Glycolysis of waste PET using Zeolites as a Catalyst

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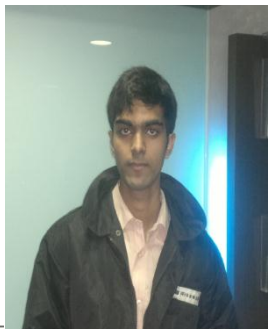

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ABSTRACT:

Polyethylene terephthalate (PET) bottle waste can be depolymerized using excess of ethylene glycol (EG) in the presence of zeolites, b-zeolite and Y-zeolite as transesterification catalyst. The glycolysis reaction can be carried out under reflux in excess of ethylene glycol for up to 8hrs. The product of glycolysis was mainly the virtual monomer, bis(2-hydroxyethyl) terephthalate (BHET) admixed with dimer as residue. The BHET obtained will be in pure crystalline form. Influence of the reaction time, PET: EG ratio, type, and concentration of catalyst on the yield of the glycolysis products were investigated. The yield of BHET monomer will be more than 60%, which is comparable with the conventionally used heavy metal catalysts such as zinc acetate and lead acetate. Melting point of zeolite is much greater than oligomer. So the oligomer+zeolite mixture can be separated by heating it to the melting point of oligomer followed by solid-liquid separation. This process of glycolysis of PET is economically viable and the catalysts are environment friendly.

Key words: polyester; recycling; monomers; oligomers; zeolites.

1. INTRODUCTION:

Polyethylene terephthalate (PET) is one of the most valuable versatile engineering plastics which are used in the manufacturing of soft drinks bottles. With increasing application and decreasing prices, PET became the symbol of disposability in consumerism and hence a noxious material of concern in the relatively recent environmental protection issue, as it is resistant to atmospheric and biological agents. Therefore the necessity of finding a simple economic route for the recycling of waste PET is an important practice for suitable recycling and contributes to the conservation of raw petrochemical products and energy[1]. The amount of plastic production has been increasing significantly year by year, with uses including fiber, packing, container, building materials, etc. Plastics offer a tremendous convenience for our life. However, the proliferation of plastic uses has raised waste disposal issues. In recent years, disposal of waste materials has come into focus as an environmental problem that affects everyone. PET resin, a common form of plastics, has excellent characteristic features such as thermal stability, clarity, transparency, light, and is processible. The amount of PET consumption has rising each year, used for producing fibers, textiles, video and audio tapes, food packing and containers. With the increasing of PET consumption, its recycling has received considerable attention for the ecological and economic considerations[2].

There are two distinct approaches to the recycling of postconsumer polyester waste. It may be reused directly through **physical reprocessing** of grinding, melting, and reforming[4].

Chemical Depolymerization of PET can be done by using several methods such as hydrolysis, methanolysis, aminolysis, glycolysis etc. **Hydrolysis** of PET can be carried out by water, acid or alkali under pressure. The ultimate products are terephthalic acid (TPA) and ethylene glycol (EG). During **Methanolysis**, PET waste is treated with methanol under pressure to recover dimethyl terephthalate (DMT) and ethylene glycol (EG) in the presence of catalyst. **Aminolysis** is the reaction of PET with different aqueous amine solutions to yield the corresponding diamides of TPA and EG[3].

Glycolysis of PET can produce the BHET monomer, which has been widely used in the production of unsaturated polyesters and rigid or flexible polyurethanes, the glycolysis process was chosen for further investigation in our study. This process is very sluggish without a catalyst. So

depolymerization of PET with ethylene glycol (EG) must be done in the presence of catalyst. Glycolysis proceeding under the influence of EG is the true reverse reaction to the polycondensation of PET, reproducing the BHET monomer. Usually a partial hydrolysis of the PET wastes with EG is applied to obtain a low molecular mixture of oligomers and BHET. The mixture is re-circulated to the PET synthesis process or used in the synthesis of co-polyesters[9] (see Figure 1)

