECTS CENTRAL NERVOUS SYSTEM.

**Label Precautions:**
Do not breathe vapor or mist.
Use only with adequate ventilation.
Keep container closed.
Avoid contact with eyes, skin and clothing.
Wash thoroughly after handling.

**Label First Aid:**
If inhaled, remove to fresh air. If not breathing, give artificial respiration. If breathing is difficult, give oxygen. In case of contact, immediately flush skin or eyes with plenty of water for at least 15 minutes. Call a physician if irritation develops or persists. If swallowed, give water or milk to drink and induce vomiting. Never give anything by mouth to an unconscious person. In all cases call a physician.

**Product Use:**
Laboratory Reagent.

**Revision Information:**
MSDS Section(s) changed since last revision of document include: 8.

**Disclaimer:**
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F2. Terephthalic Acid Material Safety Data Sheet
1. Chemical Product Identification

Product Name: AMOCO TA-22

MANUFACTURER/SUPPLIER:
Amoco Chemical Company
200 East Randolph Drive
Chicago, Illinois 60601 U.S.A.

EMERGENCY HEALTH INFORMATION:
1 (800) 447-8735

EMERGENCY SPILL INFORMATION:
1 (800) 424-9300 CHEMTREC (USA)

OTHER PRODUCT SAFETY INFORMATION:
(312) 856-3907

2. Composition/Information on Ingredients

<table>
<thead>
<tr>
<th>Component</th>
<th>CAS#</th>
<th>Range % by Wt.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Terephthalic acid</td>
<td>100-21-0</td>
<td>100</td>
</tr>
</tbody>
</table>

(See Section 8.0, "Exposure Controls/Personal Protection", for exposure guidelines)

3. Hazards Identification

Emergency overview: This product has been evaluated and does not require any hazard warning on the label under OSHA criteria. Handling and/or processing of this material may generate airborne fibers and particles which can cause mechanical irritation of the eyes, skin, nose and throat.

Potential health effects:
Eye contact: No significant health hazards identified. Particles or fibers may cause slight discomfort similar to getting dust in the eye.
Skin contact: No significant health hazards identified.
Inhalation: No significant health hazards identified.
Ingestion: No significant health hazards identified.
HMIS code: (Health:0) (Flammability:0) (Reactivity:0)
NFPA code: (Health:0) (Flammability:0) (Reactivity:0)

4. First Aid Measures

Eye: Flush eyes with plenty of water.
Skin: Wash exposed skin with soap and water.
Inhalation: If adverse effects occur, remove to uncontaminated area. Get medical attention.
Ingestion: If a large amount is swallowed, get medical attention.

5. Fire Fighting Measures

Flash point: Not applicable.
UEL: Not determined.
LEL: 0.05
Autoignition temperature: 1250°F (678°C)
Flammability classification: None
Extinguishing media: Agents approved for Class A hazards (e.g., foam, steam) or water fog.
Unusual fire and explosive hazards: High dust concentrations have a potential for combustion or explosion. High-voltage static electricity buildup and discharge must be avoided when significant quantities of dust are present.
Fire fighting equipment: Firefighters should wear full bunker gear, including a positive pressure self-contained breathing apparatus.
Precautions: Take precautionary measures against static discharges, including thorough electrical interconnecting, grounding of equipment, and conveyance, under inert gas.
Hazardous combustion products: Incomplete burning can produce carbon monoxide and/or carbon dioxide and other harmful products.

6. Accidental Release Measures

Y. Banat & Z. Abu El-rub
Contain and remove by mechanical means.

### 7. Handling and Storage

**Handling:** Take appropriate measures to prevent static discharges, which may include thorough electrical interconnecting, grounding of equipment, and/or conveyance under inert gas.

**Storage:** No special requirements.

### 8. Exposure Controls / Personal Protection

**Eye:** None required; however, use of eye protection is good industrial practice. Use dust goggles if high dust concentration is generated.

**Skin:** None required; however, use of protective gloves/clothing is good industrial practice.

**Inhalation:** None required; however, use of adequate ventilation is good industrial practice. If ventilation is inadequate, use respirator that will protect against dust/mist.

