

# Alkaline Hydrolysis of PET waste in presence of CTAB and (C<sub>16</sub>Mim) Br.

Shital P. Kharwade<sup>1</sup>, Vijendra Batra<sup>2</sup>, Sushil Kapoor<sup>3</sup> and Dilip B. Patil<sup>4</sup>

<sup>1</sup>Department of Environmental Science, Government Institute of Science, Nagpur 440 010, India

<sup>2</sup>Department of Chemistry, Sarvodaya Mahavidyalaya, Sindewahi, Chandrapur 441 222, India

<sup>3</sup>Department of Chemistry, Art, Commerce, and Science College, Tukum, Chandrapur 442 402, India

<sup>4</sup>Department of Chemistry, Government Institute of Science, Nagpur 440 010, India

(Received 10 July, 2021; Accepted 30 August, 2021)

## ABSTRACT

Alkaline hydrolysis of poly (ethylene terephthalate) PET waste has been carried out by sodium hydroxide in presence and absence of cethyltrimethyl ammonium bromide (CTAB) and 1-hexadecyl-3-methylimidazolium bromide [C<sub>16</sub>Mim]Br under atmospheric pressure. The optimum parameters for alkaline hydrolysis such as amount of sodium hydroxide, reaction temperature, reflux time and particle size of PET waste has been determined. The average rate constant,  $k'$  for alkaline hydrolysis is  $12.26 \times 10^{-4} \text{ min}^{-1}$  at optimum conditions. The energy of activation  $E_a$  and frequency factor  $A$  are found to be  $13.68 \text{ KJ mole}^{-1}$  and  $1.43 \times 10^{-3}$  respectively. The average rate constant,  $k'$  in presence of CTAB and [C<sub>16</sub>Mim] Br are  $16.50 \times 10^{-4} \text{ min}^{-1}$  and  $1.90 \times 10^{-3} \text{ min}^{-1}$  respectively and the values of energy of activations are  $9.57 \text{ KJ mole}^{-1}$  and  $5.47 \text{ KJ mole}^{-1}$ . The corresponding frequency factors are  $1.83 \times 10^{-3}$  and  $2.03 \times 10^{-3}$ . The catalytic constants for  $k_{\text{CTAB}}$  and  $k_{[\text{C}_{16}\text{Mim}]\text{Br}}$  are 3.50 and 3.63.

**Key words :** Chemical recycling, PET, Alkaline hydrolysis, Catalytic constant, CTAB, [C<sub>16</sub>Mim] Br.

## Introduction

Poly(ethylene terephthalate) is commonly known as PET. It is extensively used worldwide. It is widely used in the manufacturing of fibres, disposable soft drink bottles, photographic films and packaging for food industry. Every year large amounts of PET was produced and consumed, hence huge amount of PET waste is generated. Although it does not creates hazard to environment, it does not degrade readily in nature. It is resistive to environment and biologically agents and hence non-biodegradable.

Because of serious disposal and treatment problems, PET waste becomes an important issue worldwide (Williams, 2006; Edge *et al.*, 1991; Cesare *et al.*,

2006; Karayannidis *et al.*, 2007). Therefore, recycling process must be established for preservation of resources and protection of the global environment (Hayden, 2013). Last few decades, many researcher focused their attention on chemical recycling of PET waste to obtain valuable products. Numerous methods for recycling of PET waste have been reported in the literature (Nickles *et al.*, 2013; Firas *et al.*, 2005; Miller, 2002; Pawlak *et al.*, 2000; Oromiehie *et al.*, 2004; Fann *et al.*, 1996). Among these important are glycolysis, methanolysis, hydrolysis, supercritical methanolysis and supercritical hydrolysis (Liu *et al.*, 2005; Scheirs, 1998; Paszun, 1997). Several researcher studied the hydrolysis of PET waste by acid or base catalysis, including hydrochloric acid,

sulphuric acid, nitric acid and sodium hydroxide (Revens,1960; Davis *et al.*, 1962; Brown *et al.*, 1976; Pustaseri, 1982; Yoshiaka *et al.*, 1994; Yoshiaka *et al.*,1998; Tabekh *et al.*, 2012; Achilias *et al.*, 2004; Subramian,2000; Guclu *et al.*, 2003; Grause *et al.*, 2004; Rosmaninho *et al.*, 2006; US Patent, 2003; Patent WO, 2001; Carta *et al.*, 2003).

