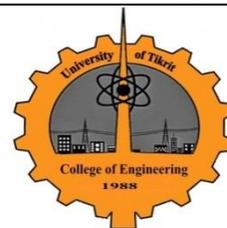


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Alkaline Depolymerization of Polyethylene Terephthalate Plastic Waste

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ABSTRACT

Depolymerization reaction is considered one of the most significant ways of converting waste polyethylene terephthalate in to terephthalic acid. The water polyethylene terephthalate bottle waste was collected from different places in Baghdad. The collection step shows that there is plenty amount of polyethylene terephthalate suitable to be an important source of terephthalic acid production.

PET plastic waste conversion to terephthalic acid by depolymerization process was examined. The effect of ethylene glycol amount, reaction time (up to 90 minutes) and reaction temperature (from 70 to 170° C) on the polyethylene terephthalate conversion was obtained.

The kinetic study shows that the ordination of the depolymerization reaction of PET is first order irreversible reaction with 31103.5 J/mole activation energy.

A 97.9 % terephthalic acid purity has been obtained by purification with N, N-dimethylformamide.

Keywords: Depolymerization, Polyethylene terephthalate plastic, Terephthalic acid, Kinetic study, Domestic municipality waste.

التحلل القلوي لمخلفات البولي إيثيلين التيرفثاليكية

الخلاصة

يعتبر تفاعل التحلل واحد من الطرق المعتبرة لتحويل مخلفات بولي إيثيلين ترفثاليك الى حامض الترفثاليك. تم تجميع مخلفات قناني الماء المصنوعة من بلاستيك بولي إيثيلين ترفثاليك من مناطق متفرقة من بغداد. اشارت هذه الخطوة الى توفر كميات وافرة من بلاستيك بولي إيثيلين ترفثاليك والذي يعتبر مصدر مهم لانتاج حامض الترفثاليك. تمت دراسة تفاعل التحليل لبلاستيك بولي إيثيلين ترفثاليك الى حامض الترفثاليك. وتم الحصول على تأثير كل من كمية وجود الايثيلين كلايكول و زمن التفاعل (حتى 90 دقيقة) و درجة حرارة التفاعل (من 70 و حتى 170 درجة مئوية) على تحول بلاستيك بولي إيثيلين ترفثاليك. دراسة حركية التفاعل اشارت الى ان التفاعل غير عكسي و من الدرجة الاولى بطاقة تنشيط مقدارها 31103.5 جول لكل مول. تم الحصول على حامض الترفثاليك بنقاوة مقدارها 97.9 % بعد تنقيته بالداي ميثيل فورماميد.

الكلمات الدالة: لجنة الإضاءة الدولية , فضاء الألوان , الألوان الأساسية , تحليل الصورة.

Abbreviations

EG: Ethylene glycol.

PET: Polyethylene terephthalate.

pTPA: Producing terephthalic acid.

sTPA: Standard terephthalic acid.

TPA: Terephthalic acid.

Nomenclatures

C_{PET} : The concentration of PET.

$(C_{PET})_0$: The initial concentration of PET.

E : The depolymerization reaction activation energy (J/mole).

k : The depolymerization reaction coefficient (min).

k_0 : The frequency factor of the Arrhenius equation (min).

R : The Universal gas constant (8.314 J/mole.K).

r_{PET} : The PET depolymerization reaction rate (mole/min).

t : The depolymerization reaction time (min).

T : The depolymerization reaction temperature (K).

x_{PET} : The PET conversion (calculated from Eq. 1).

Introduction

Through the recent years, plastics portion in the municipal solid waste increases dramatically. Plastics are occupied between 5 to 15 wt.% (20 to 30 vol. %) of municipal solid waste [1].

Most plastics are non-degradable and possibly take hundred years to decompose naturally.

The published statistics for Western Europe estimate the yearly consumption of plastic products about 100 kg per person for a total of over 39.1 million tones [2]. Over 78 wt.% of this total corresponds to thermoplastics such as high density polyethylene (HDPE), low density polyethylene (LDPE), polypropylene (PP), poly-vinyl chloride (PVC) and polyethylene terephthalate (PET). The remaining 22 wt.% to thermosets (mainly epoxy resins and polyurethane) [3].

