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Original Research Article

Alkaline Solvolysis of Poly(ethylene terephthalate) in Butan–1–ol Media: Kinetics and Optimization studies

5 ABSTRACT

6 This study was carried out to examine the thermo-chemical decomposition of postconsumer poly(ethylene 7 terephthalate) (PET) in alkaline solution of butan-1-ol. The effect of various process parameters such as 8 reactor temperature, time and sodium hydroxide concentration on the degree of PET degradation and 9 products yield were studied and it was found that the decomposition of PET was essentially complete in 10 an hour, with terephthalic acid and ethylene glycol being the main products. A kinetic study of the 11 process showed that the alkaline solvolysis of PET is a second order reaction.

12 1. Introduction

13 Poly(ethylene terephthalate) (PET) is a linear thermoplastic, bluish-white resin made from terephthalic acid and ethylene glycol through poly-condensation (Aguado et al., 1999). It is an indispensable material 14 owing to its low cost (Thompson et al., 2009), excellent tensile strength, chemical resistance, clarity, 15 processability, and reasonable thermal stability (Caldicott, 1999). It is mainly applied in the textile 16 17 industry, where more than 60% of the entire PET produced worldwide is consumed. Enormous amounts 18 are also used for other applications including manufacture of video and audio tapes, X-ray films, thermoformed products and food packaging (Carraher, 2000; ILSI, 2000; Olabisi, 1997). In food 19 20 packaging, PET has become the choice especially for beverages mainly due to its glass-like transparency coupled with adequate gas barrier properties for retention of carbonation. It provides an excellent barrier 21 against oxygen and carbon dioxide in the carbonated soft drink sector, which has been growing more 22 23 rapidly than other applications. In addition, it exhibits a high toughness/weight property ratio, which 24 allows lightweight and securely unbreakable containers with large capacity (Welle, 2011).

25 Combining the relative simplicity of the polymerization process with the durable mechanical properties of PET, industries throughout the world have used PET as the staple polymer for beverage packaging. Along 26 27 with this widespread use of PET is the inevitable creation of large amounts of post-consumer PET waste 28 due to its increasing consumption rate and non-biodegradability, thus creating serious environmental concerns. PET does not have any side effects on the human body, and does not create a direct hazard to 29 the environment. However, due to its substantial fraction by volume in the waste stream and its high 30 resistance to the atmospheric and biological agents, it is considered as a noxious material (Paszun and 31 Spychaj, 1997). With the increase in the amount of PET wastes, its disposal began to pose serious 32 33 economical and environmental problems. The recycling of PET does not only serve as a partial solution to the solid waste problem but also contributes to the conservation of raw petrochemical products and 34 35 energy. Products made from recycled plastics can result in 50-60% capital saving as compared to making 36 the same product from virgin resin (Sinha et al., 2008).

37 Recycling is assumed to be one of the best approaches to solve the problems of PET wasted accumulation. Various methods such as primary recycling (Hopewell et al., 2009; Al-Salem et al., 2009), 38 39 mechanical recycling (Aguado and Serrano, 1999; Bartolome et al., 2012) and chemical recycling (Campanelli et al., 1993; Yoshioka et al., 2003; Hopewell et al., 2009; IPTS 2012) have been considered 40 41 to recycle the PET. Among the various methods of PET recycling, only chemical recycling conforms to 42 the principles of sustainable development because it has potentials for yielding the raw materials from which PET is originally made. However, the various chemical recycling routes reported in various works 43 (such as hydrolysis, alcoholysis and aminolysis) are fraught with shortcomings such as the need for high 44 pressure and corrosion resistant equipment (Genta et al., 2007), high temperature (Campanelli et al., 45 1993), and long reaction times (Yoshioka et al., 2003). Taking into account the cost and energy 46 47 consumption, chemical reclamation methods are the most effective recycling methods for PET. Alkaline

solvolysis was chosen for this study because it operates under less hazardous conditions, effectively
eliminating the need for corrosion resistant pressure vessels (since it can be carried out at atmospheric
pressure).