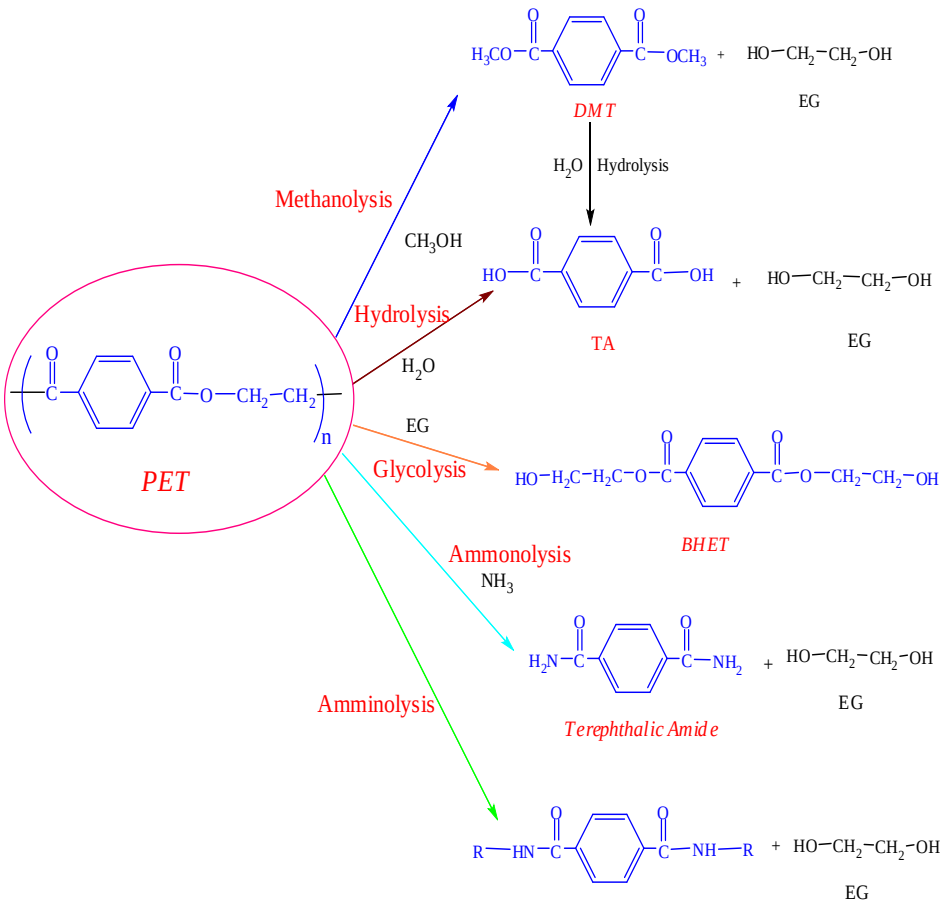

Fig. 1: Schematic representation of various methods of chemical depolymerization of PET.

*from ref no. 4

2. Glycolysis of PET waste:

The PET fiber waste is treated with ethylene glycol at a molar ratio of 1 : 6 (PET : EG) under reflux in the presence of different catalysts for time periods up to 8 hrs. Various catalysts are used in this process concentrations ranging between 0.3 and 1% (w/w). At the end of the reaction, distilled water is added in excess to the reaction mixture with vigorous agitation. The glycolyzed product is obtained as a residue after filtration. The filtrate contains unreacted ethylene glycol, bis-2-hydroxyethylene terephthalate (BHET), and small quantities of a few water-soluble oligomers. White crystals of BHET were obtained by first concentrating the filtrate by boiling and then chilling it. The glycolyzed residue is then boiled with water to extract any remaining BHET. White crystalline powder of BHET is purified by repeated crystallization from water, dried in an oven at 80^0C and weighed to estimate the yield[5]. (see Table 1)(see Figure 2)

Table 1: Chemicals used in glycolysis

Chemicals	Molecular formula	Molecular weight	Density (g/cm^3) at 20^0C	Melting point (^{0}C)	Water solubility at 90^0C
PET	$(C_{10}H_8O_4)_n$	192	1.4	240-270	Insoluble
EG	$C_2H_6O_2$	62	1.113	-12.9	Miscible in all proportion
Water	H_2O	18	1.0	0	-
BHET	$C_{12}H_{14}O_6$	254		109-112	Soluble