In Arab countries (Saudi Arabia as an example), the amount of plastic waste is about 15 wt. % in the domestic municipality waste [4]. According to the report of Jackson and Bertényi [5], each three tons of plastic waste contain about one ton of PET which equal to 20000 PET bottles.

The depolymerization of PET was conducted by various alcohols with sodium hydroxide under atmospheric pressure. PET was depolymerized to EG and disodium terephthalate ($\text{Na}_2\text{-TPA}$). The depolymerization reaction is illustrated in Figure 1.

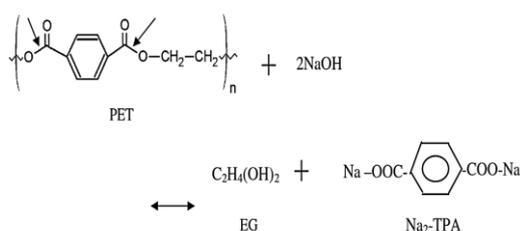


Fig.1,Depolymerization reaction of PET [6]

The depolymerization reaction of PET is a kind of trans-esterification reaction

triggered by the addition of alcohol under basic conditions. Transesterification is the process of substituting the alkoxy group of an ester compound with that of an alcohol [6].

Oku et al. [7] was produced terephthalic acid from PET by reacting it with NaOH solution at boiling point of the reaction mixture (about 200°C). The result show that terephthalic acid can be produced at this temperature within 20 minutes the produced mixture after that washed by water firstly followed by H_2SO_4 solution and then water again.

Ben-Zn Wan et al. [8] made hydrolytic depolymerization of PET flakes in a potassium hydroxide solution. The reaction was carried out in a stirred batch reactor at 120, 140 and 160° C for 30 minutes and under pressure of about 1.7, 2.9 and 4.9 atm. Zinc acetate was used as catalyst in the reaction with sulfuric acid into the filtrate to neutralize the potassium hydroxide and TPA produced was by water.

Abbas et al. [9], reported that the maximum yield of terephthalic acid from PET by the depolymerization reaction in the presence of ethylene glycol can be obtained at 40 minutes and 170°C.

Yusuke Asakuma et al. [6], studied the depolymerization reaction of virgin PET bottles on the basis of both experimental data and numerical data obtained from quantum chemistry calculations. Various alcohols were used as solvents in the search for the reaction mechanism. The maximum PET conversion through the depolymerization reaction in presence of ethylene glycol was about 30% at 78°C after 3 hours.

The present work, was intended to study the depolymerization reaction of collecting waste PET bottles with NaOH in order to produce terephthalic acid. The effects of the initial amount of ethylene glycol, reaction temperature and time were considered.

Experimental Work

Materials

1. PET bottle waste, collected from different places in Baghdad, was used. Water bottles with thickness 0.4 mm and density is 1.18 g/cm³.

- Sodium hydroxide (NaOH): NaOH molecular weight 40 and purity of 99.8%. (RIEDELDEHAEN AG SEELZEHANNOVER Chem. rian, plozchen, DAB7, B.P.1968 M.Wt. 40)
- Ethylene glycol (C₂H₆O₂), BDH Chemicals Ltd.
- Sulfuric acid: H₂SO₄ of molecular weight of 98.07 and specific gravity of 1.84 was used.
- N, N-dimethylformamide (DMF): DMF (C₃H₇NO) of molecular weight 73.10 was used as purification agent because of its highly selective dissolver of terephthalic acid rather than by product of depolymerization reaction.
- Standard terephthalic acid: Terephthalic acid of 98.3 % purity was used as standard. The standard terephthalic acid is from Aldrich Chemical Co. Ltd.

Apparatus

The apparatus used in this study for depolymerization (saponification) reaction is shown in Figure 2. The batch scale system consists of the followings:

- 3 Necks flask (500 ml).
- Heat flat magnetic stirrer (Stuart CB302 / USA).
- Reflux Condenser (Germany), 37 cm.
- Mercury thermometer from zero to 250 °C.