- 51 Preliminary studies on the alkaline solvolysis of postconsumer PET in methanol or ethanol media showed
- 52 that it is possible to decompose PET according to the reaction mechanisms shown below (Sanda *et al.*,
- 53 2012; Sanda *et al.*, 2016):
- 54 **Step 1**: The long polyester chain in PET is broken down using a suitable alcohol. This yields the corresponding dialkyl terephthalate and ethylene glycol:

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- 57 This step is the alcoholysis step, similar to the methanolysis process reported by Kondo and Genta (2001)
- 58 Step 2: The dialkyl terephthalate from the alcoholysis step reacts with an alkali such as sodium hydroxide
- 59 (NaOH) to yield the corresponding salt:

- Step 3: The sodium salt can be broken down to yield terephthalic acid and the corresponding salt of the
 alkali used using a mineral acid:
 - Na-O-C-O-C-O-Na + 2HX \rightarrow H-O-C O-C-O-H + 2NaX Terephthalic acid

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64 where HX is a monobasic acid such as HCl or $HNO_{3.}$

The aim of this study is to explore the applicability of a higher molecular weight primary alcohol such as butan–1–ol for the alkaline solvolysis of PET with a view to examining the effects of various parameters

- 57 such as process temperature, reaction time and alkali dosage on the process. The study also examined the
- various products formed in the decomposition process and proposes reaction mechanisms where possible.

69 2. Experimental

70 **2.1.** Materials

- Postconsumer PET bottles used for the study were sourced from restaurants, fast foods outlets and hotels
 in Ile-Ife, Nigeria. Butan-1-ol (Lobachemie), sodium hydroxide (J. T. Baker) and pyridine (Merck
 Millipore) were obtained from reputable chemical stores in Lagos, Nigeria. All reagents were used asreceived.
- The PET bottles collected were shredded after separating from the non-PET components such as labels and caps. The shredded PET pieces were washed and dried in an oven at 110 °C for 4 h and after drying,
- 77 stored in airtight plastic containers prior use.

78 2.2 Alkaline Solvolysis of PET

- 79 For each run, about 5 g of PET flakes was placed in a two-neck 500 cm³ flask with 100 cm³ of 40 g.dm³ 80 sodium hydroxide in butan-1-ol. The flask was dipped in a thermostatic oil bath with the temperature of the bath maintained between 120 and 150 °C. The mixture was heated for 10-60 min under reflux and at 81 82 the end of each run, 100 cm³ of distilled water was added to dissolve the solid products. The mixture was 83 then filtered through a Whatman No. 1 filter paper to separate the unreacted PET from the mother liquor and the residue was washed with additional 50 cm³ of distilled water. Terephthalic acid (TPA) was 84 precipitated from the filtrate by the addition of 1 mol.dm⁻³ hydrochloric acid and removed with a 85 Whatman No. 1 filter paper. The unreacted PET and the TPA produced were dried in an oven for 2 h at 86 87 105 °C and weighed. The percent decomposition of PET was determined by gravimetry using the 88 expression below:
 - % Decomposition of PET = $\left(\frac{W_o W_f}{W_o}\right) \times 100$ (1)
- 90 where W_o is the initial mass of PET flakes and W_f represents the mass of unreacted PET at the end of 91 experiment. The terephthalic acid yield is given by:

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$$TPA \text{ yield} = \frac{\text{mass of terephthalic acid produced}}{\text{mass of PET fed into the reactor}}$$
(2)

93 In order to optimize the alkaline solvolysis process, a three-level-three factor Box-Behnken design was 94 employed for this study, with 15 experimental runs per alcohol. The factors investigated in this study 95 were temperature (°C), reaction time (min) and alkali concentration (g.dm⁻³). The coded and uncoded 96 levels of the independent factors are shown in Table 1.

