Use of High Pressure Autoclave for Chemical Recycling of Plastic Wastes

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Abstract — High pressure autoclave of 500 mL capacity, facilitated with temperature control panel working under maximum pressure up to 100 kg/cm² or 1500 psi, and maximum temperature up to 250°C was found to shorten the reaction time for chemical recycling of plastic wastes. Depolymerisation of polyester waste was carried out by saponification reaction. Yield of depolymerised product was obtained up to 85% for 2.5 h reaction time. Product obtained was characterized by chemical as well as instrumental analysis such as M.P. (sublimation), acid value and FTIR Spectra. The results agree with pure Terephthalic acid (TPA). Chemical kinetics of this reaction shows that it is a first order reaction with respect to polyethyleneterephthalate (PET) concentration which is in the order of $10^{-2}$ min⁻¹.

Keywords — Depolymerization, Kinetics, Thermodynamics, Terephthalic acid

I. INTRODUCTION

Polyethylene terephthalate (PET) is semi-crystalline thermoplastic polyester widely used in the form of fibers, sheets and films. PET is characterized by high mechanical strength and low permeability to gases, with good aesthetic appearance. It is non-toxic material having high resistance to atmospheric and biological agents.

PET is condensation thermoplastic polymer produce by the reaction of terephthalic acid (TPA) with mono ethylene glycol. PET was first used commercially in the 1950s as Terylene and Dacron in the form of fiber. Now a day PET is commonly and widely used in the form of film for X-ray photographs, magnetic recording tapes, packaging and many industrial uses. In the 1970s technology was developed to use PET as rigid container. Since then the container market has grown very rapidly. Particularly the mineral bottles, soft drink bottles made by PET are accepted by the society. Polyester is the major fiber used in non-woven interlinings, interfacing, filtration media, surgical and medical products, agricultural clothes, coated and laminated packaging.

Since the first recycling of PET in 1977 (Miller 2002), many studies have been conducted to investigate PET recycling methods (Helwani et al. 2009; Patterson 2007; Yoshioko et al. 1994, 2001), and the recovery rate of consumed PET has been consistently increasing. The world consumption of PET packaging is expected to about 19.1 million tons by 2017, with 5.2% increase per year between 2012 and 2017 (Smithers Pira 2012). The recycling of plastic wastes is well illustrated by Figure 1.

Figure 1 Recyling loop.
II. EXPERIMENTAL

A. High Pressure Autoclave

It was provided with vent valve, liquid sampling valve, gas inlet valve, automatic cooling system, temperature alarm system etc. Liquid sample after definite time interval can be withdrawn from liquid sample valve. The autoclave was equipped with silver rupture disc having a burst rating of 1600 psi pressure at 250°C. In order to mix the reaction mixture homogeneously autoclave was facilitated with stirrer having magnetic drive. The magnetic drive was of zero leakage and maintenance free, which was facilitated with magnetic coupling directly driven by the motor. High energy permanent magnet was fixed inside the inner rotor and on inner side of the external shell.

B. Depolymerization of PET waste at high temperature and high pressure:

The PET waste was chilled for its brittleness and grounded in to desired particle size of 425μm to create maximum surface area for heat and mass transfer in the reaction vessel. 0.5 L capacity high pressure auto autoclave was used for all hydrolytic depolymerisation experiments. The autoclave was well equipped with constant rotating stirrer at the speed of 500 rpm, which ensures the proper mixing of reaction mixture.

10 g of PET waste and 300 mL water of very high purity of HPLC grade (1:30 w/v), were charged in vessel of autoclave. The vessel was heated for 2 hours. After the specified time interval and the reaction temperature, the vessel was cooled suddenly and removed from heating collar. The vessel was subsequently opened and the product was removed. It was treated with sodium hydroxide to form sodium salt of terephthalic acid then acidified with hydrochloric acid; a white pure precipitate of TPA was obtained. It was filtered, dried and weighed. Sodium hydroxide treatment followed by hydrochloric acid was given in order to obtain pure TPA. After drying it was grounded up to fine powder using mortar and pestle.

Similar experimental procedure was repeated for various pressures such as 100, 200, 300, 400, 500, 600, 700, and 800 psi. at 100, 150, 200 and 250°C respectively. Similarly for kinetic and thermodynamic studies, the experiments were carried out for the reaction time 30, 60, 90, 120 and 150 min. at 200 and 250°C maximum temperatures. All these experimental processes were carried out in batches.

III. RESULT AND DISCUSSION

A. Kinetics of hydrolytic depolymerisation of PET waste

The kinetic study of depolymerisation was under taken on the basis of product depolymerised and its residue. The velocity constant of depolymerisation was calculated by using formula, 

\[ k = \frac{[2.303/t]}{\log \frac{a}{(a-x)}} \]

Where, \( a \) = initial weight of PET waste in gram, 

\( k \) = velocity constant of the reaction, 

\( x \) = amount of PET depolymerised in gram at time \( t \).

On the basis of results obtained, the velocity constants 1.773x10⁻² min⁻¹ and 6.909 min⁻¹ were recorded for the depolymerization reaction at 200 and 250°C

B. Verification of First Order Kinetics

The straight line natures of the graph of \( \log \{a / (a-x)\} \) versus time in minute and almost passing through origin shows the first order reaction kinetics. Slope gives the values of velocity constants 1.773x10⁻² and
6.909 \times 10^{-2} \text{ min}^{-1} \text{ at 200 and 250 } ^\circ \text{C respectively.}

Fig. 3 - Verification of First Order Kinetics of Depolymerisation of PET Waste at 200 and 250\(^\circ\)C Temperatures.

Parallel nature of the Fig. 4 shows that the velocity constants remain constant at both the temperatures. At higher temperature i.e. 250\(^\circ\)C it is about four times higher than at 200\(^\circ\)C.

The energy of activation and frequency factor are obtained by plotting Arrhenius graph log k versus 1/T at various pressures as shown in Figs. 5 and 6. The intercept and slop of the Arrhenius plot give frequency factor and energy of activation respectively. These two thermodynamic parameters at various pressures are shown in Table 1. It is clear from above results that there is no significant increase in values of energy of activation and frequency factor with varying the pressure from 500 to 800 psi.

Table 1 shows the values of intercepts and slopes at various pressures 200, 300, 400, 500, 600, 700, and 800 psi. These values provide frequency factors and energy of activations.

The enthalpy of activation was calculated by using values of energy of activations at 200\(^\circ\)C.

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<th>Pressure psi</th>
<th>Slope</th>
<th>(E_a) Kmol(^{-1})</th>
<th>(A) Kmol(^{-1})</th>
<th>Intercept</th>
<th>Frequency factor (A) x10^5 min(^{-1})</th>
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IV. CONCLUSIONS

1. High pressure autoclave was found to be the effective reactor to shorten the reaction time.
2. Neutral water hydrolysis of PET is only possible using High pressure autoclave above 200 psi pressure.
3. Neutral water hydrolysis (depolymerization) of PET was found to be first order kinetics having velocity constant value in the order of $10^{-2}$ min$^{-1}$.
4. Energy and enthalpy of activations decreases with increase in pressure indicating less amount of energy is required for reaction.

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REFERENCES