The most frequently used method for PET recycling is chemical recycling. In this method total degradation of PET to monomer or partial degradation to oligomers and other chemical substances takes place. This process results in the formation of monomer which can be again used for the production of PET.

The comparison of acid-base hydrolysis of PET with and without catalyst has been reported by few workers (Kosmidis *et al.*, 2001; Karayannidis *et al.* 2002; Achilias *et al.*, 2004). Efficient glycolysis of PET by various kind of catalyst, such as acetate, chloride, oxides and phosphates of various metals have also been used by researchers (Ghaemy *et al.*, 2005; Baliga *et al.*, 1989; Troev *et al.*, 2003; Wang *et al.*, 2010; Yoshika *et al.*, 2005). All these researchers found that these catalyst are noxious to environment and cannot be separated from reaction mixture. Since last decade, ionic liquids (Parvulescu *et al.*, 2007; Liu *et al.*, 2009; Wang *et al.*, 2009); has attracted many researchers for their desirability as green solvents or catalyst and their unique features such as thermal stability, electrochemical stability, non volatility, strong solvent power for organic and inorganic compounds low flammability and structural adjustability of cation and anion.

Literature survey reveals that glycolysis of PET using ionic liquid is the most widely studied process (Hideki *et al.*, 2003; Chen *et al.*, 1999; Xi *et al.*, 2005; Firas *et al.*, 2005). But to the best of our knowledge, work on ionic liquid catalysed hydrolysis of PET waste is very scanty.

This work has been particularly focused on analyzing the PET waste degradation by means of alkaline hydrolysis in presence of cethyltrimethyl ammonium bromide (CTAB) and 1-hexadecyl-3-methylimidazolium bromide [ $C_{16}$ Mim] Br as a catalyst. The specific objectives of this study are, on one hand to study the alkaline hydrolysis of PET waste under atmospheric pressure; the influence of various reaction parameters such as base concentration, temperature, reflux time and particle size. The kinetic parameters such as average constant, energy of activation and frequency factor has been determined

and on other hand to evaluate the catalytic performance of CTAB and [ $C_{16}$ Mim] Br by determining their catalytic constants.

## Experimental

All the chemicals used in the present study were of analytical grade. The required solutions were prepared in doubly glass distilled water. The PET waste used in all the experiments was procured from local corporation area of Nagpur, Maharashtra, India. The PET waste was washed with Teepol and then with hot double distilled water. Then the PET waste was dried with hot air blower. The PET waste was chilled in cryostat to increase its brittleness, then crushed, ground and sieved into different particle sizes.

### Optimum parameter

The optimum parameters for alkaline degradation of PET waste were determined by gravimetric measurement of un-reacted PET waste. Degradation was carried out in 500 ml three vertical neck round bottom flask fitted with extralong water condenser, digital thermometer and microstirrer. The optimum parameters were determined so as to get maximum degradation of PET waste to terephthalic acid (TPA). The general procedure adopted was consisting of charging three vertical neck round bottom flask by required quantity of PET waste, NaOH and pyridine. The flask was heated on hot oil bath for fixed time. After heating time at particular temperature, reaction mixture was cooled and filtered for operation of un-reacted PET waste. Unreacted PET waste was washed with water and weighed on digital balance. The filtrate was treated with hydrochloric acid (HCl) to get TPA. To ensure the degradation of PET waste, TPA was characterized by FTIR spectra.

### Kinetics of PET Degradation

In each degradation experiment, 12g PET waste (100  $\mu$ m), 3ml pyridine, 7.0 g NaOH and 100 ml of distilled water was added into reaction flask placed in oil bath. The reaction flask was heated to desire temperature. Aliquots of the reaction mixture were withdrawn at various time intervals. At each time interval unreacted PET waste was separated using a filter glass. Unreacted PET waste was measured gravimetrically.