**Engineering controls:** Control airborne concentrations below the exposure guidelines.

**Exposure guidelines:**

<table>
<thead>
<tr>
<th>Component</th>
<th>CAS#</th>
<th>Exposure Limits</th>
</tr>
</thead>
<tbody>
<tr>
<td>Terephthalic acid</td>
<td>100-21-0</td>
<td>ACGIH TLV-TWA: 10 mg/m³</td>
</tr>
</tbody>
</table>

### 9. Chemical and Physical Properties

**Appearance and odor:** Crystals. White. Odorless.

**pH:** 3.9

**Vapor pressure:** Less than 0.01 mm Hg at 20 °C

**Vapor density:** Not determined.

**Boiling point:** 756°F (402°C) (sublimes)

**Melting point:** 801°F (427°C)

**Solubility in water:** Negligible, below 0.1%.
Specific gravity (water=1.0): 1.58

10. Stability and Reactivity

Stability: Stable.
Conditions to avoid: None identified.
Materials to avoid: None identified.
Hazardous decomposition: Incomplete burning can produce carbon monoxide and/or carbon dioxide and other harmful products.
Hazardous polymerization: Will not occur.

11. Toxicological Information

Acute toxicity data:
   - Eye irritation: This product had a primary eye irritation score (PEIS) of 10/110 (rabbit)
   - Skin irritation: This product had a primary skin irritation score (PDIS) of 0.2/8.0 (rabbit)
   - Dermal LD50: greater than 2000 mg/kg (rabbit).
   - Oral LD50: greater than 5000 mg/kg (rat).
   - Inhalation LC50: greater than 2000 mg/m3 (rat)

Other toxicity data:
This product contains terephthalic acid. Terephthalic acid is non-irritating to eyes and skin. The maximum eye irritation score was 10.0/110 after one hour (rabbit). The Primary Dermal Irritation Score for terephthalic acid was 0.2/8.0 (rabbit). The dermal LD50 was greater than 2000 mg/kg body weight (rabbit).
The oral LD50 was greater than 5000 mg/kg body weight (rat). Terephthalic acid produced urinary calculi when fed to rats at very high levels in the diet during chronic studies. Humans are not expected to produce urinary calculi by skin exposure or by inhalation exposure.
The 2 hour LD50 was greater than 2000 mg/m3 (rat). No fatalities occurred when rats were exposed to 25 mg/m3 terephthalic acid, 6 hours per day, 5 days a week, for 4 weeks. The weight gain of the test animals was lower than normal.
Exposing pregnant rats to concentrations of terephthalic acid as high as 10 mg/m³ during the major organogenesis period did not result in any significant toxic or teratogenic effects in the dam or the fetus.

12. Ecological Information

PTA is relatively non-toxic to aquatic organisms. Test results of the acute toxicity of terephthalic acid and its sodium salt for several freshwater species are tabled below:

<table>
<thead>
<tr>
<th>Species</th>
<th>Time (hr)</th>
<th>Endpoint</th>
<th>EC50</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water flea, Daphnia magna</td>
<td>48</td>
<td>EC50</td>
<td>&gt;982 mg/l</td>
</tr>
<tr>
<td>Golden orfe fish, Leuciscus idus melanotus</td>
<td>96</td>
<td>LC50</td>
<td>&gt;922 mg/l</td>
</tr>
<tr>
<td>Green alga, Scenedesmus subspicatus</td>
<td>96</td>
<td>No effect</td>
<td>922 mg/l</td>
</tr>
<tr>
<td>Microbes (activated sludge)</td>
<td>3</td>
<td>EC50</td>
<td>1390 mg/l</td>
</tr>
</tbody>
</table>

The above tests were conducted following relevant OECD protocols and in compliance with Good Laboratory Practices (GLP). Terephthalic acid has been shown to biodegrade in water under several test methods and in soil suspension inoculum, according to published reports. In a modified Sturm test (OECD Guideline 301B), over 60% of the theoretical CO2 was generated within 5 days, and over 80% of theoretical CO2 was generated within 14 days, at two concentrations of terephthalic acid, meeting the criteria for "readily biodegradable."

