Study of Chemical Recycling of Poly (ethylene terephthalate) Waste

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Abstract
Chemical recycling of Poly (ethylene terephthalate), PET wastage has been investigated in this work. The aim of this work is terephthalic acid and ethylene glycols recovery from PET waste. This process has been done in two stages. First stage was reaction of PET waste with sodium hydroxide that produced ethylene glycol and sodium terephthalate solution and second stage was reaction of obtained sodium terephthalate with hydrochloric acid that led to terephthalic acid production. Variables such as operational temperatures and pressures, and quantity of consuming sodium hydroxide and hydrochloric acid have been studied. The needful quantities of sodium hydroxide and hydrochloric acid were achieved 50gr and 166gr per 1kg of PET waste, respectively. Operational temperature and pressure was achieved 180 °C and 1.5bar in the first stage respectively.

Keywords: poly (ethylene terephthalate), terephthalic acid, ethylene glycol, chemical recycling

Introduction
Due to upward usage of polymers and plastic materials especially in throwaway applications, wastage generation of these products is daily and relatively in large volume. Considering that plastic materials often are not resolvable with microorganisms and lead to environmental pollutions, it is necessary to recycle and return of these materials to the usage cycle. Of course environmental aspect aside, concerning to very high latent value of these materials economically, it can be attached great importance to recycling of them.

Generally, plastics such as: polyethylene, polystyrene, poly (ethylene terephthalate), polypropylene and poly (vinyl chloride) which used in packaging industries are interested to be recycled.

One of the most important thermoplastic polyesters which widely used in applications such as textile fibers, films and packing industries is Poly (ethylene terephthalate) (PET). Due to properties such as: high transparency in blown containers, high mechanical strength for minimum thickness walls, negligible permeability to CO\textsubscript{2} and relatively low cost, soft drink bottles is the most important application of PET, which produce a significant household and municipal waste. Therefore it is necessary to gain greater attention for recycling, PET waste bottle due to ecological factor and for obtaining valuable products.

Generally there are two global methods for recycling of PET waste, mechanical and chemical methods. In mechanical methods, generally beverage bottle can be recycled to the usage cycle by chipping them into very fine scraps, heating, melting and remodeling to new products. Frequently in mechanical methods the reground scrap PET is blended with virgin PET, the other polymers, and also mineral to achieve useful materials for different purposes. Frounchi M. et al, (1997) studied mechanical recycling of PET beverage bottle. They blended recycled PET with virgin PET to increase mechanical property of it. They found that mechanical blending can be used for recycling purposes without sacrificing of the virgin PET, and to reduce material cost in bottle fabrication [1]. Verney V. et al (2005) blended PET waste with polycarbonate (PC) to improve physical properties of mechanically recycled PET. They found that the blends have better

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properties than neat PET [2]. Navarro R. et al (2007) studied the influence of polyethylene cap of the bottle in the mechanical recycling of PET. They found that it is not necessary to totally separate polyethylene contents, because small percentages of PE may facilitate subsequent processing of the material using injection [3].