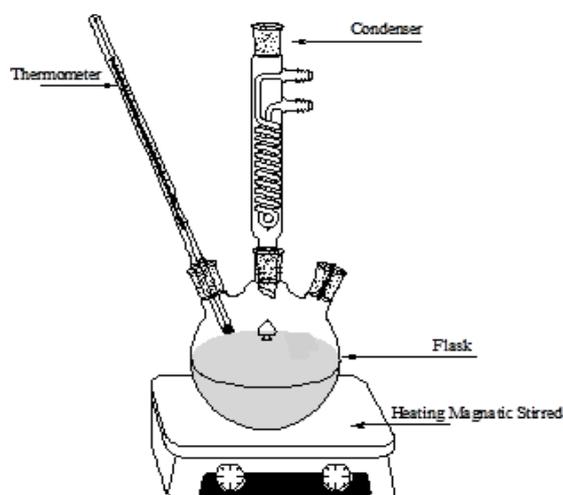


Fig.2, Schematic diagram of the reactor

Depolymerization of PET procedure

50 g of waste PET flakes of the dimension of about 5*5*0.4 mm, with 25 g of

NaOH (about 20% excess of the stoichiometric amount) and different amounts of ethylene glycol (200, 300 and 400 ml) were entered in a flask under atmospheric pressure. The mixture was heated to 70 to 170°C with stirring. A sample of the reaction mixture was used up (every 15 minutes) and pour directly in a 20 ml of distilled water of room temperature to stop the reaction, and the unreacted PET was filtered. Furthermore, a small amount of H₂SO₄ was added until neutralized to the filtrate, and the terephthalic acid (TPA) was precipitated.

Conversion of PET through reaction was calculated as:

$$PET, \text{ conversion}(x_{PET}) = \frac{\text{Initial PET weight} - \text{Filtered PET weight}}{\text{Initial PET weight}} \quad \dots 1$$

In order to purification of TPA, the precipitated amount of TPA was filtered and then dried in oven at 85 °C overnight to get rid of the moisture. The produced dry TPA was dissolved in DMF, the un-dissolved materials were removed by filtration and TPA is recovered by evaporation of DMF. The characterization tests of producing TPA were compared with those for standard TPA.

Testing methods

Final produce terephthalic acid sample was tested for:

- Melting point: according to ASTM D-127-05, the test was done in the Ministry of Industry and Minerals, General Commission for Research and Industrial Development, Chemical and Petrochemical Research Center.
- Acid number: according to ASTM D664-06, the test was done in the Ministry of Industry and Minerals, General Commission for Research and Industrial Development, Chemical and Petrochemical Research Center.
- Ash residue: according to ASTM D1951-86, the test was performed at the University of Baghdad, College of Engineering, Chemical Engineering Department.
- Infra-red (IR) analysis: IR-scan, with wavelength between 4000 and 400, for producing TPA was accomplished by IR-

spectrophotometer made by Shimadzu of model FTIR-8400S. This test was done in the Central Organization of Standardization and Quality Control.

Results and Discussion

Collection of PET bottles waste

PET bottles were collected from different places in Baghdad (Iraq), these places were 17 houses from different neighborhoods of the capital Baghdad, 1 kindergarten, and 1 coffee-shop. These places serve about 397 persons per day. The collection was done in different days in March and April, 2013.

Table 1 shows the classification and weight of the collected PET bottles, while Table 2 summarized the places, numbers of persons and the average collected waste bottles per days.

The average weight of PET waste per person (15.92 g) means 509.44 tons per day for Iraq (Iraq population is approximately 32 million persons). This huge amount of only one single type of plastics (PET) causes an environmental nightmare for any country. But when the filled half of the cup seen, this massive amount of PET plastic waste is considered a plenty sources for different chemicals production such as terephthalic acid.

The estimation results of PET waste amount in Iraq, about 5.8 kg per person yearly, is very close to the reported estimation values of Western Europe and Saudi Arabia [2, 3].