Abiotic degradation, such as by photolysis or hydrolysis, is not expected to be significant. Terephthalic acid is not expected to bioconcentrate or bioaccumulate. A low bioconcentration factor of 19 is predicted using the estimated octanol-water partition coefficient (log Kow) of 2 for undissociated terephthalic acid. Significant bioconcentration is unlikely if bioconcentration factors are less than 100 to 1000. Other evidence supports the expected lack of bioconcentration,
including the biodegradability and the elimination of terephthalic acid and its metabolites in mammalian studies.

13. Disposal Information

Enclosed-controlled incineration is recommended unless directed otherwise by applicable ordinances.

14. Regulatory Information

Cercla Sections 102a/103 Hazardous Substances (40 CFR Part 302.4): This product is not reportable under 40 CFR Part 302.4.

SARA Title III Section 302 Extremely Hazardous Substances (40 CFR Part 355): This product is not regulated under Section 302 of SARA and 40 CFR Part 355.

SARA Title III Section 311/312 Hazardous Categorization (40 CFR Part 370): This product is not regulated under SARA Title III Section 311/312.

SARA Title III Section 313 (40 CFR Part 372): This product is not regulated under Section 313 of SARA and 40 CFR Part 372.

U.S. Inventory (TSCA): Listed on inventory.


WHMIS Controlled Product Classification: Not a Controlled Product under Canada’s Workplace Hazardous Material Information System.

EC Inventory (EINECS/ELINCS): In compliance.

Japan Inventory (MITI): Listed on inventory.

Australia Inventory (AICS): Listed on inventory.

Korea Inventory (ECL): Listed on inventory.

Canada Inventory (DSL): All of the components of this product are listed on the DSL.

Philippine Inventory (PICCS): Not determined.

Food Contact Status

FDA:
This product is approved for use by the FDA under the following sections of 21 CFR:
Part 175.300 as a component of resinous and polymeric coatings for food contact surfaces when used in accordance with the specifications of this subpart.
Part 175.320 as a component of resinous and polymeric coatings of polyolefinic food contact surfaces when used in accordance with the specifications of this subpart.

15. Other Information

Prepared by:
Environment, Health and Safety Department

Issued: April 05, 1996
Supersedes: March 14, 1995

AMOCO TA-22
MSDS No. 01092000 ANSI/ENGLISH

MATERIAL SAFETY DATA SHEET

This material Safety Data Sheet conforms to the requirements of ANSI Z400.1. This material safety data sheet and the information it contains is offered to you in good faith as accurate. We have reviewed any information contained in this data sheet which we received from sources outside our company. We believe that information to be correct but cannot guarantee its accuracy or completeness. Health and safety precautions in this data sheet may not be adequate for all individuals and/or situations. It is the user’s obligation to evaluate and use this product safely and to comply with all applicable laws and regulations. No statement made in this data sheet shall be construed as a permission or recommendation for the use of any product in a manner that might infringe existing patents. No warranty is made, either express or implied.

F3. Polyethylene Terephthalate Material Safety Data Sheet
1. Chemical Product and Company Identification

**Product Name** Polyester Resin

**CAS#** Mixture/None Assigned

**Generic Name** Organic Resin

**Formula** Polymer

**Chemical Name:** Polyethylene terephthalate polymer

**Hazard Label** PET-001

**Manufacturer Information**
Johns Manville Engineered Products Group
Mats and Reinforcements Division
P.O. Box 5108
Denver, CO 80127, CO 80127
Telephone: 303-978-2000
Internet Address: http://www.jm.com
Emergency: 800-424-9300 (Chemtrec)

**Trade Names:** Polyester Resin Type (17,18,26,32,38)

2. Composition / Information on Ingredients

<table>
<thead>
<tr>
<th>CAS #</th>
<th>Component</th>
<th>Percent</th>
</tr>
</thead>
<tbody>
<tr>
<td>25038-59-9</td>
<td>Polyethylene terephthalate polymer (PET)</td>
<td>100</td>
</tr>
<tr>
<td>75-07-0</td>
<td>Acetaldehyde*</td>
<td>*</td>
</tr>
</tbody>
</table>

**Additional Component Information**
* May be released when product is heated above 383°F (195°C).

3. Hazards Identification
Emergency Overview

Appearance and Odor:
Product form varies: chips, dice noodles or lace. Colors vary: milky white to black; several levels of translucence or luster. Under normal conditions of use, this product is not expected to create and unusual emergency hazards.