From the amount of un-reacted PET waste at

various time intervals, reaction rate constant  $k$ , was calculated using first order rate equation. From these values, average rate constant,  $k'$  for the alkaline degradation of PET waste was calculated. Such average rate determinations were made at various temperature from the result, kinetic parameters such as energy of activation and frequency factor were evaluated. The similar procedure have been carried out by adding the catalyst such as CTAB ( $1 \times 10^{-4}$ ) and  $[C_{16}Mim] Br$  under the same experimental conditions. In each case average rate constants, energy of activation and frequency factors were determined. Further in order to check the catalytic action, the catalytic constants of CTAB and  $[C_{16}Mim] Br$  were determined by using various concentrations of catalysts.

## Results and Discussion

### Optimum parameters

The results of optimum parameters for alkaline degradation of PET waste by NaOH are summarized in Table 1. It is observed that maximum degradation of PET waste occurred at 12.0g of PET waste. The optimum amount of NaOH required for optimum hydrolysis of PET is found to be 7.0g. Further increase in amount of NaOH decreases the degradation of

**Table 1.** Alkaline Degradation of PET Waste : Optimum Parameters

Sr.No.	Parameters	Optimum Value
1.	Amount of PET Waste	12.0g
2.	Amount of NaOH	7.0g
3.	Particle Size of PET waste	100 $\mu$ m
4.	Reflux Time	130min
5.	Temperature	70°C

PET waste.

The particle size of PET waste was varied from 100  $\mu$ m to 800  $\mu$ m. The results showed that increase in particle size from 100  $\mu$ m to 800  $\mu$ m, there is decrease in degradation of PET waste. This concludes that smaller the particle size of PET waste, greater is the degradation of PET waste. This is due to the large surface area provided by the small particle size, large heat and mass transfer.

The increase in the reflux time increases the degradation of PET waste. The maximum degradation takes place at 130 min. Beyond this time, degrada-

tion decreases. It is also observed that increase in temperature increases the degradation of PET waste up to 70°C. Further increase in temperature, decreases the degradation of PET waste.

The product of alkaline degradation of PET waste is terephthalic acid (TPA). The degradation product is confirmed by FTIR spectroscopy and melting point. It is found that the FTIR spectra of TPA product is very much similar to standard FTIR spectra of TPA (fig.1 and fig.2). The melting point of TPA is observed to be 297°C which is very near to pure TPA.

### Average rate constant

The degradation study for determination of average rate was carried at previously determined optimum parameters. The degradation of PET waste by NaOH has been carried out on the basis of measurement of weight of unreacted PET waste at various time intervals during the course of reaction. The rate constant at each time interval has been calculated using the first order equation,  $K = 2.303/t \log C_o/C_t$  where  $C_o$  is the initial weight of PET waste and  $C_t$  is the weight of unreacted PET waste after the reaction time,  $t$ . From these values of rate constants, average rate constant,  $k'$  is calculated.

Similarly, average rate constant determinations has been carried out under the same experimental conditions in presence of CTAB and  $[C_{16}Mim] Br$  as

**Table 2.** Alkaline Degradation of PET waste : Average Rate Constant

Sr. No.	Degrading Agent/ Catalyst	Average rate constant, $k'/\text{min}^{-1}$
1.	NaOH	$12.26 \times 10^{-4}$
2.	CTAB	$16.50 \times 10^{-4}$
3.	$[C_{16}Mim] Br$	$1.90 \times 10^{-3}$

a catalyst (Table 2).

### Energy of activation

The energy of activation of alkaline degradation of PET waste is obtained using Arrhenius equation,  $\ln k' = \ln A + E_a/RT$  where  $k'$  is the average rate constant,  $E_a$  is energy of activation,  $T$  is temperature in Kelvin and  $R$  is gas constant. In each case, average rate constants has been determined at various temperature ranging from 40°C to 80°C (Table 3).

From the slope of the Arrhenius plot for NaOH, CTAB and  $[C_{16}Mim] Br$  and intercepts, energy of

**Table 3.** Alkaline Degradation of PET Waste : Average Rate Constant at Various Temperature

Sr. No.	Temperature °C	Average Rate Constant, k'		
		NaOH 10 <sup>-4</sup> min <sup>-1</sup>	CTAB 10 <sup>-4</sup> min <sup>-1</sup>	[C <sub>16</sub> Mim] Br 10 <sup>-3</sup> min <sup>-1</sup>
1.	40	10.07	14.31	1.78
2.	50	10.86	15.10	1.82
3.	60	11.56	15.80	1.85
4.	70	12.26	16.50	1.90
5.	80	12.04	16.72	1.87

activation and frequency factors has been evaluated (Table 4). The result showed that energy of activation is lowered in case of CTAB and [C<sub>16</sub>Mim] Br, as compared to NaOH degradation of PET waste.



