

Chapter one

Introduction

Poly ethylene terephthalate (PET) is a thermoplastic polyester widely used in the manufacture of video and audio tabs, X-ray films, food packaging and especially in the manufacture of soft-drink bottles (Yue et al (2011)). Due to properties such as, high transparency in blown containers, high mechanical strength for minimum thickness walls, negligible permeability to CO₂ and relatively low cost, soft drink bottles is the most important application of PET, which produce household and municipal waste (*Vakili and Haghshenas Fard.* (2010)).

Global consumption of polyethylene terephthalate (PET) packaging is forecasted to reach 19.1 million tons by 2017, with a 5.2% increase per annum between 2012 and 2017 (Zhang and Zong-Guo (2013)). Bottles for water, carbonated soft drinks, and other beverages account for 83–84% of global PET resin demand (Zhang and Zong-Guo (2013)). This rapid increase in PET bottle consumption has also led to the emergence of various issues. These include environmental pollution health concerns for scavengers, and low utilization efficiency for reclaimed PET bottles (Zhang and Zong-Guo (2013)).

Increased environmental awareness and public demand for environmental sustainability are leading to an increased interest in plastics recycling. It is very important for a wide number of reasons such as conservation of oil, reduction of greenhouse gas emissions, saving of landfill space, conservation of energy, and benefits of reuses (López-Fonseca et al (2010)).

There are two global methods for recycling of PET waste, mechanical and chemical methods. In mechanical methods, generally beverage bottle can be recycled to the usage cycle by cutting it into fine scraps, heating, melting and remolding to new products (Vakili and Haghshenas Fard. (2010)). in chemical recycling of PET waste consist of depolymerization by hydrolysis, methanolysis, glycolysis and aminolysis to obtain various monomers (Vakili and Haghshenas Fard. (2010)).

1.2 Production of Terephthalic acid:-

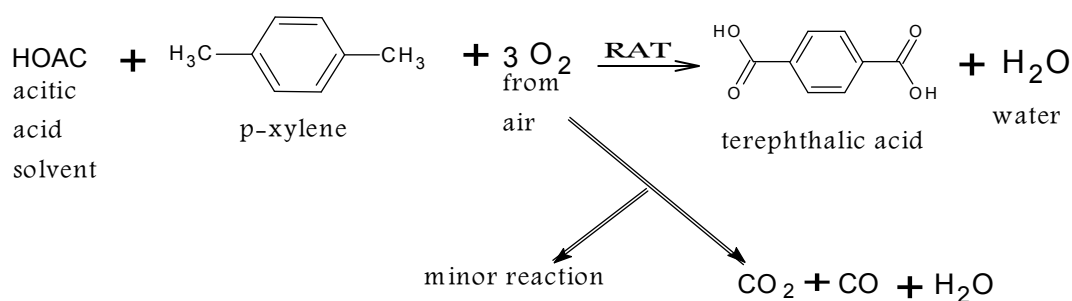
PET is formed through a reversible poly condensation reaction, so it can be transformed back to its monomer by pushing the reaction to the opposite direction through the addition of a condensation product (Terephthalic acid & Ethylene glycol).

In industrial scale, Terephthalic acid is produced by oxidation of p-xylene by oxygen from air.

Thermal and hydrolysis depolymerization of PET has also been studied by Sao and Cloyd (Sao and Cloyd (1991)). Methanolysis of PET waste is used to form monomers, dimethyl terephthalate (DMT) and ethylene glycol (EG). Neutral hydrolysis of waste PET with different amounts of water and different catalysts, in presence of x-ylene has been studied by Guclu et al. (2003) (Guclu et al (2003)). Ghaemy M. & Mossaddegh K. (2005) studied glycolysis of PET waste using ethylene glycol. They investigated some parameter such as: reaction time, volume of EG, catalysts and their concentrations on the yield of glycolysis (Ghaemy and Mossaddegh, (2005)).

1.2.1 P-Xylene oxidation:

The oxidation of p-xylene by air to give Terephthalic acid is almost universally carried out with cobalt and manganese salts as catalysts. A typical continuous process for the manufacture of crude Terephthalic acid (C-TPA) (Dylewski et al (1980)) as shown in “scheme 1.1”.



P-Xylene, fresh acetic acid, a catalyst system such as manganese or cobalt acetate and sodium bromide, and recovered acetic acid are combined into the liquid feed entering the reactor. Air, compressed to a reaction pressure of about 2000 kPa (290 psi) is fed to the reactor. The temperature of the exothermic reaction is maintained at about 200°C (392°F) by controlling the pressure at which the reaction mixture is permitted to boil and form the vapor stream leaving the reactor. (Durocher et al (1979)).

