Greener route for recovery of TPA by depolymerization of PET waste

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Abstract

One of the major objectives of Green Chemistry is to make existing processes and products more environment friendly. Increase in PET waste has been a major threat to environment and thus its depolymerization is being widely studied by researchers all over the world. Chemical recycling of PET waste by using water, alkali, acid, methanol, ammonia and glycol has already been studied on wide scale.Alkali hydrolysis is one of the ways to convert PET into its original raw material. According to the principle of Green Chemistry this method is an incrementally better method than the ones used in the past. In alkaline hydrolysis, PET is refluxed for different time intervals at different temperatures. Different types of catalysts have been used; acetates of zinc, lead, manganese, cobalt, calcium etc. were also studied as catalysts; but increase in pollution due to metals remains a challenge, in such situation,Phase Transfer Catalysts (PTC) are proven to be safer and more efficient. Recovery of monomers of terephthalic acid from Poly (ethylene terephthalate) waste using sodium or potassium hydroxide is a method in which more than 90% recovery of TPA is possible at lower temperature and in lesser time. Experimentally, when 10 gm PET waste was refluxed with 8gm NaOH in 100 ml distilled water, in presence of Tetrabutyl ammonium bromide 0.25% weight of PET waste in fine powder form, it was observed that yield of TPAwas 93% at 100°C when the reaction was carried out for 120 minutes.

KEYWORDS: Green Chemistry, Depolymerization, PET, Phase Transfer Catalyst, Alkaline Hydrolysis.

Introduction:

Poly(ethylene terephthalate) or PET is a condensation polymer synthesized from terephthalic acid and diol(alcohol) in a reversible reaction. TPA and Ethylene glycol (diol)both are derived from crude oil. Ester bond formation takes place during condensation. Commercially it is also called polyesteror Terelene or Dacron or Terlon.

PET is a thermoplastic polymer, which softens on heating and becomes hard on cooling. In thermoplastics, molecules are joined end to end into a series of long sole carbon chain. These longer chains are independent of each other. The backbone structure of this polymer is made by carbon and carbon, due to this reason, breaking of bond at normal condition or degradation is not easy.

PET is semi crystalline polyester of high strength, it is transparent, it is safe, and it has long shelf life. Its molecular weight may range from 15000 to 36000 g/mole. It has good mechanical properties and it is low cost plastic.PET was first used commercially as textile fibre in 1940,when itwas combined with natural fibres such as cotton. The combination of cotton and polyester yields a fabric, that dries quickly without wrinkling and has the comfort like that of cotton. PET was firstly developed for use as fibre by British Calico Printers in 1941, then patent rights were sold to Dupont and ICI. 1960 onwards it is being used as packaging material. ThePET in the form of bottles was, for the first time, presented in 1973 and became essential part of packaging in soft drink bottles, food packaging, drinking water bottles etc. because of low permeability of CO_2 and oxygen. Usage of PET is increasing continuously. The PET used in textile industry has the molecular weight ranging from 15000 to 20000 g/mole, however for bottle grade PET, molecular weight rangesfrom24000 to 36000 g/mole. Textile industry is using approximately 60% of the total production of PET worldwide, in packaging, this number is 28% and remaining PET is used in applications such as X-ray films, house hold products, engineering and building materials.

Poly(ethylene terephthalate) is non-toxic in nature, but it does not degrade easily, since its inception its usage is increasing continuously; with increase in demand its waste management began to pose serious problem. Environmentalists are deeply concerned due to huge deposits of PET in land-fills and in waterresources.Recycling of PET on the basis of method used can be classified as follows:

(i) Primary recycling

(ii) Secondary recycling or mechanical recycling

(iii) Chemical recycling or Tertiary recycling: The chemical process for converting plastic or polymer waste, back to raw material is also known as depolymerization.

(iv)Quaternary recycling.

Out of all these methods, chemical recycling is most important and widely accepted according to the principles of sustainable development. In this method formation of monomer from which polymer is originally made is recovered, therefore this is the most environment friendly technique. Chemical recycling is carried out by two ways: (i) Solvolysis (ii) Pyrolysis.

