



Catalytic Depolymerization and Kinetics of Poly(ethylene terephthalate) by Saponification

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ABSTRACT

Conductometric measurement technique has been deployed to study kinetic of depolymerization of Poly(ethylene terephthalate) and NaOH using cobalt acetate and manganese acetate catalyst. Chemical kinetic of this reaction shows second order kinetics. The specific reaction rate without catalyst is $2.88 \times 10^{-3} \text{g}^{-1} \text{s}^{-1}$ at 70°C. Specific reaction rates were determined at various temperatures ranging from 50°C to 80°C. From the data, Arrhenius constant, energy of activation were determined and found to be $5.0 \times 10^5 \text{min}^{-1}$ and 54.2KJg^{-1} respectively. Similarly the activation parameters were determined using cobalt acetate and manganese acetate as catalyst.

Key word: Kinetics, catalysis, saponification, conductometry, PET waste.

INTRODUCTION

Number of methods of recycling of PET are available in the literature¹⁻⁴. For PET saponification much research has been carried out in acidic environment. Pusztašeri⁵ studied saponification in sulphuric acid. Sato and Yoshiaka⁶ also studied saponification under acidic conditions. Alcoholysis has been carried out by different workers⁷⁻¹³. Acid, alkali and water saponification of PET in organic solvent have been reported by several workers¹⁴⁻¹⁸.

In present work, alkali saponification of PET waste powder is under taken using cobalt acetate and manganese acetate as a catalyst. A rapid online conductivity measurement are carried out to study the kinetics. In the kinetic study, specific reaction rates were determined with and without catalyst. The energy of activation, Arrhenius constant were determined for saponification of PET waste powder.

EXPERIMENTAL

All chemical used in the present work were of analytic reagent grade. The solution of sodium hydroxide was prepared using conductivity water. PET waste bottles were procured from local corporation area of Nagpur, Maharashtra, India. The bottles were washed with Teepol and then with double distilled water. All the bottles were dried with hot air blower. The dried bottles were chilled to increase its brittleness, then crushed, ground and sieved into different particle sizes ranging from 100 μ m to 800 μ m.

The optimum parameters for saponification of PET waste powder were determined by gravimetric measurement of product terephthalic acid (TPA). All kinetics measurements were carried at optimum parameters (Table 1). In kinetic measurements, three vertical neck round bottom flask was fixed with refluxed water condenser, an internal digital temperature measurement probe, a conductivity measuring cell and a micro-controller based vertical type stirrer. A digital conductivity monitoring instrument made of Equiptronic India Ltd. was used to measure conductivity. High precision thermostat and digital temperature measurement probe was used in the present work.

In kinetic experiment, 10g PET waste powder (100 μ m) and 3 ml pyridine was added into reaction flask placed in the thermostat. Conductivity cell and tip of temperature measurement probe was adjusted so that they are not struck by vertical stirrer bar. 7g of sodium hydroxide in 100ml of water was added to PET waste powder containing pyridine. Immediately stop-watch was started and conductivity measured at various time intervals up to 150 min. From specific conductivity of water

(C_w), specific conductivity of reaction mixture at various time (C_t), specific conductivity at zero time (C_0) and specific conductivity at infinity (C_∞), the values of $(C_0 - C_t)/(C_t - C_\infty)$ were determined at various time interval. From plot of $C_0 - C_t/C_t - C_\infty$ versus time, specific reaction rate were determined.

In order to evaluate kinetic and thermodynamic parameters, specific reaction rate determinations, in presence and absence of catalyst were determined at various temperatures ranging from 50°C to 80°C. From results, energy of activation, frequency factor were evaluated.

RESULTS AND DISCUSSION

Specific conductivity of unreacted sodium hydroxide solution in the reaction system at various intervals of time were determined. A plot of $C_0 - C_t/C_t - C_\infty$ versus time is plotted and found to be linear. It indicates the second order nature of this saponification reaction. The slope of the plot gives the specific reaction rate, k_2 (Table 2 and Fig. 1). The variation of specific reaction rate, k_2 , with the amount of sodium hydroxide and PET waste powder, confirms the second order kinetic of saponification.