Table 1, Classification and weight of PET waste bottles collected in Baghdad per day

Bottle size	Houses	Kinder garden	Coffee-shop
0.3 L	23	70	-
0.5 L	55	46	-
0.6 L	68	15	208
1.0 L	5	-	-
1.5 L	24	1	34
Total No.	175	132	242
Weight, kg	2.104	1.050	3.165

Table 2, Numbers of PET waste bottles collected in Baghdad per day

Place	No. person	Avg. No. PET bottles	Weight, kg
Houses	93	175	2.104
Kindergarten	104	132	1.050
Coffee-shop	200*	242	3.165
Total weight, kg			6.319
Average PET waste per person, g			15.92

*Approximate average number of customers

Effect of EG on the PET conversion

The effect of EG on the PET depolymerization was intended at 90 minutes of reaction time and at different reaction temperatures: 70, 130 and 170 °C.

The results (Figure 3) show, that there is no significant effect of the EG on the conversion of PET through the depolymerization reaction.

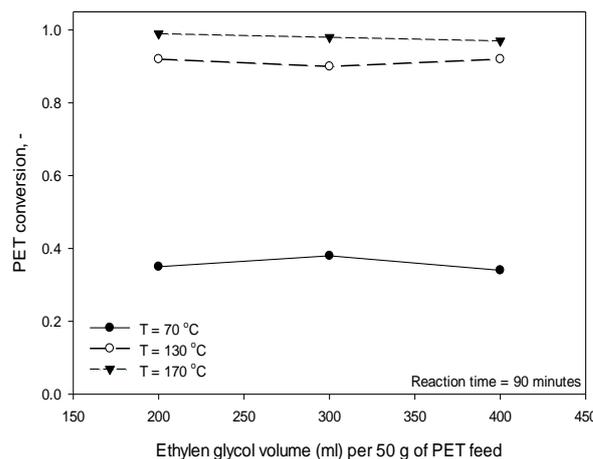


Fig.3, Effect of the ethylene glycol on PET conversion of different temperature and at 90 minutes reaction time

The addition more amount of produced material (EG) did not cause significant change in PET conversion or did not change the backward reaction or decreased the forward reaction of the depolymerization of PET. Thus, depolymerization reaction shown in Figure 1

can be considered as irreversible reaction. This result is in good agreement of Yusuke Asakuma et al. [6], and it's reinforced the next assumption of being the depolymerization reaction of PET irreversible reaction.

Effect of reaction temperature on the PET conversion

Figure 4 shows the effect of the depolymerization reaction time and reaction temperature on the conversion of PET.

As shown in Figure 4, the PET conversion increase with reaction temperature and reach the highest value (0.99) at 170 °C. While, the conversions at 70 °C were 0.04 during the first 15 minutes of reaction time and 0.35 after 90 minutes of reaction.

These results are in good agreement with those that extracted from Abbas et al. [9] which reported that the maximum yield of terephthalic acid (maximum conversion of PET) can be obtained at 170 °C. Yusuke Asakuma et al. [6], that pointed the conversion of PET through the depolymerization reaction about 10 % during the 90 minutes reaction time and at 70 °C temperature. While, Spaseska and Civkaroska [10] found that the above 90 TPA wt.% produced during 5 hours in temperature range 80 to 120 °C but with presence of trioctyl methyl ammonium bromide as a catalyst.

A marked increase in PET conversion appeared when the temperature increases to 110 °C and above. According to the collision theory [11], when temperature increases, it may cause an increase of molecular activity, and in the same time, the increasing of solubility of PET in EG and decreasing in viscosity of solution mixture. So the molecules have more energy to react and more probability to collisions together to accomplish the reaction.

As the solubility of PET increasing this means increasing of PET macromolecules which that can be easily attacked by the OH⁻ and then be depolymerized. After that, the produced terephthalate anion returns to the aqueous phase and form the di-sodium terephthalate salt with NA⁺ [12].

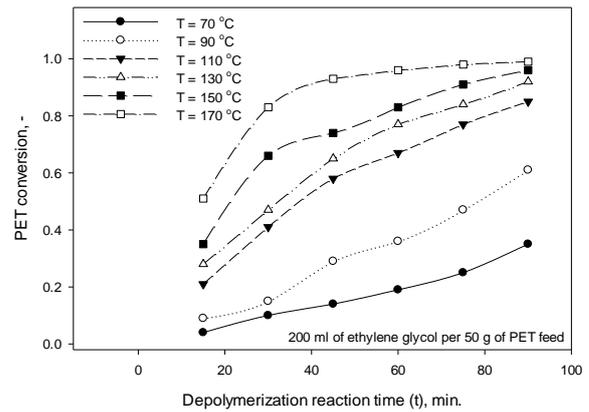


Fig.4, Effect of the depolymerization reaction time on the PET conversion of different temperatures and 200 ml of ethylene glycol per 50 g of PET feed

Kinetic model of PET depolymerization reaction

The kinetic of PET depolymerization was studied by assuming that the reaction is irreversible homogeneous first order according to PET.