In solvolysis degradation of polymer happens in presence of solvent including water.Solvolysis is further divided as follows

(i) Hydrolysis (ii) Aminolysis (iii) Ammonolysis (iv) Methanolysis (v) Glycolysis;while pyrolysis involves degradation of polymer by heat in absence of air or oxygen.

Depolymerization of PET by Hydrolysis: Recovery of monomer terephthalic acid (TPA) from polymer PET is widely studied. This method is a matter of interest because in this process both the starting materials terephthalic acid and ethylene Glycol are recovered. Hydrolysis of PET is possible in alkaline medium, acidic medium or in neutral medium.Alkaline hydrolysis of PET is carried out usually in

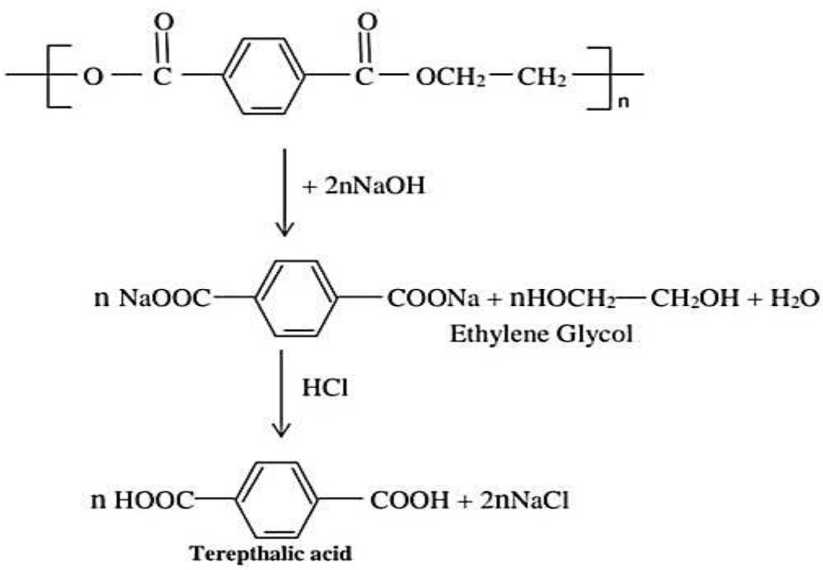


Fig: Alkaline hydrolysis of PET wasteby usingNaOH.

aqueous solution of NaOH or KOH, this process is also known as saponification with alkali. Recovery of monomer by alkaline NaOH depends upon quantity of NaOH, particle size of polymer, temperature and time duration of reflux. Normally alkaline hydrolysis requires higher temperature(between 100 to 200^{o}C) and longer time period to yield satisfactory recovery.

Effect of Catalyst:

Different types of catalysts were used to improve rate of reaction and for shortening the time for monomer recovery. Acetate of zinc, lead, manganese, cobalt etc. are some of the examples, among these zinc acetate and manganese acetates are reported as good catalyst. However, environmentalisthave expressed their concern over the pollution due to toxicity and corrosive nature of these catalysts. Therefore, according to the principle of green chemistry Phase Transfer Catalystsare selected, PTC is efficient yet environment friendly. These catalysts are used in those reactions in which inorganic and organic phase both are present, where anion reacts with organic substrate. PTC is a source of lipophiliccations. Often tetra alkyl ammonium cations serve this purpose as catalyst. Tetra butyl ammonium bromide (PTC) is used in this experiment. These have covalent bond between Nitrogen and Carbon. Therefore, this catalyst has organic character. Catalytic role of PTC is to transport –OH reactive anion from NaOH (miscible part) to external surface of PET powder (solid phase), in this way, the ester linkage in PET molecule becomes easier to attack by hydroxyl ion and depolymerization increases the return of terephthalic ion to aqueous phase.