The activation parameters of depolymerisation of PET waste powder by saponification were evaluated by measuring the specific reaction rate at various temperature ranging from 50°C to 80°C. The specific reaction rate varies from $0.88 \times 10^{-3} \text{g}^{-1} \text{s}^{-1}$ to $5.12 \times 10^{-3} \text{g}^{-1} \text{s}^{-1}$.

From results, a plot of $\log k_2$ versus $1/T$ is plotted and it gives straight line (Table 3 and Fig. 2). From slope of this plot, the energy of activation is evaluated and found to be 54.2KJg^{-1} . The frequency factor is $5 \times 10^6 \text{min}^{-1}$.

Table 1: Kinetics of saponification of PET waste Powder: Optimum parameters

S. No.	Parameters	Optimum value of gravimetry
1.	Particle size	100 μ m
2.	Amount of PET waste powder	10 g
3.	Amount of NaOH	7g
4.	Amount of pyridine	3ml
5.	Temperature	70°C

The addition of small amount of manganese acetate shows a remarkable effect in enhancing the specific reaction rate of depolymerization of PET waste powder. The specific reaction rate increases from $0.88 \times 10^{-3} \text{g}^{-1} \text{s}^{-1}$ to $1.60 \times 10^{-3} \text{g}^{-1} \text{s}^{-1}$ at 50°C . The increase in temperature from 50°C to 80°C , increases the specific reaction rate from $1.60 \times 10^{-3} \text{g}^{-1} \text{s}^{-1}$ to $4.08 \times 10^{-3} \text{g}^{-1} \text{s}^{-1}$.

A plot of $\log k_2$ versus $1/T$ is linear and the values of energy of activation, in presence of manganese acetate is 28.4 KJg^{-1} . which is lower than in absence of added manganese acetate i.e. 54.2 KJg^{-1} (Table 4 and Fig. 3). All these facts strongly suggest that the manganese acetate has a catalytic effect on depolymerization of PET waste powder.

Table 2: Kinetics of Depolymerisation of PET waste powder

Amount of PET waste powder	:	10.0 g.
Amount of sodium hydroxide	:	7.0 g.
Volume of pyridine	:	3.0 cm^3
Temperature	:	70.0°C
Specific conductance of conductivity water	:	$1.45 \mu\text{s/cm}$
Specific Conductivity of solution, C_0	:	$668.1 \mu\text{s/cm}$
Specific Conductivity at infinity, C_∞	:	$180.3 \mu\text{s/cm}$

Time t/min.	Specific conductance of solution $C_0/\mu\text{s/cm}$	Specific conductance, $C_t/\mu\text{s/cm}$	$C_0 - C_t$	$C_t - C_\infty$	$\frac{C_0 - C_t}{C_t - C_\infty}$
00	668.1	666.6	—	—	—
25	631.9	630.5	36.2	450.2	0.08
50	604.1	602.6	64.0	422.3	0.15
75	580.8	579.4	87.3	399.1	0.22
100	556.8	555.4	111.3	375.1	0.30
125	536.7	535.3	131.4	355.0	0.37
150	519.8	518.4	148.3	338.1	0.44

Slope of the graph of $\frac{C_0 - C_t}{C_t - C_\infty}$ versus time = specific reaction rate, $k_2 = 2.88 \times 10^{-3} \text{g}^{-1} \text{s}^{-1}$

Table 3: Kinetics of Depolymerisation of PET waste powder: effect of temperature

Amount of PET waste powder	:	10.0g
Amount of sodium hydroxide	:	7.0g
Volume of pyridine	:	3.0 cm^3

Temperature t/ $^\circ\text{C}$	Temp. T/K	$1/T/10^{-3} \text{K}^{-1}$	Specific reaction rate, $k_2/10^{-3} \text{g}^{-1} \text{S}^{-1}$	Log k_2
50	323	3.10	0.88	-3.05
60	333	3.00	1.68	-2.77
70	343	2.92	2.88	-2.54
80	353	2.83	5.12	-2.29