The first order homogenous reaction kinetic model is [13]:

$$-r_{PET} = -\frac{dC_{PET}}{dt} = kC_{PET} \quad \dots 2$$

But:

$$C_{PET} = (C_{PET})_o (1 - x_{PET}) \quad \dots 3$$

$$(C_{PET})_o \frac{dx_{PET}}{dt} = k(C_{PET})_o (1 - x_{PET}) \quad \dots 4$$

The integration of Equation 4 gives the regular first order reaction model:

$$\ln \frac{1}{(1-x_{PET})} = kt \quad \dots 5$$

$$x_{PET} = 1 - e^{-kt} \quad \dots 6$$

And:

$$k = k_o e^{\left(\frac{-E}{RT}\right)} \quad \dots 7$$

A plot of $\ln \frac{1}{(1-x_{PET})}$ versus t , as shown in Figure 5, gives straight lines with zero intercepts and slopes equal to the reaction coefficients (k).

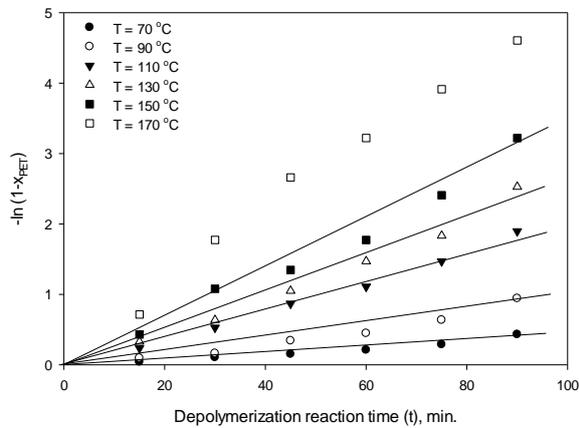


Fig.5, First order kinetic model of the PET depolymerization

The numerical values of depolymerization reaction coefficients versus temperature are summarized in Table 3.

Table 3, Values of the depolymerization reaction coefficients versus temperature

Temperature, °C	Temperature, K	k, min.
70	343	0.0041
90	363	0.0088
110	383	0.0198
130	403	0.0256
150	423	0.0330
170	443	0.0530

The activation energy of the reaction and frequency factor for the first order homogeneous depolymerization reaction are calculated according to the Arrhenius' equation (Eq. 7). The plot of $\ln(k)$ versus $\frac{1}{T}$ gives straight line with slope of $\left(\frac{-E}{R}\right)$ and intercept of the value if $\ln(k_o)$ this plot is called Arrhenius' plot.

Arrhenius' plot of depolymerization reaction are shown in Figure 6.

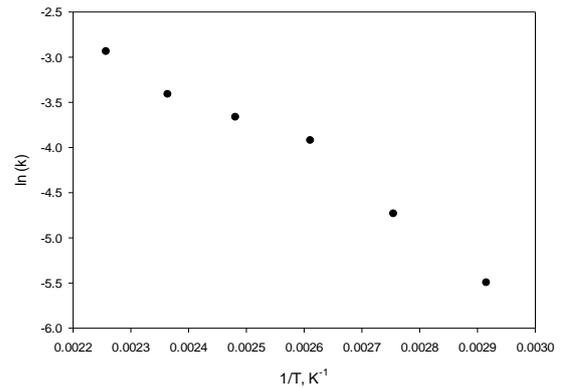


Fig.6, Arrhenius' plot of depolymerization reaction of PET

The value of the straight line slope of the Arrhenius' plot $\left(\frac{-E}{R}\right)$ equal to -3741.1 then the value of the activation energy of the depolymerization reaction of PET is 31103.5 J/mole, and the intercept value $\ln(k_o)$ is 5.5646 then the value of the frequency factor of the depolymerization reaction of PET k_o is 261.02 minutes.