Experimental: Conversion of PET waste powder into Terephthalic Acid

Conversion of PET waste powder was carried out in 250 ml Borosil round bottom flask equipped with reflux water condenser. This setup was placed on top of heating mantle. The whole experiment was carried out at 1 atmospheric pressure. On second mouth of round bottom flask magnetic stirrerwas placed and the third mouth was fixed with digital thermometer.In round bottom flask 10 gm of PET waste of 100 µm particle size was taken along with 8 gm of NaOH in 100 ml of double distilled water. The mixture was refluxed for the various time intervals ranging from 30 to 150 minutes. The reaction mixture was filtered for the separation of unreacted PET waste powder. The filtrate was treated with concentrated HCl till the solution became acidic in nature. After addition of required quantity of HCl, white precipitate of Terephthalic Acid (TPA) was obtained. This process was carried out repeatedly for different time intervals and temperatures.

It was washed repeatedly with double distilled water to remove excess HCl for complete removal of HCl. It was tested by addition of dilute Silver Nitrate solution for absence of HCl. The white ppt of TPA was dried in vacuum at 100°C and was weighed. The melting point of dried TPA was found to be 261°C.Recovery of TPA in NaOH from PET waste in 150 minutes at different temperatures was also observed.

The same process was performed in presence of Phase Transfer Catalyst (PTC), Tetrabutyl Ammonium Bromide and effect of catalyst was also observed.

Table No. 1: Recovery of TPA from PET waste of 100μm withNaOH at 100°C

Sr. No.	Time	% of TPA
1	30	22.5
2	60	40
3	90	66
4	120	73
5	150	80

Table No. 2: Recovery of TPA in 150 minutes at different temp.

Sr. No.	Temp	% of TPA
1	30	28
2	60	52
3	90	68
4	120	78
5	150	86

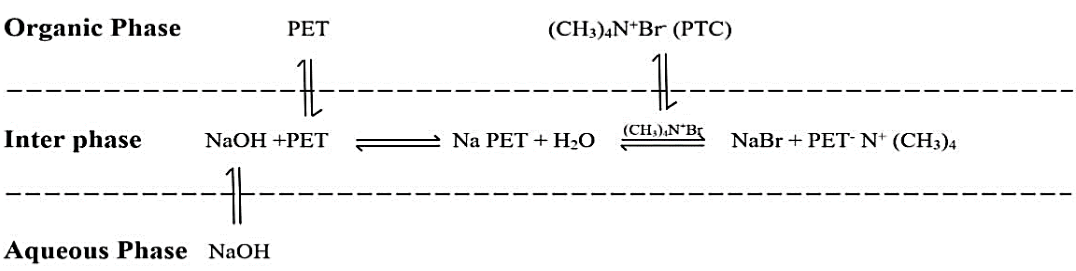
Table No. 3: Effect of catalyst, TPA recoveryat 100°C for various time intervals

Sr. No.	Time	% of TPA
1	30	52
2	60	72
3	90	70
4	120	93
5	150	92

Table No. 4: Effect of catalyst: Recovery in 150 minutes at different temp.

Sr. No	Temp	% of TPA
1	30	42
2	60	74
3	80	82
4	100	93

Phase Transfer catalyst plays an important role to improve recovery of monomer at relatively lower temperature and in lesser time because of an ion exchange reaction with the inorganic salt in aqueous phase and formation of an ion pair, which can cross the solid liquid interface due to lipophilic nature. In the organic phase, these ions undergo nucleophilic substitution reaction with the organic reagent to form the product. The new ion pair again goes back to aqueous phase and the cycle goes on and thus the product recovery becomes fast.



Conclusion:

Recovery of Terephthalic acid by alkaline hydrolysis in absence of catalyst consumes more time and requires higher temperature. At 150^{o}C, when reflux time was 150 minutes, only 86% yield was observed. When similar experiments were performed in presence of tetra butyl ammonium Bromide (PTC), 0.25% of PET waste weight at lower temp 100^{o}C and in 120 minutes, 93% recovery of monomer was observed. Use of PTC catalyst is thus, less time and energy consuming; and usage of PTC is a prudent step towards safer environment.

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