The oxidation and product recovery portion essentially consists of the Mid-Century oxidation process, whereas the recovery and recycle of acetic acid and recovery of methyl acetate are essentially as practiced by dimethyl terephthalate (DMT) technology. The purpose of the DMT process is to convert the Terephthalic acid contained in C-TPA (crude Terephthalic acid) to a form that will permit its separation from impurities. C-TPA is extremely insoluble in both water and most common organic solvents (Dylewski, S. W. (1981)).

1.2.2 Hydrolysis:-

The hydrolysis of PET relies on the use of aqueous systems at elevated temperatures and pressures to obtain Terephthalic acid and ethylene glycol. Each cleavage of the polymer chain consumes one molecule of water and creates two functional groups, carboxylic and hydroxylic, at the scission place. The growing interest in this method is associated with the development of the PET synthesis directly from EG and TA, which eliminates toxic methanol from the

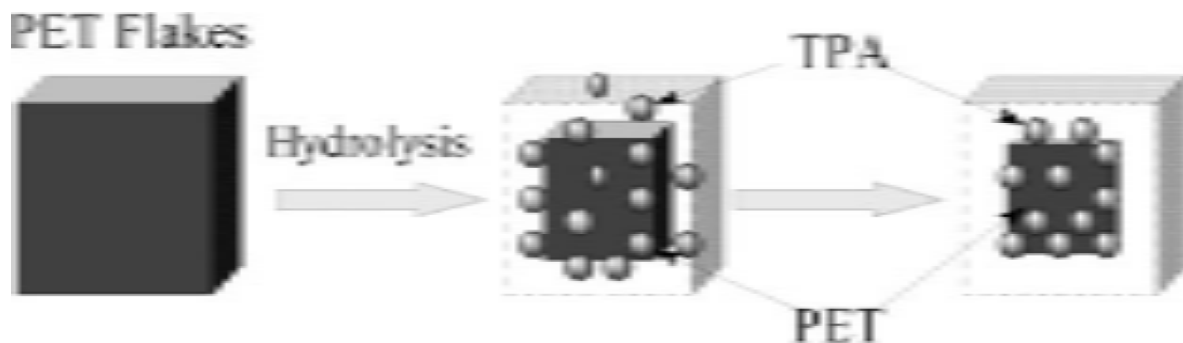
technological cycle. Hydrolysis of PET waste can be performed as an acid-catalyzed, base-catalyzed, or neutral process, and is used on a commercial scale. However, this method is not as widely applied as methanolysis and glycolysis since the cost associated with the purification of the recycled TA is rather high. PET hydrolysis was first described in patents issued in the years 1959-1962 (Spychaj (2000)).

Alkaline hydrolysis of PET is usually carried out by the use of an aqueous solution of sodium hydroxide or potassium hydroxide (Lazarus et al (1967)) or with an aqueous ammonia solution. According to literature data, PET waste containing impurities up to 40wt% can be processed by hydrolysis with NaOH solutions (Scheirs (1998)). Sodium hydroxide-catalyzed hydrolysis processes are performed in alkaline solutions of a concentration of 3-20 wt% under pressures of 1-2MPa (or under atmospheric pressure) at temperatures of 100-250°C. However, in order to obtain reaction rates applicable to industrial processes, hydrolysis should be conducted at a temperature above the polymer melting point. Catalysts may also be used in the alkaline hydrolysis of PET, e.g., amines with dissociation constant $K > 10^{-5}$ (Alter (1986)). Representative examples of PET hydrolysis using alkaline solutions are given below. Pitat et al. (Pitat et al (1959)) have patented a method of PET alkaline hydrolysis in an 18 wt% solution of NaOH. The most advantageous results are achieved at a PET/NaOH weight ratio of 1:20 at about 100°C for 2h. The sodium salt of TA formed has relatively good solubility in aqueous

solutions of alkaline hydroxides; however, by maintaining the NaOH concentration at a constant level of 18 wt%, it is possible to achieve its complete precipitation.

After separation, the salt is dissolved in a small amount of water so as to obtain a nearly saturated solution. After acidification, TA is precipitated from the solution, filtered off, rinsed, and dried. EG formed during the reaction remains in the aqueous phase and is fed back into the process after addition of NaOH. The EG content in the solution increases and, therefore, its recovery by vacuum distillation becomes feasible. The process can be run under either high or atmospheric pressure as well as under conditions using lower hydroxide concentrations. (Spychaj (2000)).

