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Ultrasound assisted alkaline hydrolysis of poly(ethylene terephthalate) in presence of phase transfer catalyst

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ABSTRACT

Alkaline hydrolysis of poly(ethylene terephthalate) (PET) flakes from waste packaged drinking water bottles was carried out with and without influence of ultrasound waves rated 20 kHz frequency and 190 W power. Alkali used for hydrolysis was 10% NaOH (w/w). Tetrabutyl ammonium iodide (TBAI) was used as phase transfer catalyst (PTC) to enhance rate of hydrolysis. The experiment yields terephthalic acid (TA) and ethylene glycol as products of hydrolysis. Minimum time required for ultrasound assisted (UA) reaction and without ultrasound assistance (WUA) reaction to complete was investigated and compared. PTC: PET ratio = 0.03:1 w/w, temperature (90 °C) and NaOH concentration (10% w/w) were kept constant. All reactions were carried out at atmospheric pressure. For UA reaction, time required for 100% conversion of PET was found to be 45 min. For WUA reaction, the time required for 100% conversion of PET was found to be more than 65 min. Yield of TA was found to be >99% on the basis of moles of repeating units of PET fed. Melting point of product was found nearly equal to standard TA. Product TA was confirmed by comparing Fourier-transform infrared spectroscopy (FTIR) spectra of product with that of standard TA. Ratio of PTC to PET was fine-tuned for UA reaction keeping reaction time constant at 45 min.

1. Introduction

Increasing demand of petroleum products and incapability of mankind to serve the niche is now compelling people to reuse or recycle materials. Poly(ethylene terephthalate) (PET) is one of those materials since, it is commercially manufactured from polymerization of terephthalic acid (TA) and ethylene glycol. TA is manufactured from paraxylene, a downstream petrochemical industry product. PET is observed to be an abundant waste material because of tremendous increase in the use of packed drinking water in India. According to a report [1], 5,00,000 ton/year of PET is manufactured in India while only 1,40,000 ton/year is recycled. Remaining PET ends up in landfills or accumulates in environment. Recent trends in the field of PET waste recycling [2] reveal that, PET is physically recycled by melting and casting into pellets. However 100% use of recycled PET to replace virgin polymer cannot be done since it leads to the quality degradation. Unsustainable physical recycling of PET brings our attention towards chemical recycling of PET. The cause of unimplemented chemical recycling of PET is high cost of raw materials and energy involved in the process.

Paszun and Spychaj [3], suggested six ways to degrade PET into monomers. Out of those, we have focused on hydrolysis for study since it appeared to be most efficient with respect to use of chemicals and yield of TA. Hydrolysis of PET can be done by four ways namely neutral, acidic, enzymatic hydrolysis and alkaline hydrolysis. Neutral hydrolysis of PET was carried out by Güçlü et al. [4] but temperature as high as 140 °C and use of xylene as a solvent increased the processing cost. Yoshioka et al. [5] studied acidic hydrolysis of PET using sulfuric acid. Chen [6] studied glycolysis of post-consumer PET bottles at 190 °C. Hydrolysis of PET using tailored enzyme was studied by Araujo et al. [7] which is not feasible because of low rate of reaction.

Alkaline hydrolysis of PET using solvent like ethylene glycol, water and mixture of both were studied at various temperatures by Oku et al. [8], Gupta and Guria [9], Rahman [10] and López-Fonseca et al. [11]. All studies mentioned require either high temperature of reaction or long reaction time reducing financial feasibility of chemical recycling of PET. A phase transfer catalyst (PTC) can be employed to make chemical recycling of PET feasible. Alkaline hydrolysis of PET bottle flakes under the influence of different PTCs was studied by Das et al. [12]. In that study benzalkonium chloride was found to be most effective catalyst with respect to maximum

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PET conversion compared to the amount of catalyst used per unit weight of PET.

Use of new ways like microwave (MW) and ultrasonic assisted reactions to carry PET depolymerization has rarely been explored. Microwave (MW) assisted depolymerisation of waste PET bottles was studied by Khalaf and Hasan [13]. Reaction time to achieve 100% hydrolysis of PET was found to be 60 min and temperature of reaction was reported to be 90–98 °C. Ultrasound irradiation in the pool of reacting liquid species is reported to alter the kinetics of chemical reaction by Suslick [14]. Kang and Hoffman [15], Laulghrey et al. [16], Walton [17], Gogate and Pandit [18] and Okitsu [19] studied various sonolytic degradation reactions. Above mentioned studies support the positive impact of ultrasound in the degradation of organic chemicals. Sonolytic degradation of various polymers was studied by several researchers. Ultrasonic degradation of polybutadiene was studied by Chakraborty et al. [20]. Desai et al. [21,22] studied polypropylene and low density polyethylene (LDPE) degradation under acoustic induced cavitation. Kinetics of ultrasonic degradation of poly alkyl methacrylate was studied by Daraboina and Madras [23]. Mohod and Gogate [24] studied ultrasonic degradation of carboxymethyl cellulose and polyvinyl alcohol (PVA). Commercially very important polymers butadiene and styrene and their copolymers implemented in rubber industry were ultrasonically degraded by Sathiskumar and Madras [25]. All mentioned studies support the concept of ultrasound assisted depolymerization.