Chemical recycling of PET waste consist of depolymerization by hydrolysis, methanolysis, glycolysis and aminolysis to obtain various monomers. The hydrolysis of PET in presence of acid and base using suitable solvents has been reported by several researchers [4]. Neutral hydrolysis of waste PET with different amounts of water and different catalysts, in presence of xylene has been studied by Guclu G. et al (2003) [5]. Thermal and hydrolysis depolymerization of PET has also been studied by Sao and Cloyed [6]. Methanolysis of PET waste is used to form monomers, dimethyl terephthalate (DMT) and ethylene glycol (EG). Kurokawa H. et al (2003) studied methanolysis of PET in the presence of aluminium tisoproxide catalyst to form monomers. They found that using a toluene/methanol mixed solvent (20 vol. % toluene) instead of pure methanol, lead to obtain maximum yield of monomers, 88% for DMT and 87% for EG [7]. Genta M. et al (2006) used supercritical methanol for PET depolymerization instead of vapor methanol. They found that the rate of PET depolymerization in supercritical methanol is faster than that of PET depolymerization in vapor methanol [8]. Yang Y. et al (2002) study effect of some parameter on methanolysis of PET waste in supercritical methanol. They found that both yield of DMT and degree of PET depolymerization were seriously influenced by the temperature, weight ratio of methanol to PET and reaction time, whilst the pressure has no considerable effect, when it is above critical point of methanol [9]. Ghaemy M. and Mossaddegh K. (2005) studied glycolysis of PET waste using ethylene glycol. They investigated some parameter such as: reaction time, volume of EG, catalysts and their concentrations on the yield of glycolysis [10]. Karayannidis G.P. et al (2004) used glycolysis of waste PET to produce alkyd resins. They found that mechanical properties of produced resin are comparable with conventional general purpose resin [11]. Dullius J. et al (2006) also applied chemical recycling of waste PET to alkyd resins synthesis [12]. Shukla S.R. et al (2006) used glycolysis method for recycling waste PET into useful auxiliaries. The advantages of this method were that chemicals used during depolymerization of PET are inexpensive and comparatively less harmful to the environment [13]. Aminolysis is another method of chemical recycling of PET waste, which has been little explored as compared to other technique. Shukla S.R. et al (2006) method to produced bis (2-hydroxy ethylene) terephthalate (BHETA) by aminolysis of PET waste. They used excess of ethanolamine in the presence of different simple chemicals, namely glacial acetic acid, sodium acetate and potassium sulphate, as catalyst. They obtained good yield of BHETA as 91% [14]. Parra J.B. et al (2004) obtained High value carbon materials from PET recycling use of pyrolysis and subsequent activation of PET [15]. Barriocanal C. et al (2004) also studied producing of carbon materials from PET recycling [16].

In present work hydrolysis with sodium hydroxide was used for recycling of Pet waste has been studied. End of this work was recovery of Terephthalic acid and ethylene glycols from PET waste. Variables such as operational temperatures and pressures, and quantity of consuming sodium hydroxide and hydrochloric acid have been studied.

**Experimental**

Method used for this work was a two stage process. First stage was reaction between PET and sodium hydroxides according to the following reaction:

\[
\text{PET} + 2n\text{NaOH} \rightarrow n\text{Na}_2\text{C}_8\text{H}_4\text{O}_4 + n\text{C}_2\text{H}_6\text{O}_2
\]
Products of above reaction is ethylene glycol that was as first product of process, and sodium terephthalate that reacted with hydrochloride acid at second stage of process according to the following reaction:
\[
\text{Na}_2\text{C}_8\text{H}_4\text{O}_4 + \text{HCl} \rightarrow \text{C}_8\text{H}_6\text{O}_4 + 2\text{NaCl}
\]

**Materials and Equipment**

The PET used in all experiments was procured from Poly (ethylene terephthalate) beverage bottles. Reactions were carried out in water as solvent. Before charging the PET in the reactor, bottles was cut into 1mm $\times$ 1mm to about 6mm $\times$ 6mm flakes. Sodium hydroxide 85% by weight and hydrochloric acid 1molar was used for experiments.

A 10litres, high pressure pilot-plant reactor was used for all experiments. The reactor was well-equipped with an anchor impeller to ensure proper mixing. It was also equipped with a shell around it to circulate hot oil used for heating the reactor contents. Heat transfer oil be heated with a thermal element in a vessel and be recycled through the whole heating system by a pump.

Reactor was equipped with a condenser at the top of it to condense and collect vapors exit from reactor that can be collected in a small vessel and discharged through a valve as a product. All or part of these condensed vapors can be returned into the reactor from a recycling line.

**First stage**

1kg PET and 4lit water were charged in the reactor. Then 20gr sodium hydroxide was added to reactor. Water was used as solvent for reactants. The temperature of reactor was set to 110 °C. This temperature was provided with circulating hot oil in the shell around the reactor. Reactor contents were mixed by impeller. When temperature reached to the set value, in 5min intervals, pH of the reactor solution was measured until it became nature. If still there was some unreacted PET in the reactor, 20gr sodium hydroxide was added to the reactor and pH was measured as above again. This was continued until all of PET in the reactor was consumed.