The response for each alcohol was evaluated using Minitab statistical software (version 16.1.1) and fitted 97 98 to the quadratic model below:

 $Y = \delta_0 + \delta_1 X_1 + \delta_2 X_2 + \delta_3 X_3 + \delta_{12} X_1 X_2 + \delta_{13} X_1 X_3 + \delta_{23} X_2 X_3 + \delta_{11} X_1^2 + \delta_{22} X_2^2 + \delta_{33} X_3^2$ (3) 99 Where Y is the predicted response (% PET decomposition or TPA yield), δ_o is the intercept term, δ_1 , δ_2 , 100 δ_3 are the linear coefficients, δ_{12} , δ_{13} , δ_{23} are the interactive coefficients and δ_{11} , δ_{22} , δ_{33} are the 101 quadratic coefficients. In addition, the terms X1, X2 and X3 are the coded factors, which are related to the 102 actual factors x_1 , x_2 and x_3 in Table 1 by equation (4): 103

$$X_i = \frac{x_i - x_o}{\Delta x}$$
(4)

105 where:

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 X_i = coded value for the *i*th input (that is, X_i),

107 $x_{\rm o} =$ mid value for the experimental design, and

108 $\Delta x = (x_{high} - x_o) = (x_o - x_{low}).$

The terms X_{high} and X_{low} represent the chosen upper and lower design limits, respectively. Table 1: Coded and uncoded levels of variables for the RSM Box–Behnken design. 109

Variable	Symbol	Coded factor levels		
Variable	Symbol	-1	0	+1
Oil bath Temperature (°C)	x_I	120	135	150
Time (min)	x_2	15	37.5	60
[NaOH] <mark>(g.dm⁻³)</mark>	<i>x</i> ₃	10	30	50

111 2.3. Acid value determination

About 1 g of the crude terephthalic acid obtained from each of the alkaline solvolysis runs was accurately 112 weighed into a 100 cm³ beaker containing 25 cm³ of pyridine. The mixture was stirred till the sample 113 completely dissolved, after which 25 cm³ of water and 2 - 3 drops of phenolphthalein indicator were 114 added. The solution was titrated against 0.5 mol.dm^{-3} potassium hydroxide solution till a permanent pink 115 end point was obtained. A blank determination was also carried out, excluding the sample. The acid value 116 was determined from the formula: 117

$$AV (mg KOH/g) = \frac{56.1 \times M \times (V_s - V_B)}{m}$$
(5)

Where M is the molarity of the KOH solution ($mol.dm^{-3}$), V_s and V_B are the titre values of sample and 119 blank, respectively, and w (g) is the mass of sample taken for test. 120

121 **Instrumental analysis** 2.4.

Differential thermal analysis of the solid product was carried out on a Netzsch Diffential Thermal 122 Analyzer (Model DTA 404 PC Eos) at a heating rate of 10 °C/min. Infrared spectroscopy was carried out 123 on a Thermo Nicolet iS5 FT-IR equipped with iD3 Attenuated Total Reflectance (ATR) accessory and 124 125 Omnic FTIR software for spectra processing and analysis.

The analysis of the liquid products was done on an Agilent 6890/5973 GCMS System with 5% phenyl 126 127 methyl siloxane capillary column. Helium was used as the carrier gas at a flow rate of 1.5 ml/min. The oven temperature was programmed as follows: 35 °C for 5 min, then 4 °C/min to 150 °C for 2 min, and 128 finally at 20 °C/min to 250 °C for 5 min. The quadrupole temperature was set at 150°C. Methanol was 129 130 used as solvent.

Results and Discussion 131 3.

PET depolymerization kinetics 132 3.1.

The overall chemical equation for the alkaline solvolysis of PET to yield disodium terephthalate 133 134 (Na_2TPA) and ethylene glycol (EG) may be written as shown:

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$$PET + 2NaOH \xrightarrow{butan-1-ol} Na_2TPA + EG$$
(6)

The kinetics of PET depolymerization in alkaline butan-1-ol was studied by assuming that the reaction is
 irreversible homogeneous second order with respect to PET and NaOH. The second order homogeneous

reaction kinetic model is given by (Lopez-Fonseca *et al*, 2008):

$$-\frac{ac_{PET}}{dt} = kC_{PET}C_{NaOH} \tag{7}$$

where C_{PET} and C_{NaOH} represent the quantity of PET and NaOH present per unit volume of the reaction mixture at any given time, respectively.