Slope of the graph of $\log k_2$ versus $1/T = -2829 \text{ K}$

Energy of activation, $E_a = 54.2 \text{ KJ g}^{-1}$

Table 4: Kinetics of Depolymerisation of PET waste powder: effect of temperature in presence of manganese acetate

Amount of PET waste powder : 10.0g
 Amount of sodium hydroxide : 7.0g

Temperature t/°c	Temp. T/K	1/T/10 ⁻³ K ⁻¹	Specific reaction rate, k ₂ /10 ⁻³ g ⁻¹ S ⁻¹	Log k ₂
50	323	3.10	1.60	-2.79
60	333	3.00	2.32	-2.63
70	343	2.92	3.12	-2.50
80	353	2.83	4.08	-2.39

Slope of the graph of log k₂ versus 1/T = -1481.5 K

Energy of activation, Ea = 28.4 KJ g⁻¹

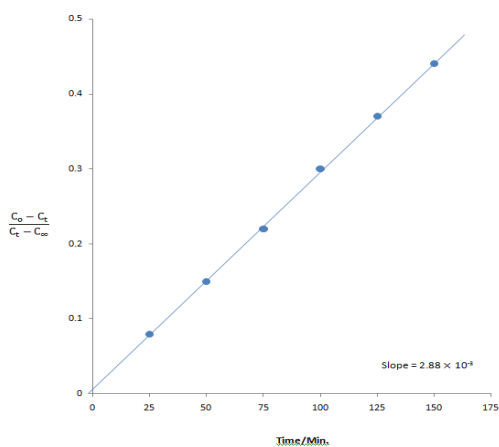
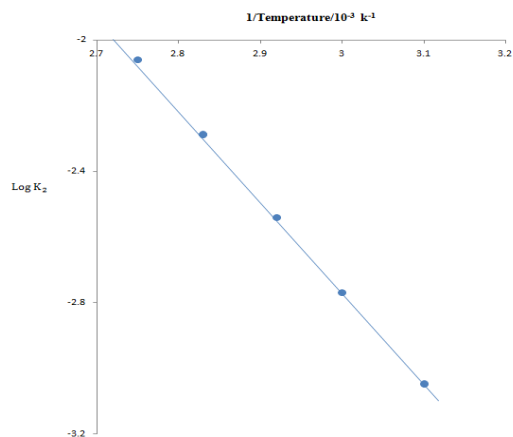
Table 5: Kinetics of Depolymerisation of PET waste powder: effect of temperature in presence of cobalt acetate

Amount of PET waste powder : 10.0g
 Amount of sodium hydroxide : 7.0g

Temperature t/°c	Temp. T/K	1/T/10 ⁻³ K ⁻¹	Specific reaction rate, k ₂ /10 ⁻³ g ⁻¹ S ⁻¹	Log k ₂
50	323	3.10	1.68	-2.77
60	333	3.00	2.48	-2.61
70	343	2.92	3.44	-2.46
80	353	2.83	4.40	-2.36

Slope of the graph of log k₂ versus 1/T = -1444.4 K

Energy of activation, Ea = 27.6 KJ g⁻¹

**Fig. 1: Kinetics of depolymerisation of PET waste powder:****Fig. 2: Kinetics of depolymerisation of PET waste powder: effect of temperature**

Similarly, addition of cobalt acetate increases the specific reaction rate from $0.88 \times 10^{-3} \text{ g}^{-1}\text{s}^{-1}$ to $1.68 \times 10^{-3} \text{ g}^{-1}\text{s}^{-1}$ at 50°C . Increase in temperature from 50°C to 80°C increases the specific reaction rate from $1.68 \times 10^{-3} \text{ g}^{-1}\text{s}^{-1}$ to $4.40 \times 10^{-3} \text{ g}^{-1}\text{s}^{-1}$. A

plot of $\log k_2$ versus $1/T$ gives energy of activation as 27.6 KJg^{-1} , which is also lower than that in absence of cobalt acetate. It indicates that cobalt acetate also has catalytic effect on depolymerization of PET waste (Table 5 and Fig. 4)