Decrease in activation energy for CTAB and [C<sub>16</sub>Mim] Br indicates that less energy is required for the alkaline degradation of PET waste. From the results, it is quite obvious that CTAB and [C<sub>16</sub>Mim] Br acts as a catalyst for the alkaline degradation of PET waste. It is also indicative of strong catalytic action of [C<sub>16</sub>Mim] Br as compared to CTAB.

The frequency factors for NaOH, CTAB and [C<sub>16</sub>Mim] Br are in the order of,



The higher value of frequency factor for CTAB and [C<sub>16</sub>Mim] Br indicates the maximum numbers of collisions between the reactants which leads to the rapid degradation of PET waste as compare to simple alkaline hydrolysis.

In order to study compare the catalytic action of CTAB and [C<sub>16</sub>Mim] Br, the reaction is carried out at various catalyst concentrations ranging from 1.0 ×

10<sup>-4</sup> to 5.0 × 10<sup>-4</sup>. In each case average rate constants has been determined. From the results, the catalytic constants are determined [table 5]. The catalytic constant for [C<sub>16</sub>Mim] Br is higher than the CTAB. It indicates that though CTAB acts as a catalyst, [C<sub>16</sub>Mim] Br has stronger catalytic action than CTAB.

## Conclusion

In present work, the alkaline degradation of PET waste was found to be dependent on the concentration of CTAB and [C<sub>16</sub>Mim] Br. Both CTAB and [C<sub>16</sub>Mim] Br exhibited good catalytic action to alkaline degradation of PET waste. In addition, the alkaline degradation of PET waste follows first order reaction kinetics at temperature range irrespective of the presence of CTAB and [C<sub>16</sub>Mim] Br. The energy of activation and frequency factor shows low requirement of energy for alkaline degradation of PET waste using CTAB and [C<sub>16</sub>Mim] Br. In conclusion [C<sub>16</sub>Mim] Br can be used as catalyst for alkaline degradation of PET waste.

## References

- Achilias, D.S. and Karayanridis, G. P. 2004. The Chemical Recycling of PET in the framework of Sustainable Development. *Water Air and Soil Pollution. Focus 4*: 384-396.
- Achilias, D.S. and Karayanridis, G. P. 2004. The Chemical Recycling of PET in the framework of Sustainable Development. *Water Air and Soil Pollution: Focus 4*: 384-396.
- Baliga, S. and Wong, W. T. 1989. Depolymerisation of Poly(ethylene terephthalate) Recycled from Post Consumer Soft Drink Bottles. *Journal of Polymer Sci-*

**Table 4.** Alkaline Degradation of PET Waste: Kinetic Parameter

Sr. No	Degradation Agent/ Catalyst	Slope	Intercept	Energy of Activation, E <sub>a</sub> /KJ/mole	Frequency Factor, A/ 10 <sup>-3</sup>
1.	NaOH	-714.28	- 6.550	13.68	1.43
2.	CTAB	-500.00	-6.300	9.57	1.83
3.	[C <sub>16</sub> Mim] Br	-285.71	-6.200	5.47	2.03

**Table 5.** Alkaline Degradation of PET Waste : Catalytic Constant

[Catalyst] / 10 <sup>-4</sup>	1.0	2.0	3.0	4.0	5.0	Catalytic Constant
Average Rate Constant, k' / 10 <sup>-4</sup> min <sup>-1</sup> CTAB	16.50	18.12	18.45	18.78	19.17	3.50
Average Rate Constant, k' / 10 <sup>-4</sup> min <sup>-1</sup> [C <sub>16</sub> Mim] Br	17.8	22.7	26.0	29.4	32.6	3.63