142 If the initial amount of PET is given to be $(C_{PET})_o$, then it can be said that:

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$$C_{PET} = (C_{PET})_o (1 - X_{PET})$$

144 where X_{PET} is the fractional conversion of PET, which is given by:

$$X_{PET} = \frac{W_o - W_f}{W_o} \tag{9}$$

146 where W_o and W_f are the initial and final masses of the PET samples, respectively.

147 Equation (7) can be written for the chemical reaction in (6) as:

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$$\frac{dX_{PET}}{dt} = k(C_{PET})_o (1 - X_{PET})(M - 2X_{PET})$$
(10)

where M is the initial NaOH to PET molar ratio. If it is assumed that the volume of the reaction mixture isconstant, the integration of equation (10) gives:

$$\left(\frac{1}{M-2}\right)\ln\left[\frac{M-2X_{PET}}{M(1-X_{PET})}\right] = k(\mathcal{C}_{PET})_{o}t$$
(11)

152 where k is the rate constant.

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The PET dissolution kinetics plots are presented in Figure 1 with the initial mass of PET and the initial concentration of sodium hydroxide kept constant at 5 g and 40 g.dm⁻³, respectively (NaOH:PET molar ratio, M = 3.84) while the temperature of the oil bath was varied from 120 - 150 °C (393 – 423 K).

156 A plot of $\left(\frac{1}{M-2}\right) \ln \left[\frac{M-2X_{PET}}{M(1-X_{PET})}\right]$ against t gives straight lines with zero intercepts as shown in Figure 2 157 while the numerical values of depolymerization rate constants at different oil bath temperatures are

presented in Table 2. Each of the plots was found to fit the kinetic model presented in equation (11) with P^2 values of 0.08, or better

159 R^2 values of 0.98, or better.



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(8)

Figure 1 Alkaline Solvolysis of PET in 40 g.dm⁻³ NaOH in Butan-1-ol at different oil bath
 temperatures

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 Table 2:
 Kinetic Data Obtained for the alkaline solvolysis of PET

Temperature of Oil bath, T (K)	Apparent rate constant, k(C _{PET}) _o (min ⁻¹) × 10 ³	R² value
393	12.1	0.9904
408	18.9	0.9962
413	23.3	0.9987
423	36.7	0.9808

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172 3.2. Analysis of PET alkaline solvolysis products

From the theory of PET alkaline solvolysis, the expected primary product is terephthalic acid. For each
experimental run, a white powder was obtained and this was subjected to various physical and chemical
tests.

176 3.2.1. Acid value

The acid values of the solid products obtained from the alkaline solvolysis of PET in the alcoholic media
under the different conditions studied gave an average of 670.6 mg KOH/g for the butan-1-ol media.
Comparing this average value with the theoretical acid number of TPA (that is, 675 mgKOH/g), it can be

180 said that the observed variations might have been a result of impurities and other reaction perturbations.

181 3.2.2. FTIR analysis

182 The FTIR spectrum of the product obtained from the decomposition of PET using 40 g.dm³ NaOH in the

alcohol is shown in Figure 3. A look at the IR spectra indicated that each product is a *p*-substituted

aromatic compound, considering the absorption bands at 1600 and 1420 cm⁻¹ (-C-C- stretch for aromatic

185 compounds), and the sharp absorption band around 750 cm⁻¹. The very broad –OH band occurring