Hydrolysis of PET “scheme 1.2”



1.3 Uses of Terephthalic acid:

1. The hydrolysis products may be used to produce virgin PET, in this way the environment is not surcharged and there is no need for extra resources for the production of PET, or may be converted to more expensive chemicals like oxalic acid.
2. Polyester fibers based on PTA provide easy fabric care both alone and in blends with natural and synthetic fibers.
3. Polyesters films are used widely in audio and video recording tapes, photographic films, labels and other sheet material requiring both dimensional stability and toughness.
4. PTA derivative , poly ethylene terephthalate (PET) has become the primary container resin for application such as: carbonated beverage bottles, while other terephthalate provide dimensional stability, good heat resistance and durability for engineering applications
5. - Terephthalic acid is also used in the pain as a carrier.
6. It is used in the pharmaceutical industry as a raw material for certain drugs.
7. In addition to these end uses, Terephthalic acid based polyester and polyamides are also used in hot melt adhesives.

8. PTA is an important raw material for lower molecular weight saturated polyesters for powder and water-soluble coatings.
9. The analgesic drug comes as a terephthalate salt; however, the more usual salt of oxycodone is hydrochloride.
10. It is used as filler in some military smoke grenades, most notably the American M83 smoke grenade, producing a thick white smoke when it burned. (Richard (2002)).

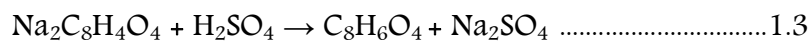
1.4 Problem statement:

In this project, different types of PET wastes will be utilized for the production of Terephthalic acid (TPA) and ethylene glycol. The process, involves depolymerization of PET to Terephthalic acid (TPA) and ethylene glycol through hydrolysis in alkaline media.

The experimental works will be carried out in two steps. In the first step, a reaction between PET and sodium hydroxide will be conducted (Eq. 1.2)



Ethylene glycol and sodium terephthalate will be produced from this step. Then, sodium terephthalate will be treated with Sulphuric acid in the second step (Eq. 1.3)



1.5 Objectives:-

The objective of this study is to find a suitable chemical recycling process of poly ethylene terephthalate waste products.

In this work, the depolymerisation process will be conducted to produce Terephthalic acid.

1.6 Significance of the study:-

- ❖ The research will be value to those who are interested in recycling and in environmental protection.
- ❖ To industries to save economical cost of raw material to produce new PET bottles or any other PET product.
- ❖ Even to open new industrial work at this domain (recycling).

Chapter two

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Experimental

2.1 Samples collection

In this project, PET beverage bottles and X-rays photograph films wastes were collected from different places in Khartoum state to be used as sources of Terephthalic acid (TPA) and ethylene glycol.

2.2 Material and glass wares:-

- Ethylene glycol solution.(NICE)
- Sodium hydroxide “solid”.(NICE “96%”)
- Poly ethylene terephthalate (PET) wastes.
- Sulphuric acid. (LOBA Chemi “98%”)
- Hydrochloric acid. (LOBA “35_36%”)

2.3 Glass wares:-

Sensitive balance- beakers (250mL) - glass funnels- graduated cylinder (50 mL, 25 mL) - benzene burner- glass rod – filter papers (witman 41).

PET wastes (beverages and mineral water bottles and X-ray Films) were cut into small pieces from 2mm×5mm to 3mm×6mm and washed by soap then by water and distilled water. A mixture of ethylene glycol(22mL) and sodium hydroxide (5.5g) were well mixed in a 500 mL beaker and heated with continuous stirring in a flame burner for about 15 min until the mixture reached its boiling point (200°C). The beaker was removed from the burner and allowed to cool at room temperature, then 100 mL of distilled water were added to the mixture and stirred well, more quantities (50 mL) of distilled water were added and the mixture was well stirred further to dissolve all solids which were in the original plastic shape. Then the solution was filtered using filter paper. 30 mL of concentrated sulphuric acid was added drop wise to the filtrate solution then a white precipitate was appeared. The mixture was well stirred again and allowed to settle down and the white precipitate was separated by filtration. The white solid was placed on a strong cotton fabric and hardly pressed to remove the remaining water. This crude Terephthalic acid was mixed again with 250 mL distilled water and separated by filtration and hard pressing to obtain pure Terephthalic acid. The same procedure was repeated using different source of PET. The effect of many parameters was studied, such as PET: NaOH weight ratio, source of acid, PET: EG weight ratio and solvent.