It was seen that pH became constant at basic range in two sequential pH measurements. It was shown that reaction was stopped. Therefore this process was repeated for a higher temperature and insomuch was continued until reaction was completed at a proper temperature and needful quantity of sodium hydroxide. Pressure of reactor depended on its temperature. Ethylene glycol obtained from reaction as vapor went to the condenser during the process and collected in a vessel in liquid state. At the end of reaction Sodium terephthalate was discharged from reactor and was washed and dried.

**Second stage**

In this stage terephthalate salt obtained from former stage react with hydrochloric acid and produce terephthalic acid. To perform this reaction obtained salt be washed with water to remove residual sodium hydroxide and then be dried. 453gr sodium terephthalate obtained from first stage and 166gr hydrochloric acid with 2lit water were charged in the reactor and temperature was set on 40 °C. In 5min intervals, reaction solution pH was measured. Upswing of pH was shown that reaction was completing, otherwise temperature was increased and reaction was repeated until it was completed.

Obtained terephthalic acid was insoluble in water and was settled at the bottom of reactor. it was discharged from reactor through a valve from bottom of reactor, washed with water and dried.
Results
Figure 1 shows conversion variation of first reaction with temperature. It is seen that maximum conversion is about 92% that occurred at 180 °C and increasing temperature has no considerable effect on conversion. At this temperature the pressure of reaction is 1.5bar. Figure 2 shows variation of needful sodium hydroxide quantity with conversion in the first reaction. It is seen that 500gr of sodium hydroxide is needful per 1kg of PET for 92% conversion.
Figure 3 shows conversion variation of second reaction with temperature. It is seen that maximum conversion is about 88% that occurred at 90 °C. Figure 4 shows variation of reaction time of two reactions with conversion. It is seen that reaction time for 92% conversion is about 180min for first reaction and reaction time for 88% conversion is about 90min for second reaction.
IR tests were performed on obtained product and compared with IR spectrum of proof samples. Figure 5 and figure 6 show IR spectrums of obtained ethylene glycol from reaction between PET and sodium hydroxide and pure ethylene glycol as proof sample, respectively. It is seen that IR spectrum of ethylene glycol obtained from reaction nearly coincide on IR spectrum of proof sample and alcoholic group specified with 3425 number, can be observed on the spectrum. Figures 7 and 8 show IR spectrums of obtained terephthalic acid from reaction between terephthalate sodium and hydrochloric acid and pure terephthalic acid as proof sample, respectively. It is seen that IR spectrum of terephthalic acid obtained from reaction nearly coincide on IR spectrum of proof sample. At the IR spectrum of proof sample numbers of 3434 is relate to carboxylic group, 1383 is relate to aromatic cycle and 1687 relate to carbonyl group while these number at IR spectrum of terephthalic acid obtained from reaction are 3432, 1393 and 1583 respectively.
Conclusion

Concerning to various methods of chemical recycling of PET, it was seemed that hydrolysis of PET with sodium hydroxide is easier to operation and also purity of product is acceptable. In this method poly (ethylene terephthalate) waste bottles were converted to ethylene glycol and sodium terephthalate salt by reaction with sodium hydroxide and then sodium terephthalate salt reacted with hydrochloric acid to produce terephthalic acid. The needful sodium hydroxide for reaction with 1kg of PET was obtained 500gr. Optimum value of temperature for reaction between PET and sodium hydroxide was obtained 180°C. At this temperature reaction conversion was 92%. This reaction continued about 180min. the amount of produced ethylene glycol was 200ml and terephthalate salt was 453 per 1kg of consuming PET.

Optimum value of temperature for reaction between sodium terephthalate and hydrochloric acid obtained 90°C at 88% conversion. This reaction continued about 90min. in this stage 166gr hydrochloric acid per 453gr sodium terephthalate was used and 433gr terephthalic acid was obtained.

References