- between 3000 and 3500 cm⁻¹, and the -C=O band around 1700 cm⁻¹ is an indication that the product is a carboxylic acid. The IR spectrum for terephthalic acid is shown in Figure 4 for comparison.
- 188 3.2.3. Thermal analysis of the solid products
- 189 The DTA scans for the solid product obtained from the alkaline solvolysis runs show that its melting
- 190 point is above 380 °C (Figure 5). The melting point of terephthalic acid is between 300 and 402 °C, while
- 191 that of PET is around 260 °C (Venkatachalam et al., 2012). Since the thermograph in Figure 5 does not
- 192 show any endothermic peak around 260 °C, it can be concluded that solid product is different from PET.
- 193 In addition, the high melting points are close to that of terephthalic acid. However, the appearance of
- 194 additional endothermic peaks at 122.1, 210.8 and 297 °C suggests the formation of other products other 195 than terephthalic acid.





cm⁻¹





Figure 5: DTA Thermograph for the solid Product

3.3. PET Solvolytic Decomposition study Using Response Surface Methodology

The relationship between the responses (% decomposition of PET and terephthalic acid yield) and three independent variables (reaction time, temperature and alkali concentration) were studied in order to optimize the alkaline solvolysis of PET. The design matrix in actual terms and the experimental results of RSM are presented in Table 3. The experimental data were fitted to Equation (3) to obtain mathematical regression quadratic models for the relationship between the responses (% decomposition of PET and TPA yield) and the experimental factors:

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$$\begin{split} Y_{\text{PET}} &= 89.067 + 2.425 X_1 + 7.075 X_2 + 19.550 X_3 - 5.058 X_1^2 - 4.158 X_2^2 - 12.008 X_3^2 + \\ &\quad 1.350 X_1 X_2 + 4.100 X_1 X_3 - 2.700 X_2 X_3 \qquad (R^2 = 0.9902) \quad \textbf{(12)} \\ Y_{\text{TPA}} &= 0.73925 + 0.02013 X_1 + 0.05872 X_2 + 0.16226 X_3 - 0.04198 X_1^2 - 0.03451 X_2^2 - \\ &\quad 0.09967 X_3^2 + 0.01120 X_1 X_2 + 0.03403 X_1 X_3 - 0.02241 X_2 X_3 \quad (R^2 = 0.9900) \quad \textbf{(13)} \end{split}$$

where Y_{PET} and Y_{TPA} represent the percentage decomposition of PET and TPA yield, respectively. 213 214 ANOVA for studying the significance of fit from the quadratic equations for the experimental data is shown in Tables 4 and 5, with P-values lower than 0.05 indicating significant model terms. In addition, 215 the lack-of-fit for the model is insignificant with a P-value of 0.846 for PET decomposition and 0.844 for 216 217 TPA yield, indicating that the models are suitable for fitting the experimental data. The quadratic models 218 are significant (P < 0.001), accounting for over 98 % of the observations. The extent of PET decomposition depends on the process temperature and the concentration of NaOH for the alcohol 219 220 studied.

	Temperature	Time	[NaOH],	% Decom	position of PET	TPA yield	l (g/g PET)
Run	(°C)	(min)	g/L	Actual	Predicted	Actual	Predicted
1	120	15	30	70.6	71.70	0.586	0.595
2	150	15	30	72.6	73.85	0.603	0.613
3	120	60	30	84.4	83.15	0.701	0.690
4	150	60	30	91.8	90.70	0.762	0.753
5	120	37.5	10	54.4	54.12	0.452	0.449

221 Table 3: Actual and Predicted Responses for the Alkaline Solvolysis of PET in Butan-1-ol Media

6	150	37.5	10	51.2	50.77	0.425	0.421
7	120	37.5	50	84.6	85.03	0.702	0.706
8	150	37.5	50	97.8	98.08	0.812	0.814
9	135	15	10	44.4	43.57	0.369	0.362
10	135	60	10	61.6	63.13	0.511	0.524
11	135	15	50	89.6	88.08	0.744	0.731
12	135	60	50	96.0	96.83	0.797	0.804
13	135	37.5	30	84.6	89.07	0.702	0.739
14	135	37.5	30	91.4	89.07	0.759	0.739
15	135	37.5	30	91.2	89.07	0.757	0.739