The undepolymerized PET was collected, dried, and weighed. The conversion of PET is defined by Eq. 2.1

$$\text{Conversion percentage of PET} = (w_0 - w_1 / w_0) \times 100\% \dots\dots\dots 2.1$$

Where:

W_0 represents the initial weight of PET.

W_1 represents the weight of undepolymerized PET.

Chapter Three

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Results and discussion

3.1-Effect of solvent type:-

Chemical recycling of PET by hydrolysis reaction involves a partial to full depolymerization of high molecular weight polymer consisting of terephthalate and ethylene glycol. The presence of glycol in reaction mixture causes chain scission by attacking the ester linkages along the polymer backbone water couldn't do this.

The effect of solvent type on the conversion of PET and the yield of PET were examined and the results are presented in table (3-1). From the conversion of PET increases distinctly with ethylene glycol and the hydrolysis conversion was achieved 95.7% moreover.

Table 3-1: Effect of solvent type:

Solvent type	PET: NaOH Molar ratio	PET: Sol* Molar ratio	PET (g)	NaOH (g)	Residual PET (g)	PTA(g)	Reacted PET (%)	PTA* (%)
Water	2:1	1:2.5	11.0	5.005	10.74952	0.2552	2.31	2.31
EG	2:1	1:2.5	11.1	5.5	1.529	10.83	86.16	98.00

**Sol= solvent, **PTA= purified Terephthalic acid. (PET: solvent molar ratio is 1:2.5, 200°C, 15 minutes)*

3-2: Effect of PET: EG molar ratio:

The PET to EG ratio is also a very important parameter for the hydrolysis. The effect of PET to EG ratio on the depolymerization reaction is summarized in table 3-2. Under the optimum weight ratio of PET:EG is (1:2.5), reaction temperature 200°C and time 15 minutes , the conversion of PET and the yield of PTA were 98%. The PET conversion and PTA yield all increased with dosage of EG growing, at PET: EG ratio is 1: 2.5.

It may be attributed to the dissolution of PET when we increase value of PET: EG ratio.

Table 3-2: Effect of PET: EG molar ratio:

PET: NaOH Molar ratio	PET:EG Molar ratio	PET* (g)	NaOH (g)	Residual PET (g)	PTA(g)	Reacted PET (%)	PTA** (%)
2:1	1:2.5	11.1	5.5	1.529	10.83	86.16	98.00
2:1	1:2	11.0	5.5073	2.101	9.465	80.92	85.9

*PET=poly ethylene terephthalate, ** PTA= purified Terephthalic acid. (PET: NaOH molar ratio is 2:1, 200°C, 15 minutes).

3.3 -Effect of PET: NaOH molar ratio on PTA yield:-

The effect of PET: NaOH molar ratio on the conversion of PET and the yield of PTA was investigated and the results are shown in table (3-3). From table (3-3), it can be seen that a great increase in the PET conversion and the PTA yield with decreasing in PET: NaOH molar ratio was observed. When molar ratio was (3:1), the PET conversion was only 81.59%. Subsequently, with decreasing PET: NaOH molar ratio, the conversion of PET increased

apparently and rapidly reaches 99.33% when the molar ratio was (2.5:1). Furthermore, the yield of PTA increased as the molar ratio was decline. Thus, low PET: NaOH molar ratio was beneficial to the formation of PTA from the hydrolysis of PET. So, the PET: NaOH molar ratio is a critical fact in the hydrolysis of PET.

Table 3-3: Effect of PET: NaOH molar ratio.

<i>PET: NaOH Molar ratio</i>	<i>PET:EG Molar ratio</i>	<i>PET* (g)</i>	<i>NaOH(g)</i>	<i>Residual PET (g)</i>	<i>PTA(g)</i>	<i>Reacted PET (%)</i>	<i>PTA** (%)</i>
3:1	1:2.5	11.03	3.71	3.22	9.00	70.80	81.59
2.5:1	1:2.5	11.00	4.40	1.375	10.92	87.50	99.33

*PET= poly ethylene terephthalate, **PTA= purified Terephthalic acid (200⁰C, 15 minutes)

3.4 Effect of acid:

The influence of the acid source on the conversion of PET and the yield of PTA is shown in table (3-4). It showed that the conversion of PET was increased with Sulphuric acid. The 98.0% conversion of PET was obtained when the Sulphuric acid was used. That is because sulphuric acid is more acidic than Hydrochloric acid.

Table 3-4: Effect of acid.