Polyesters can burn if exposed to flame. Molten polymer generates small amounts of volatile degradation products (off-gases), one of which is acetaldehyde. Acetaldehyde vapors form explosive mixtures with air that can spontaneously ignite (auto-ignite) at temperatures above 347°F (175°C). Combustion products may include compounds of carbon, hydrogen, and oxygen; exact composition depends on conditions of combustion.

In the event of fire, use normal fire fighting procedures to prevent inhalation of smoke and gases.

Potential Health Effects

Summary
Nuisance dust hazards are associated with the dry resin. Heating resin above 383°F (195°C) may cause gas and vapor that are potent irritants.

Inhalation
Irritation of the upper respiratory tract, coughing, and congestion may occur.

Skin
Molten resin will cause thermal burns.

Absorption
Not applicable

Ingestion
Not applicable

Eyes
Temporary irritation (itching) or redness may occur.

Target Organs
Upper respiratory passages, skin, and eyes.

Primary Routes of Entry (Exposure)
Respiratory system, skin, and eye.

4. First Aid Measures

First Aid: Inhalation
Remove to fresh air. Drink water to clear throat, and blow nose to remove dust.
First Aid: Skin
If contact with molten resin occurs the affected area should be flushed with plenty of water. Prompt medical attention is advised for burns.

First Aid: Ingestion
Not applicable

First Aid: Eyes
Flush eyes with large amounts of water for 5-15 minutes. If irritation develops, or persists, seek medical attention.

5. Fire Fighting Measures

Flash Point: Not applicable
Method Used: Not applicable
Upper Flammable Limit (UFL): Not applicable
Lower Flammable Limit (LFL): Not applicable
Auto Ignition: Not determined
Flammability Classification: Not determined
Rate of Burning: Not determined

General Fire Hazards
Polyesters can burn if exposed to flame. Molten polymer generates small amounts of volatile degradation products (off-gases), one of which is acetaldehyde. Acetaldehyde vapors form explosive mixtures with air that can spontaneously ignite (auto-ignite) at temperatures above 175°C (347°F). Combustion products will be comprised of compounds of carbon, hydrogen, and oxygen. The exact composition will depend on the conditions of combustion.

Hazardous Combustion Products
Acetaldehyde, carbon, hydrogen and oxygen.

Extinguishing Media
Class A or Class B fire extinguishers or water fog.

Fire Fighting Equipment/Instructions
Firefighters should wear full-face, self-contained breathing apparatus and impervious protective clothing. Firefighters should avoid inhaling any combustion products.

6. Accidental Release Measures
Containment Procedures
Sweep up small spills and put into an appropriate container. Stepping or walking on resin chips or pellets can cause falls; avoid accumulation on floors and walkways. Pick up large pieces.

Clean-Up Procedures
Wastes are not hazardous as defined by the Resource Conservation and Recovery Act (RCRA; 40 CFR 261). Comply with state and local regulations for disposal of these products. If you are unsure of the regulations, contact your local Public Health Department, or the local office of the Environmental Protection Agency (EPA).

7. Handling and Storage

Handling Procedures
Customary personal hygiene measures, such as washing hands after working with these products are recommended.

Storage Procedures
No special precautions are required.

8. Exposure Controls / Personal Protection

Exposure Guidelines
No information available for the product.
A: Component Exposure Limits

OSHA: 100 ppm TWA; 180 mg/m3 TWA

150 ppm STEL; 270 mg/m3 STEL

B: Exposure Limits for Chemicals which may be generated during processing:
This material has no components listed.

Personal Protective Equipment

Personal Protective Equipment: Eyes/Face
Wear safety glasses with side shields.