Table 4: ANOVA for the Response Model for the % PET Decomposition in Butan-1-ol Media

Source	Df^{a}	SS ^b	MS^{c}	F	Р
Model	9	4236.98	470.78	56.02	< 0.001
Temperature ($^{\circ}$ C) (X ₁)	1	47.04	47.04	5.60	0.064
Time $(\min)(X_2)$	1	400.44	400.44	47.65	0.001
[NaOH], g/L (X ₃)	1	3057.62	3057.62	363.86	< 0.001
X_1^2	1	94.47	94.47	11.24	0.020
${X_2}^2$	1	63.85	63.85	7.60	0.040
X_3^2	1	532.43	532.43	63.36	0.001
X_1X_2	1	7.29	7.29	0.87	0.394
X_1X_3	1	67.24	67.24	8.00	0.037
X_2X_3	1	29.16	29.16	3.47	0.122
Lack of fit	2	12.07	4.02	0.27	0.846
Pure error	3	29.95	14.97		
Total	14				
a: Degrees of freedom b: Sa	um of squares	<i>C</i> : <i>1</i>	Mean squares		

Table 5: ANOVA for the Response Model for TPA yield

Source	\mathbf{Df}^{a}	$\mathbf{SS}^{\ b}$	MS ^c	F	Р
Model	9	0.2917	0.0324	54.98	< 0.001
Temperature ($^{\circ}$ C) (X ₁)	1	0.0032	0.0032	5.50	0.066
Time (min) (X_2)	1	0.0275	0.0275	46.63	0.001
[NaOH], g/L (X ₃)	1	0.2106	0.2106	357.20	< 0.001
X_1^2	1	0.0039	0.0065	11.00	0.021
X_2^2	1	0.0027	0.0044	7.42	0.042
X_3^2	1	0.0367	0.0367	62.21	0.001
X_1X_2	1	0.0005	0.0005	0.82	0.406
X_1X_3	1	0.0047	0.0047	7.96	0.037
X_2X_3	1	0.0020	0.0020	3.36	0.126
Lack of fit	3	0.0009	0.0003	0.27	0.844
Pure error	2	0.0021	0.0010		
Total	14				

a: Degrees of freedom b: Sum of squares c: Mean squares

- 231 The response surface 3D and contour plots for PET decomposition in relation to temperature, sodium
- hydroxide concentration and reaction time are illustrated in Figures 6 and 7, with sodium hydroxide
- concentration, time and temperature kept at their mid-point levels in (a), (b) and (c), respectively. From
- the studies, it was found that temperature and alkali concentration play an important role in the alkalinesolvolysis of PET in butan-1-ol media.
 - The optimum PET decomposition and terephthalic acid yield for the conditions under study were found
 - to be 99.85 % and 0.8289 g TPA/g PET, respectively for an optimum temperature, NaOH concentration
 - and reaction time of 139.1 °C, 45.13 g.dm⁻³ and 50.71 min, respectively as shown by the Minitab 16
 - 239 Optimization plots in Figure 8.

240 **3.4.** Analysis of the liquid product by gas chromatography

The chromatograph for the filtrate obtained from the solvolysis run is shown in Figure 9. From the theory of the alkaline solvolysis process, the liquid phase obtained at the end of each run is expected to contain ethylene glycol and the alcohol used. Most of the compounds identified from the chromatograph are actually presented in form of combinations of the actual compounds of interest due to the conditions specified for the analyses (up to 300 °C).



Figure 6: Response surface 3D plot for % decomposition of PET.



Figure 7: Response surface contour plot for % decomposition of PET.