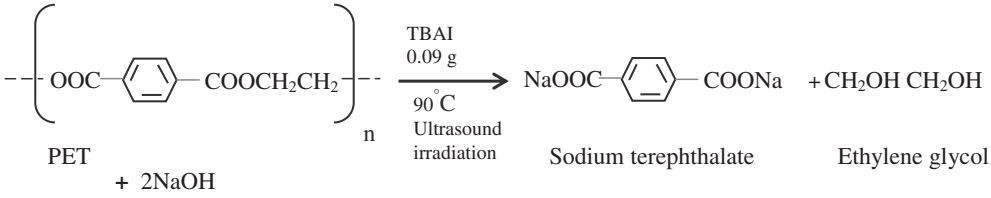
Degradation of PET under influence of ultrasound in presence of PTC was never studied and it could be quite feasible based on the studies mentioned above. Also generation of ultrasound is quite easy and large scale ultrasound processing equipment has already been commercialized [26]. Here in this paper we have provided a comparative account of ultrasound assisted (UA) and without ultrasound assisted (WUA) catalyzed alkaline hydrolysis of PET.

2. Materials and methods

PET bottle flakes were procured from local supplier and were ground further in mixer grinder for reducing the of flakes to the range of 0.2–0.5 mm. Size distribution of PET flakes was confirmed by screening analysis. Molecular weight of PET used in manufacturing bottles is near to 30,000 [27] with polydispersity index 2 [28]. Standard TA (1, 4-benzenedicarboxylic acid) of 98.0% purity was purchased from SD fine chemical limited Mumbai (Maharashtra, India). PTC tetrabutyl ammonium iodide (TBAI 99.98% pure) was procured from Tatva Chintan pharma chem. Pvt. Ltd. Ankleshwar (Gujarat, India). Ultrasonics ultrasound horn (diameter 15 mm) based equipment was used For ultrasound assisted reaction. H_2SO_4 (98% pure) and NaOH (96% pure) were purchased from Finar and Rankem respectively. Remi magnetic stirrer-heater assembly was used to maintain temperature. Shimadzu DRS 8400-s was used for doing FTIR.

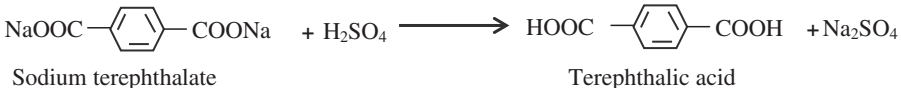
2.1. Alkaline hydrolysis

Hydrolysis reaction takes place in two steps. Step 1, which is a bottleneck step is actual alkaline hydrolysis of PET (Reaction (1)). Splitting of ester linkage in PET takes place in this reaction and the product of this reaction is formation of disodium salt of TA. In second step of reaction (Reaction (2)), disodium salt of TA is acidified by adding concentrated H_2SO_4 to precipitates TA as dispersed slurry. Multiple trials were taken to find out the optimum time required for 100% conversion of PET for with and without irradiation of ultrasound. The reaction occurring in flask can be visualized as Reaction (1). Formation of disodium salt of TA (Na_2TA) by treating with NaOH solution with TBAI as PTC takes place in this reaction.



(1)

Step 1 was repeated for UA and WUA reaction followed by step two. Two different sets of observations were taken for each UA and WUA reactions which are plotted further. After carrying out step 1, any unreacted amount of PET was determined to find out the conversion and then step 2 was carried out. Product of Reaction (2) i.e. TA was dried and weighed to determine yield.



(2)

Quantities and parameters were maintained as per report [12]. Percent consumption of PET is calculated on weight of PET consumed to the initial weight of PET taken basis (Eq. (3)).

$$\%\ \text{PET Conversion} = \left(\frac{W_{\text{PET},i} - W_{\text{PET},f}}{W_{\text{PET},i}}\right) \times 100 \tag{3}$$

Where $W_{\text{PET},i}$ is initial weight of PET and $W_{\text{PET},f}$ is final weight of PET which remains on filter paper after filtration. Yield is calculated on moles of repeating unit basis.

$$\%\ \text{Yield} = \frac{N_{\text{TA}}}{N_{\text{TA},o}} \times 100 \tag{4}$$

Here in Eq. (4), N_{TA} refers to number of moles of TA precipitated and $N_{\text{TA},o}$ refers number of moles of TA that could have theoretically been precipitated based on 100% PET conversion. As per above calculation (Eq. (4)) and stoichiometry, 100% conversion of 3 grams (g) PET should yield 2.5960 g of TA for 100% yield based on TA. Since 3 g of PET consist of 0.0156 mol of terephthalate group and hence as