Personal Protective Equipment: Skin
Leather or cotton gloves should be worn to prevent skin contact and irritation.

Personal Protective Equipment: Respiratory
Respiratory protection is not required when using this product. However, exposure to chemical
substances may occur as a result of heating this resin. Use a NIOSH-approved full-face respirator to protect against toxic gases.

**Ventilation**

Local exhaust ventilation should be provided at areas of cutting to remove airborne dust and fibers. General dilution ventilation should be provided as necessary to keep airborne dust and fibers below the applicable exposure limits and guidelines. The need for ventilation systems should be evaluated by a professional industrial hygienist, while the design of specific ventilation systems should be conducted by a professional engineer.

**Personal Protective Equipment: General**

Loose-fitting, long-sleeved clothing should be worn to protect the skin from irritation. Exposed skin areas should be washed with soap and warm water after handling.

### 9. Physical & Chemical Properties

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Appearance</strong></td>
<td>Products in form of chips, dice noodles or lace.</td>
</tr>
<tr>
<td>Colors range from milky white to black; variable translucence or luster.</td>
<td>Odor: Odorless</td>
</tr>
<tr>
<td><strong>Physical State:</strong> Solid</td>
<td>pH: Not applicable</td>
</tr>
<tr>
<td><strong>Vapor Pressure:</strong> Not applicable</td>
<td>Vapor Density: Not applicable</td>
</tr>
<tr>
<td><strong>Boiling Point:</strong> Not determined</td>
<td>Melting Point: 260ºC/500ºF</td>
</tr>
<tr>
<td><strong>Solubility (H2O): Nil</strong></td>
<td>Specific Gravity: 1.33-1.45</td>
</tr>
<tr>
<td><strong>Freezing Point:</strong> Not applicable</td>
<td>Evaporation Rate: Not applicable</td>
</tr>
<tr>
<td><strong>Viscosity:</strong> Not applicable</td>
<td>Percent Volatile: 0</td>
</tr>
<tr>
<td><strong>VOC:</strong> Not applicable</td>
<td></td>
</tr>
</tbody>
</table>

### 10. Chemical Stability & Reactivity Information
Chemical Stability
This is a stable material. This product is not reactive.

Hazardous Decomposition
Combustion products will be comprised of compounds of acetaldehyde, carbon, hydrogen, and oxygen.

Hazardous Polymerization
Will not occur.

11. Toxicological Information

Acute Toxicity
Acetaldehyde can cause irritation to eyes, nose and upper respiratory tract; eye, skin burns; dermatitis; conjunctivitis; cough; central nervous system depressant/depression; delayed pulmonary edema.

A: Component Analysis - LD50/LC50
Acetaldehyde* (75-07-0)
Inhalation LC50 Rat : 13300 ppm/4H
Inhalation LC50 Mouse : 23 gm/m3/4H
Oral LD50 Rat : 661 mg/kg
Oral LD50 Mouse : 900 mg/kg
Dermal LD50 Rabbit : 3540 mg/kg

Carcinogenicity
The Occupational Safety and Health Administration (OSHA), National Toxicology Program (NTP), International Agency for Research on Cancer (IARC), and American Conference of Governmental Industrial Hygienists (ACGIH) have not classified this product in its entirety as a carcinogen.

A: Component Carcinogenicity

NTP: Suspect Carcinogen (Possible Select Carcinogen)

IARC: Monograph 71, 1999; Supplement 7, 1987; Monograph 36, 1985 (Group 2B (possibly carcinogenic to humans))

Chronic Toxicity
No long-term health hazards are associated with polyester or polyethylene terephthalate polymer.
In animals acetaldehyde has caused: kidney, reproductive, teratogenic effects. The International Agency for research on cancer classified acetaldehyde a Group 2B possible carcinogen. The National Toxicology Program classifies it a suspect carcinogen. The American Conference of Governmental Industrial Hygienists classified acetaldehyde an A3 animal carcinogen.
12. Ecological Information

Ecotoxicity
No data available for this product.