Figure 9: Gas chromatograph for the filtrate obtained from the alkaline solvolysis of PET in butan-1-ol
media

The gas chromatograph for the liquid product obtained from the alkaline solvolysis run shows that in addition to ethylene glycol, various products were formed as a result of series of chemical reactions such as chain elongation, formation of glycol ethers or rearrangement reactions (Table 6). Since the reactions

were carried in the presence of air, there is a possibility of the partial oxidation of butan-1-ol to give butanal, which further combined with butan-1-ol to give 1,1-dibutoxy butane according to the reactions below:

$$CH_3 CH_2 CH_2 CH_2 OH \xrightarrow{[0]} CH_3 CH_2 CH_2 CH0$$
(I)

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$$2 CH_3 CH_2 CH_2 CH_2 OH + CH_3 CH_2 CH_2 CH0 \rightarrow CH_3 CH_2 CH_2 CH_2 - O - \begin{matrix} | \\ C - O - CH_2 CH_2 CH_2 CH_3 + \\ | \\ CH_2 CH_2 CH_3 \end{matrix}$$
262
$$H_2 O \quad (II)$$

The reaction (II) would normally occur in the presence of an anhydrous acid such as hydrogen chloride (Morrison and Boyd, 1993) which probably came from the acid used in precipitating the terephthalic acid. Some of the compounds (for example, butoxy-2,4-dimethyl-1-pentene and 2-Ethylnon-1-en-3-ol) are likely to be from the decomposition of a terephthalate.

Peak no	Identified component	RT (min)	Peak Area%
1	2-Methyl-1-butanol	12.824	8.16
2	Butyl acetate	13.783	4.74
3	2-Butoxyethanol	14.749	1.29
4	2-Ethyl-1-hexanol	17.718	1.41
5	(E)-Nonen-1-ol	18.307	1.56
6	1-Butoxy-1-isobutoxy-butane	21.795	4.96
8	2-Oxooctanoic acid	22.439	1.85
7	1,1-Diisobutoxy-isobutane	23.280	7.67
9	1,1-Dibutoxy-butane	24.827	30.44
10	2-Hydroxy-tetradecanoic acid	27.396	2.01
12	Butoxy-2,4-dimethyl-1-pentene	29.941	2.53
11	2-Ethylnon-1-en-3-ol	31.819	6.90

267 Table 6: Some of the identified components in the filtrate

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269 4. Conclusion

This study has shown that alkaline solvolysis of PET is a simple and effective thermo-chemical route for processing postconsumer PET into value added products. The rate of decomposition of PET depends on the concentration of alkali, process time and temperature, with a predicted optimum conversion of over 99 % within an hour. Chemical analyses showed that the solid products obtained have properties similar to those of terephthalic acid while the liquid products contain ethylene glycol in addition to the solvent used, along with various products of side reactions, implying that postconsumer PET can be a good source of terephthalic acid, ethylene glycol and other value-added products.

277 References

278 Aguado J. and Serrano D.P. (1999) Feedstock Recycling of Plastic Wastes. Clark J. H, ed., The Royal

279 Society of Chemistry, Cambridge

Al-Salem S. M., Lettieri P. and Baeyens J. (2009) Recycling and recovery routes of plastic solid waste