- ence A: *Polymer Chemistry*. 27 (6): 2071-2082.
- Brown, G.E. and Jr. Obrien, R.C. 1976. Method for Recovering Terephthalic Acid and Ethylene Glycol from Polyester Materials, *U. S. Patent*. 3 : 952, 053.
- Carta, D., Cao, G. and Angeli, C. D. 2003. Chemical Recycling of Polyethylene Terephthalate (PET) by Hydrolysis and Glycolysis. *Environmental Science and Pollution Research*. 10 (6) : 390-394.
- Cesare, L., Piero, M., Corrado, B. and Giancarlo, B. 2006 *Journal of Polym Environ*. 14(89).
- Chen, J.W. and Chen, L.W. 1999. The Glycolysis of Poly(ethylene terephthalate). *Journal of Applied Polymer Science*. 73 : 35-40.
- Davis, T., Goldsmith, P. L., Revens, D. A. S. and Ward, I. M. 1962. The Kinetics of the Hydrolysis of Polyethylene Terephthalate Film. *J. Phys. Chem*. 66: 175.
- Edge, M., Hayes, M., Mohammadian, M., Allene, N.S., Jewitt, T.S., Brems, K. and Jones, K. 1991. Aspect of Poly(ethylene terephthalate), Degradation of Achieve life and Environmental Degradation, *Polymer Degradation and Stability*. 32 (2) : 131-153.
- Fann, D. M., Huang, S. K. and Lee, J. Y. 1996. Kinetics and Thermal Crystallinity of Recycled PET. I. Dynamic Cooling Crystallization Studies on Blend Recycled with Engineering PET. *Journal of Applied Polymer Science*. 63(8) : 1375-1385.
- Firas, A. and Dumitra, P. 2005 Recycling of PET. *European Polymer Journal*. 41 (7) : 1453-1698.
- Firas, A. and Dumitru, P. 2005. Recycling of PET, *Eur. Polym. Journal*. 41 : 1453-1477.
- Ghaemy, M. and Mossaddegh, K. 2005. Depolymerisation of Poly(ethylene terephthalate) fiber waste using ethylene glycol. *Polymer Degradation and Stability*. 90 (3): 570-576.
- Grause, G., Kaminsky, W. and Fahrback, G. 2004. Hydrolysis of Poly (Ethelene Terephthalate) in a Fluided Bed Reactor. *Polymer Degradation and Stability*. 85(1) : 571-575.
- Guclu, G., Yalcinyuva, T., Ozgumus, S. and Orbay, M. 2003. Hydrolysis of Waste Polyethylene Terephthalate and Characterization of Product by Differtial Scanning Calorimetry, *thermochimica Acta*. 404 (1): 193-205.
- Hayden, K. W., Jaimys, A. Russell, J. C. and Elena, P.I. 2013 Plastic Degradation and its environmental implications with special reference to poly(ethylene terephthalate). *Polymers*. 5 : 5-18.
- Hideki, K., Masa-aki, O., Kazuo, S. and Miura, H. 2003. Methanolysis of Polyethylene terephthalate (PET) in presence of aluminium ti isopropoxide catalyst to form dimethyl terephthalate and ethylene glycol. *Polymer Degradation and Stability*. 79 : 529-533.
- Karayannidis, G. P. and Archilias, D. S. 2007 *Macromol Mater Eng*. 292 (128).
- Karayannidis, G., Chatziavgoustis, A. and Archilias, D. S. 2002 PET Recycling and Recovery of Pure Terrphthalic Acid by Alkaline Hydrolysis, *Adv. Polym. Technol*. 21 : 250-259.
- Kosmidis, V., Archilias, D.S. and Karayannidis, G. 2001. Poly (ethyleneterephthalate) recycling and recovery of pure terephthalic acid, kinetics of phase transfer catalysed alkaline hydrolysis. *Macromol. Mater. Eng*. 286: 640-647.
- Liu, F., Cui, S. X., Yu, S.T., Li, Z. and Ge, X.P. 2009. Hydrolysis reaction of Poly (ethylene terephthalate) using ionic liquids as solvent and catalyst. *J. Appl. Polym. Sci*. 114 : 3561-3565.
- Liu, L., Zhang, D., An, L., Zhang, H. and Tian, Y. 2005. Hydrolytic Depolymerization of Poly (Ethelene Terephthalate) under microwave irradiation. *J. Appl. Polym. Sci*. 95(3) : 719-723.
- Miller, C. 2002. Polyethylene Terephthalate Waste Age. 35(5) : 102-106.
- Nickles, D. E. and Farahat, M. S. 2013 New Motivation for the Depolymerisation Products Derived from Poly(ethylene terephthalate) (PET) Waste: a Review, *Macromolecular Materials and Engineering*. 290:13-30.
- Oromiehie, A. and Mamizadeh, A. 2004. Recycling PET Beverages Bottles and Improving Properties. *Polymer International*. 53 : 728-732.
- Parvulescu, V.I. and Hardacre, C.R. 2007. *Catalysis in ionic liquids chemical Reviews.*, 107 (6) : 2615-2665.
- Paszun, D. and Szychaj, T. 1997. Chemical recycling of Poly(Ethelene Terephthalate). *Ind. Eng. Chem. Res*. 36: 1373-1383.
- Patent WO/2001/068581: 2001 The Method of Recycling of Polyethylene Terephthalate Waste.
- Pawlak, A. 2000. Characterization of scrap poly(Ethelene Terephthalate). *European Polymer Journal*. 36 (9): 1875-1884.
- Pustaseri, S. F. 1982. Method for Recovery of Terephthalic Acid from Polyester scrap. *U.S. Patent*. 4 : 355, 175.
- Revens, D. A. S. 1960. Chemical Reactivity of Poly(Ethelene Terephthalate): Heterogeneous Hydrolysis by Hydrochloric Acid. *Polymer (London)*, 1 : 375.
- Rosmaninho, M., Jardim, E., Flavia, M.C.C., Ferreira, G. Thom, V., Yoshida, M., Arauj, M. H. and Lago, R.M. 2006. Surface Hydrolysis of Post Consumer Polyethylene Terephthalate produce adsorbants for Catiomic Contaminants. *Journal of Applied Polymer Science*. 102(6) : 5284-5291.
- Scheirs, J. 1998. Chapter 4: Recycling of PET, *Polymer Recycling*, Wiley Series in Polymer Science, John Wiley & Sons. Sussex.
- Subramian, P. M. 2000. Plastic Recycling and Waste Management in the US, Resources. *Conservation and Recycling*. 28 : 253-263.
- Tabekh, H., Koulsi, Y. and Ajji, Z. 2012. Chemical Recycling of Poly(Ethelene Terephthalate) using Sulphuric Acid. *Rev. Rom. Chim*. 57(12) : 1029-1034.
- Troev, K., Grancharov, Tsevi G. R. and Gitsov, I. 2003. A