A: Component Analysis - Ecotoxicity - Aquatic Toxicity

13. Disposal Considerations

US EPA Waste Number & Descriptions
This product is not regulated as a hazardous waste by the U.S. Environmental Protection Agency (EPA) under Resource Conservation and Recovery Act (RCRA) regulations.

A: Component Waste Numbers

Disposal Instructions
Dispose of waste material according to Local, State, Federal, and Provincial Environmental Regulations.

14. Transportation Information

US DOT Information

Shipping Name: This product is not classified a hazardous material for transport.

15. Regulatory Information

US Federal Regulations
No information on this product as a whole.

A: Component Analysis
This material contains one or more of the following chemicals required to be identified under SARA Section 302 (40 CFR 355 Appendix A), SARA Section 313 (40 CFR 372.65) and/or CERCLA (40 CFR 302.4).

CERCLA: final RQ = 1000 pounds (454 kg)

State Regulations
No information available for the product.
A: Component Analysis - State
The following components appear on one or more of the following state hazardous substances lists:

<table>
<thead>
<tr>
<th>Component</th>
<th>CAS #</th>
<th>CA</th>
<th>FL</th>
<th>MA</th>
<th>MN</th>
<th>NJ</th>
<th>PA</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetaldehyde*</td>
<td>75-07-0</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
</tr>
</tbody>
</table>

The following statement(s) are provided under the California Safe Drinking Water and Toxic Enforcement Act of 1986 (Proposition 65):
WARNING! This product contains a chemical known to the state of California to cause cancer.

Other Regulatory Information
No information available for the product.

A: TSCA Status
This product and its components are listed on the TSCA 8(b) inventory. None of the components listed in this product are listed on the TSCA Export Notification 12(b) list.

B: Component Analysis - Inventory

<table>
<thead>
<tr>
<th>Component</th>
<th>CAS #</th>
<th>TSCA</th>
<th>DSL</th>
<th>EINECS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polyethylene terephthalate polymer (PET)</td>
<td>25038-59-9</td>
<td>Yes</td>
<td>Yes</td>
<td>No</td>
</tr>
<tr>
<td>Acetaldehyde*</td>
<td>75-07-0</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
</tr>
</tbody>
</table>

A: Component Analysis - WHMIS IDL
No components are listed in the WHMIS IDL.

16. Other Information

Other Information
Prepared for:
Johns Manville Engineered Products Group
Mats & Reinforcements Division
P.O. Box 5108
Denver, CO 80217-5108
Prepared by:
Johns Manville Technical Center
P.O. Box 625005
Littleton, CO USA 80162-5005

The information herein is presented in good faith and believed to be accurate as of the effective
date given. However, no warranty, expressed or implied, is given. It is the buyer's responsibility to ensure that its activities comply with Federal, State or provincial, and local laws.

<table>
<thead>
<tr>
<th>Date</th>
<th>MSDS #</th>
<th>Reason</th>
</tr>
</thead>
<tbody>
<tr>
<td>08/01/00</td>
<td>2202-1.0000</td>
<td>New MSDS authoring system.</td>
</tr>
</tbody>
</table>
Appendix G

Fire and Explosion Index
Appendix G

Fire and Explosion Index
## Appendix-G: Fire & Explosion Index

<table>
<thead>
<tr>
<th>Site:</th>
<th>Manufacturing Unit:</th>
<th>Process Unit:</th>
</tr>
</thead>
<tbody>
<tr>
<td>PET Production</td>
<td>Esterification Reactor</td>
<td>R-200</td>
</tr>
</tbody>
</table>

### Materials in Process Unit
- EG, TPA, BHET

### State of Operation
- Normal Operation

### Basic Material for Material Factor
- EG

### Material Factor

<table>
<thead>
<tr>
<th>Material Factor</th>
<th>Penalty Factor Range</th>
<th>Penalty Factor Used</th>
</tr>
</thead>
<tbody>
<tr>
<td>Base Factor</td>
<td>1.00</td>
<td>1.00</td>
</tr>
</tbody>
</table>