281 (PSW): A review. *Waste Management*, 29: 2625 – 2643

- 282 Bartolome L, Imran M, Cho B. G., Al-Masry W. A. and Kim D. H. (2012) Recent Developments in the
- Chemical Recycling of PET, Material Recycling Trends and Perspectives, Dr. Dimitris Achilias (Ed.),
 ISBN: 978-953-51-0327-1, InTech, Available from:<u>http://www.intechopen.com/books/material-</u>
- 285 recycling-trends-andperspectives/recent developments-in-the-chemical-recycling-of-pet
- Caldicott, R. (1999). The Basics of Stretch Blow Molding PET Containers. *Plastics Engineering*, 55(1):
 35–40
- 288 Campanelli J. R., Kamal M. R. and Cooper D. G. A. (1993) Kinetic Study of the Hydrolytic Degradation
- of Polyethylene Terephthalate at High Temperatures. *Journal of Applied Polymer Science*, 48: 443 451
- 290 Carraher, C. (2000). Polymer Chemistry, (5th Ed), Marcel Dekker, New York
- Genta M, Iwaya T, Sasaki M, and Goto M. (2007) Supercritical methanol for polyethylene terephthalate
 depolymerization: Observation using simulator. *Waste Management*, 27(9): 1167-1177
- Hopewell, J., Dvorak, R. and Kosior, E (2009). Plastics recycling: challenges and opportunities.
 Philosophical Transactions of the Royal Society B, 364: 2115 2126
- 295 ILSI (2000) Packaging Materials: 1. Polyethylene Terephthalate (PET) for Food Packaging 296 Applications, Europe Report Series, ISLI Press, Brussels
- IPTS (2012) End-of-waste criteria for waste plastic for conversion. IPTS Second working document,
 Seville, Spain.
- 299 Lopez-Fonseca R., Gonzalez-Marcos M. P., Gonzalez-Velasco J. R. and Gutierrez-Ortiz J. I. (2008)
- 300 Chemical recycling of PET by alkaline hydrolysis in the presence of quaternary phosphonium and
- ammonium salts as phase transfer catalysts. WIT Transactions on Ecology and the Environment, 109:
 511–520
- 303 Morrison R. T. and Boyd R. N. (1993) Organic chemistry, 6 ed. Prentice Hall Publishers, NY.
- 304 Olabisi, O. (1997). Handbook of Thermoplastics, Marcel Dekker, New York
- Paszun, D. and Spychaj, T. (1997) Chemical Recycling of Poly(ethylene terephthalate). *Industrial and Engineering Chemistry Research*, 36(4): 1373–1383
- Ravens D. A. S. (1961) The Chemical Reactivity of Poly(ethylene terephthalate): Heterogeneous
 Hydrolysis by Hydrochloric Acid. *Polymer (London)* 1, 375 383
- 309 Sanda O., Taiwo E. A. and Osinkolu G. A. (2012) Decomposition of Postconsumer PET Waste in
- Ethanolic NaOH. Proceedings of Faculty of Technology Conference (OAUTEKCONF 2012), Obafemi
 Awolowo University, Ile Ife, Nigeria. pp 1 4
- 312 Sanda O., Taiwo E. A., Akinrinsola M. G. and Osinkolu G. A. (2016) A Study of the Alkaline Solvolysis
- of Postconsumer Polyethylene Terephthalate in Primary $C_1 C_3$ Aliphatic Alcohols. *American Chemical* Science Journal, 16(1): 1-14
- Sinha, V., Patel, M., and Patel, J. (2008). PET waste management by chemical recycling: A review.
 Journal of Polymer and the Environment, 18(1): 8 25
- Thompson, R., Swan, S., Moore, C., and vom Saal, F. (2009). Our plastic age. *Philosophical*
- 318 *Transactions of the Royal Society B*, 364(1526): 1973–1976
- 319 Venkatachalam S., Nayak S. G., Labde J. V., Gharal P. R., Rao K. and Kelkar A. K. (2012) Degradation and
- Recyclability of Poly (Ethylene Terephthalate). Accessed 03 February, 2016. Available:
 http://cdn.intechopen.com/pdfs/39405/InTech-Degradation and recyclability of poly ethylene terephthalate .pdf.
- 322
- Welle, F. (2011). Twenty years of PET bottle to bottle recycling—An overview. *Resources, Conservation and Recycling*, 55(11): 865–875
- 325 Yoshioka, T., Ota, M., and Okuwaki, A. (2003). Conversion of a Used Poly(ethylene terephthalate) Bottle
- 326 into Oxalic Acid and Terephthalic Acid by Oxygen Oxidation in Alkaline Solutions at Elevated
- 327 Temperatures. Industrial and Engineering Chemistry Research, 42(4): 675-679
- 328 Yoshioka T, Okayama N. and Okuwaki A. (1998) Kinetics of hydrolysis of PET powder in nitric acid by
- a modified shrinking-core model, *Industrial and Engineering Chemistry Research*, 37: 336–340