<i>Acid used</i>	<i>PET: NaOH Molar ratio</i>	<i>PET:EG Molar ratio</i>	<i>PET* (g)</i>	<i>NaOH (g)</i>	<i>Residual PET (g)</i>	<i>PTA (g)</i>	<i>Reacted PET (%)</i>	<i>PTA** (%)</i>
<i>HCl</i>	<i>2:1</i>	<i>1:2.5</i>	<i>11.0</i>	<i>5.51</i>	<i>3.180</i>	<i>5.50</i>	<i>43.29</i>	<i>50.00</i>
<i>H₂SO₄</i>	<i>2:1</i>	<i>1:2.5</i>	<i>11.1</i>	<i>5.50</i>	<i>1.529</i>	<i>10.8</i>	<i>86.16</i>	<i>98.00</i>

*PET=poly ethylene terephthalate, **PTA=purified Terephthalic acid. (200⁰C, 15 minutes)

3.5- Effect of PET source:-

The use of various sources of poly ethylene terephthalate (PET) – X-ray photograph films and clear bottles of PET- for depolymerization of PET into PTA by hydrolysis was examined. The following operation conditions were employed for comparative purposes, 200°C, EG: PET molar ratio 1:2.5 PET after a reaction time interval of 15 minutes. Activity results are summarized in table (3-5), and concluded that when we use clear PET bottles the yield of Terephthalic acid was more than when x-ray photograph films was used because the silver layer did not cleared at first (treated as contaminant).

Table 3-5: Effect of PET source.

<i>PET source</i>	<i>PET: NaOH Molar ratio</i>	<i>PET:EG Molar ratio</i>	<i>PET* (g)</i>	<i>NaOH (g)</i>	<i>Residual PET (g)</i>	<i>PTA(g)</i>	<i>Reacte d PET (%)</i>	<i>PTA** (%)</i>
PET bottles	2:1	1:2.5	11.06	5.50	1.529	10.8	86.16	98.00
x-ray photograph Films	2:1	1:2.5	11.00	5.50	4.345	7.7	60.50	70.42

*PET=poly ethylene terephthalate, **PTA=purified Terephthalic acid. (200⁰C, 15 minutes)

Chapter Four

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Conclusion

PET waste originates from various sources (soft-drink bottles, photographic and X-ray films). It is considered as a feed-stock for chemical processing.

PET waste recycling represents the most successful and widespread example of polymer reuse.

The chemical recycling of PET can be performed with various solvolytic agents, and useful products for many applications may be obtained. The important advantages of the chemical recycling methods related to waste PET are removal of any impurities associated (physically or chemically) to the polymer chain by purification of the monomers.

(ii) The selection of the most appropriate recycling method depends on the quality of the available feed-stock and on the type of the targeted product. (Spychaj (2002))

However, some drawbacks of the PET chemical recycling processes should also be listed.

(i) Necessity to operate with well-sorted feed-stocks.

(ii) Consistency of the batch-to-batch quality.

(iii) Separation of colored PET wastes is often required.

(iv) Contaminants, such as PVC, paper, glue, should be reduced to a minimum.

(v) In addition to TA and EG, the recycled PET product contains a number of co-monomers that increase its chemical heterogeneity. (Spychaj (2002)).

The effect of various operation parameters on the hydrolysis of PET waste was investigated in order to efficiency recover of Terephthalic acid. The yield of acid was increased with an increasing in EG: PET ratio, decreasing in PET: NaOH until the reaction reached equilibrium conditions. Hence, a yield of PET close to 99.33% could be attained at 200 °C, with and PET: EG molar ratio of (1:2) and using sulphuric acid as an acid. In an attempt to find perfect PET: EG, PET: NaOH, source of acid and PET source and suitable solvent for PET, many molar ratios , sources and solvents were examined, (1:2.5) & (1:2) for PET: EG , (3:1) & (2.5:1) for PET NaOH molar ratio, sulphuric acid as source of an acid, clear PET and X-ray photograph Films were used as source of PET source and ethylene glycol and water as sources of solvent. Under these conditions PTA and Ethylene glycol were found in the reaction mixture.

On the other hand, it was demonstrated that hydrolysis with ethylene glycol appeared to be suitable for chemical recycling of PET wastes of with a more complex nature and characteristics (clear PET) than those of X-ray, used as a reference waste in this study.

Recommendations:-

- ✓ *Study effect of temperature and time of reaction.*
- ✓ *Silver layer on X-ray photograph films did have affect on TA yield or it is not important?*
- ✓ *Incouredge people environmental awareness to make life easy and safe.*
- ✓ *Ministry of Industry should support and develop this domain, open new industries and make more researches.*

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