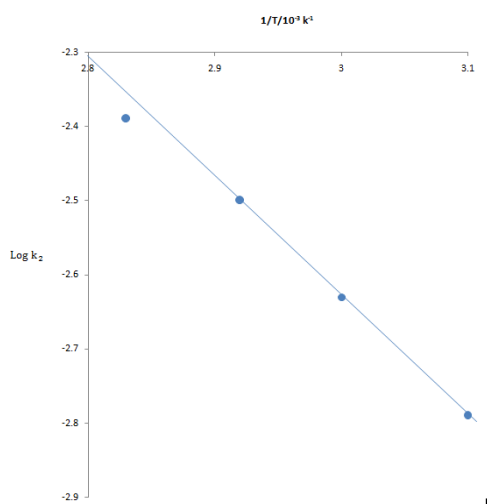


Fig. 3: Kinetics of depolymerisation of PET waste powder: effect of temperature in presence of manganese acetate

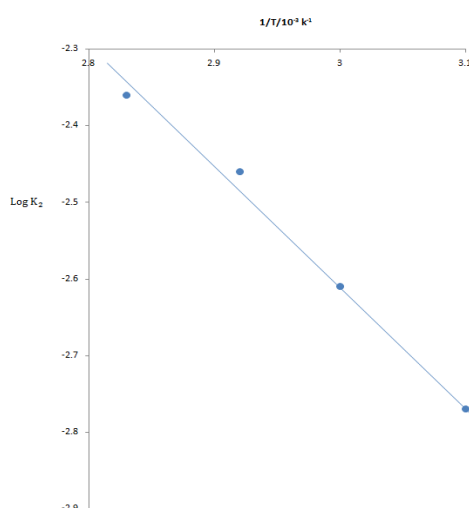


Fig. 4: Kinetics of depolymerisation of PET waste powder: effect of temperature in presence of cobalt acetate

REFERENCES

- Erlenbach, E.H. ; Laundenbach, E.S. and Obenbug, R.L.; *U.S. Pat.*,**1962**,03,037/050
- Kuroda, Y.; Yamaguchi, R. and Matsumoto, R.; *Japan kokai Pat.*,**1973**, 48,68538
- Miura, K.; Kagiya, Y. and Ichikawa, T.; *Japan, Kokai Pat.*, **1968**, 6823,449
- Baliga, S. and Wong, T. W.; *J. Polym. Sci. part A., polym chem.*, **1989**,27,2701
- Pusztanseri, S.F., *U.S. Pat.*,**1987**, 27,2701
- Yashioka, T. ; Sato, T. and Okuwaki, A., *J Appl. polym. Sci.*,**1994**,52,1353-1355
- Ref. 4
- Vaidya, V.R. and Nadkarni, V. M., *Ind. Engng. Chem. Res.*, **1998**, 27,2056
- Vaidya, V.R. and Nadkarni, V. M., *Ind. Engng. Chem. Res.*, **1987**,26, 194
- Orekov, V.N. and Rudenko, B.M., *Vest Khar'kpolytech Inst.*, **1982** , 195,10
- Snieszko, A.; Penczek, P. and Ostrysk, R., *InstIndChemwarsaw pol., Forbe lack*, **1981**,87, 1014,
- Leaversuch, R.D., *Morden plastic*, **1991**,68,41
- Mikalojezyk, B.; Lubawy, A.; Djewska, M.; Smoczynski, P., Poziniak A., Boebel, 11, *Pol. Pat PL*, **1985**, 120,009
- Yashioka, T.; Sato, T.; Okuwaki A., *J. Appl. PolymSci* , **1994**, 52,1353
- Companelli, J.R.; Kamal, M.R.; Cooper, D.G., *Appl. Polym Sci.*,**1993**, 48,443
- Yoshioka, T.; Okayama, N. and Okuwaki, A., *Ind. Engng. Chem. Res.*,**1998**,37,336-340
- Yoshioka, T.; Motoki, T. and Okuwaki, A., *Ind. Engng. Chem. Res.*,**2001**,40,75-79
- Mishra, S.; Goje, A.S.; and Zope, V.S., *International conference on plastic waste Management and Environment, proceeding, New Delhi*, **2001** , 163-169.