1. **General Process Hazards**

<table>
<thead>
<tr>
<th>Activity</th>
<th>Penalty Factor Range</th>
<th>Penalty Factor Used</th>
</tr>
</thead>
<tbody>
<tr>
<td>A. Exothermic Chemical Reaction</td>
<td>0.30-1.25</td>
<td>0.5</td>
</tr>
<tr>
<td>B. Endothermic Processes</td>
<td>0.2-0.4</td>
<td>0.0</td>
</tr>
<tr>
<td>C. Material Handling and Transfer</td>
<td>0.25-1.05</td>
<td>0.0</td>
</tr>
<tr>
<td>D. Enclosed or Indoor Process Units</td>
<td>0.25-0.9</td>
<td>0.0</td>
</tr>
<tr>
<td>E. Access</td>
<td>0.2-0.35</td>
<td>0.0</td>
</tr>
<tr>
<td>F. Drainage and Spill Control</td>
<td>0.25-0.5</td>
<td>0.25</td>
</tr>
</tbody>
</table>

**General Process Hazards Factor (F1)** = 1.75

2. **Special Process Hazards**

<table>
<thead>
<tr>
<th>Activity</th>
<th>Penalty Factor Range</th>
<th>Penalty Factor Used</th>
</tr>
</thead>
<tbody>
<tr>
<td>A. Toxic Material(s)</td>
<td>0.2-0.80</td>
<td>0.2</td>
</tr>
<tr>
<td>B. Sub-Atmospheric Pressure(&lt;500 mm Hg)</td>
<td>0.5</td>
<td>0.0</td>
</tr>
<tr>
<td>C. Operation In or Near Flammable Range</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1. Tank Farms Storage Flammable Liquids</td>
<td>0.5</td>
<td>0.0</td>
</tr>
<tr>
<td>2. Process Upset or Purge Failure</td>
<td>0.3</td>
<td>0.0</td>
</tr>
<tr>
<td>3. Always in Flammable Range</td>
<td>0.8</td>
<td>0.0</td>
</tr>
<tr>
<td>D. Dust Explosion</td>
<td>0.25-2.00</td>
<td>0.0</td>
</tr>
<tr>
<td>E. Pressure, Operating Pressure = 50.6 psig</td>
<td>0.25</td>
<td></td>
</tr>
<tr>
<td>F. Low Temperature</td>
<td>0.2-0.30</td>
<td>0.0</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Activity</th>
<th>Penalty Factor Range</th>
<th>Penalty Factor Used</th>
</tr>
</thead>
<tbody>
<tr>
<td>G. Quantity of Flammable/Unstable Material</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1. Liquids or Gasses in Process</td>
<td>0.0</td>
<td></td>
</tr>
<tr>
<td>2. Liquids or Gases in Storage</td>
<td>0.0</td>
<td></td>
</tr>
<tr>
<td>3. Combustible Solids in Storage, Dust in Process</td>
<td>0.0</td>
<td></td>
</tr>
<tr>
<td>H. Corrosion and erosion</td>
<td>0.10-0.75</td>
<td>0.10</td>
</tr>
<tr>
<td>I. Leakage-Joints and Packing</td>
<td>0.1-1.50</td>
<td>0.10</td>
</tr>
<tr>
<td>J. Use of Fired Equipment</td>
<td>0.0</td>
<td></td>
</tr>
<tr>
<td>K. Hot Oil Heat Exchange System</td>
<td>0.15-1.15</td>
<td>0.0</td>
</tr>
<tr>
<td>L. Rotating Equipment</td>
<td>0.50</td>
<td>0.5</td>
</tr>
</tbody>
</table>

**Special Process Factor (F2)** = 2.15

**Process Unit Hazards Factor (F1 × F2) = F3** = 3.7625

**Fire and Explosion Index (F3 × MF) = F&EI** = 15.05
Appendix H

HAZOP Study Tables
Appendix H: HAZARD study for the primary esterification reactor (R-200)

Table (H.1) Line No. 102: Feed to the primary esterification reactor from the mixing tank at 15.36 ton/hr and 28 °C
   Intention: Transfer EG and TPA mixture from mixing tank