- Novel catalyst for the glycolysis of Poly(ethylene terephthalate). *Journal of Applied Polymer Science*. 90 (4): 1148-1152.
- US Patent 664972: 2003. Method of Recycling of Polyethelene Terephthalate Waste.
- Wang, H., Li, Z.X., Liu, Y. Q., Zhang, X. and Zhang, S. J. 2009. Degradation of Poly (ethylene terephthalate) using ionic liquids, *Green Chem*. 11 : 1568-1575.
- Wang, H., Yan, R.Y., Li, Z. X., Zhang, X.P. and Zhang, S.J. 2010. Fe-containing magnetic ionic liquid as effective catalyst for the glycolysis of Poly(ethylene terephthalate)., *Catalysis Communication*. 11 (8) : 763-767.
- Williams, P.T. 2006. *Waste Treatment and Disposal*, 2nd Edition: John Wiley & Sons, Weinhein, Germany.
- Xi, G.X., Lu, M.X. and Sun, C. 2005. Study on Depolymerisation of waste Polyethylene terephthalate into Monomer of bis(2-hydroxyethyl terephthalate), *Polym. Degradation and Stability*. 87 : 117-120.
- Yoshiaka, T., Okayama, N. and Okuwak, A. 1998. Kinetics of Hydrolysis of PET Powder in Nitric Acid by a Modified Shrinking-Core Model. *Ind. Eng. Chem. Res.* 37 : 336-340.
- Yoshiaka, T., Sato, T. and Okuwaki, A. 1994. Hydrolysis of Waste PET by Sulphuric Acid at 1500C from Chemical Recycling. *J. Appl. Polym. Sci.* 52 : 1353.
- Yoshika, T., Handa, T., Grause, G. Li, Z.G. Innomata H. Mizoguchi, T.E. 2005. Effects of metal oxides on the pyrolysis of Poly(ethylene terephthalate)., *Journal of Analytical and Applied Pyrolysis*. 73 1 (1) : 39-144.
-