The final reaction rate equation of the depolymerization reaction of PET with a 20% excess of the stoichiometric amount of NaOH and in the presence of ethylene glycol is:

$$-r_{PET} = -\frac{dC_{PET}}{dt} = 261.02e^{\left(\frac{-31103.5}{RT}\right)} C_{PET} \quad \dots 8$$

The found values of reaction coefficients are in the same magnitude of those obtained by Yusuke Asakuma et al. [6], but the calculated activation energy of the depolymerization reaction (31103.5 J/mole) differs from the reported value for the activation energy of depolymerization reaction in the presence of EG that about 115 kJ/mole. This difference due to the wide range of the temperature studied by the present work (70 to 170 °C) on the contrary of the study of Yusuke Asakuma et al. [6], whose studied the polymerization reaction of PET in presence of different alcohols, but in the narrow range of temperature (65 to 78 °C) for depolymerization reaction in presence of EG.

Predicted values calculated from the first order model of PET depolymerization (Eq. 5), which uses the found reaction rate coefficients (Table 3), and experimental data are shown in Figure 7.

Statistical analysis of the experimental data shows that the solution of the model (Eq. 6) is proportional to the experimental results. The statistical analyses are summarized in Table 4.

The statistical analyses promote that the depolymerization reaction of PET with EG behaves as homogeneous first order reaction with a high correlation coefficient (0.9872) and low standard deviation (0.0710) and standard error (0.0467) for 36 observations (no. of experiments).

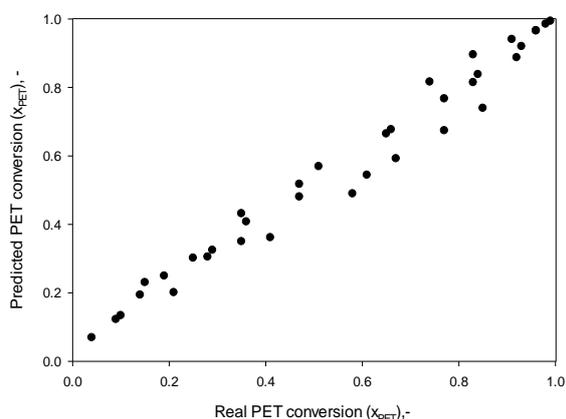


Fig.7, Experimental and predicted values of apparent rate constant by using suggested model of depolymerization of PET

Table 4, Statistical analysis of the depolymerization of PET model

Statistical analysis	Value
No. of observation	36
Correlation coefficient	0.9872
Standard error	0.0467
Standard deviation (S)	0.0710
Variance	0.0050
Confidence level	0.95

Characterization the produced TPA by PET depolymerization reaction

Depolymerization reaction of 50 g of PET with 20% stoichiometric excess of NaOH in the presence of 200 ml EG at 170 °C and 90 minutes was selected to produce TPA. The comparison of the other tested properties is shown in Table 4.

Table 5, Comparison of testing properties between producing and standard TPA

Test	pTPA	sTPA
Melting point, °C	306	304
Ash residue, ppm	13	10
Acid number, mg KOH/g	674	675

IR-spectrometer analysis shows identically of the produced terephthalic acid (pTPA) with the shows that the purity of the product sample is 97.9 % (after purification with DMF), while the standard terephthalic acid (sTPA) purity was 98.3 %.

Conclusion

1. The enormous quantity of PET plastic bottle waste (approximately 509.44 tons) throws away in Iraq daily.
2. Ethylene glycol did not effect on the conversion of PET through the depolymerization reaction with NaOH significantly.
3. Conversion of PET of about 99% can be reached by depolymerization of PET waste for 90 minutes at 170 °C.
4. The reaction of the PET depolymerization reaction was first order according to the PET.
5. The activation energy of the depolymerization reaction was 31103.5 J/mole with 261.02 minutes as the value of frequency factor.
6. The statistical analyses strengthened that the depolymerization reaction of PET with EG behaves as homogeneous first order reaction.
7. The purity of the produced TPA was 97.9 %.

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