<table>
<thead>
<tr>
<th>Date: 18 / 02 / 01</th>
<th>NR: 1 / 3</th>
<th>GUIDE OF: primary esterification reactor (R-200)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GUIDE WORD</td>
<td>DEVIATION</td>
<td>POSSIBLE CAUSES</td>
</tr>
<tr>
<td>MORE</td>
<td>FLOW</td>
<td>- Pump racing</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>LESS</td>
<td>FLOW</td>
<td>- Pump failure</td>
</tr>
<tr>
<td></td>
<td></td>
<td>- Line breakage</td>
</tr>
<tr>
<td></td>
<td></td>
<td>- Sediment</td>
</tr>
<tr>
<td>NO</td>
<td>FLOW</td>
<td>- Pump failure</td>
</tr>
<tr>
<td></td>
<td></td>
<td>- Line breakage</td>
</tr>
<tr>
<td></td>
<td></td>
<td>- Line blockage</td>
</tr>
<tr>
<td>REVERSE</td>
<td>FLOW</td>
<td>- Pump failure</td>
</tr>
<tr>
<td></td>
<td></td>
<td>- Pump failure higher than delivery</td>
</tr>
<tr>
<td>MORE</td>
<td>PRESSURE</td>
<td>- Partial blockage of vessel or line</td>
</tr>
<tr>
<td>LESS</td>
<td>PRESSURE</td>
<td>- Pump failure</td>
</tr>
<tr>
<td></td>
<td></td>
<td>- Line leakage</td>
</tr>
<tr>
<td>MORE</td>
<td>TEMPERATURE</td>
<td>- Control problem or faulty temperature signal (reads low)</td>
</tr>
<tr>
<td>LESS</td>
<td>TEMPERATURE</td>
<td>- Control problem or faulty temperature signal (reads high)</td>
</tr>
</tbody>
</table>
Table (H.2) Line 200: Produced liquid esterification mixture at 15.36 ton/hr and 240 °C
Intention: Transfer liquid reaction mixture to the unit PV-400

<table>
<thead>
<tr>
<th>Date: 18 / 02 / 01</th>
<th>NR: 2 / 3</th>
<th>GUIDE OF: primary esterification reactor (R-200)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GUIDE WORD</td>
<td>DEVIATION</td>
<td>POSSIBLE CAUSES</td>
</tr>
<tr>
<td>MORE</td>
<td>FLOW</td>
<td>- Failure of reactor level control</td>
</tr>
<tr>
<td>LESS</td>
<td>FLOW</td>
<td>- Partial failure or blockage of valve</td>
</tr>
<tr>
<td>NO</td>
<td>FLOW</td>
<td>- Failure of valve</td>
</tr>
<tr>
<td>MORE</td>
<td>PRESSURE</td>
<td>- Partial blockage in line</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>LESS</td>
<td>PRESSURE</td>
<td>- Line leakage</td>
</tr>
<tr>
<td>MORE</td>
<td>TEMPERATURE</td>
<td>- Failure of temperature control</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>LESS</td>
<td>TEMPERATURE</td>
<td>- Failure of temperature control</td>
</tr>
</tbody>
</table>
Table (H.3) Auxiliary: Steam line  
Intention: Transfer heat to the reactor vessel

<table>
<thead>
<tr>
<th>Date: 18 / 02 / 01</th>
<th>NR: 3 / 3</th>
<th>GUIDE OF: primary esterification reactor (R-200)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>GUIDE WORD</strong></td>
<td><strong>DEVIATION</strong></td>
<td><strong>POSSIBLE CAUSES</strong></td>
</tr>
<tr>
<td><strong>MORE</strong></td>
<td>MORE FLOW</td>
<td>- Failure of control valve</td>
</tr>
<tr>
<td></td>
<td></td>
<td>- Trap frozen</td>
</tr>
<tr>
<td><strong>LESS</strong></td>
<td>LESS FLOW</td>
<td>- Partial failure or blockage of valve</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>NO</strong></td>
<td>NO FLOW</td>
<td>- Failure of control valve</td>
</tr>
</tbody>
</table>

Appendix H-4