*****from Material Safety Data Sheet on internet

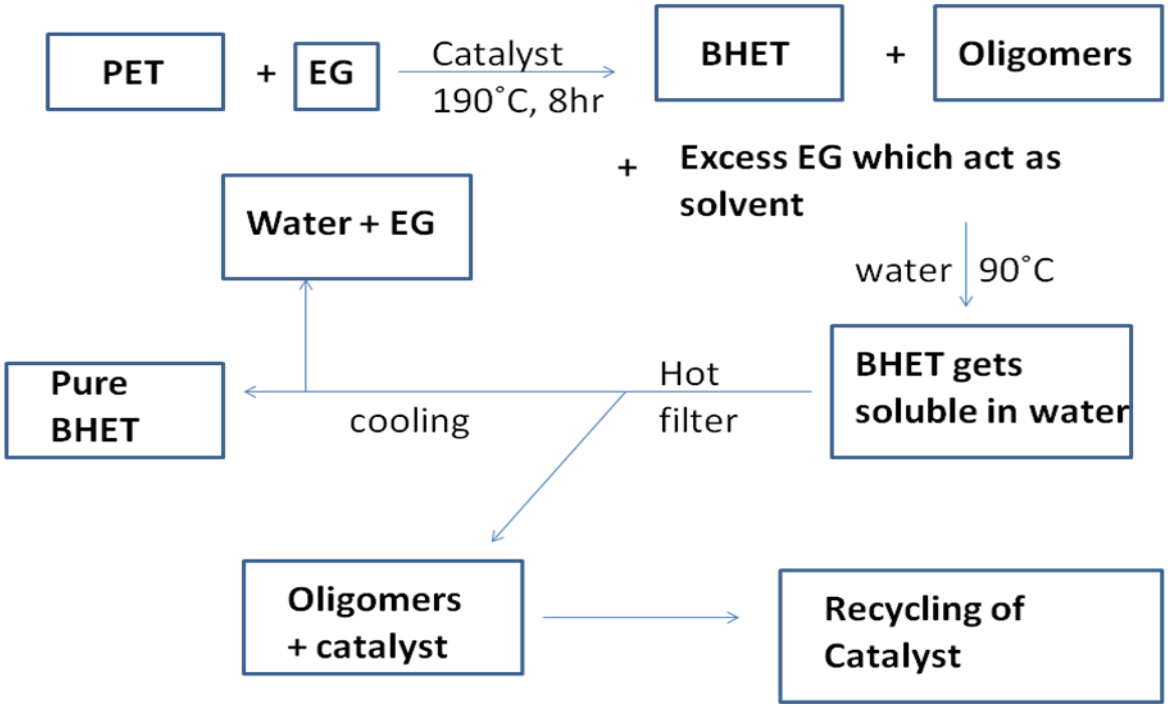

Fig. 2: Schematic representation of Glycolysis of PET. (*drawn by ourselves)

2.1 Reaction mechanism: (see Figure 3)

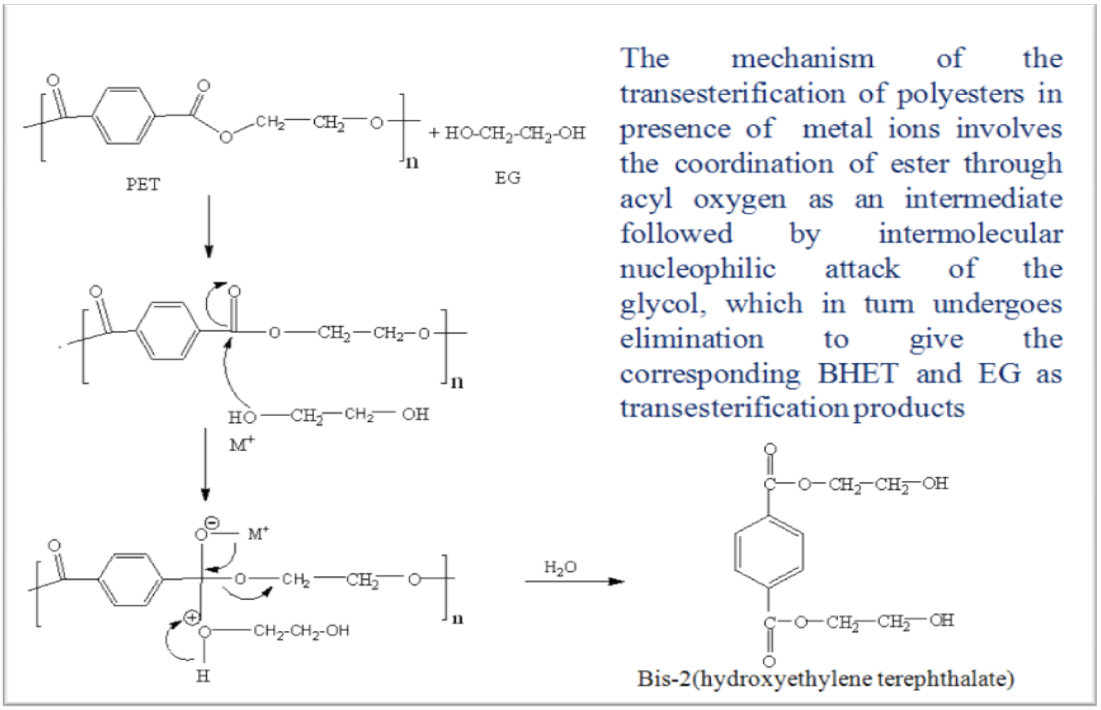

Fig. 3: Schematic representation of reaction mechanism. (*from internet google images)

3. Catalysts used for glycolysis:

Glycolysis of polyester is carried out **conventionally** at atmospheric condition using different types of metal catalysts like zinc acetate, lead acetate, titanium phosphate, solid super acids etc. The simple chemicals such as glacial acetic acid or salts of simple metal cations lithium, sodium, and potassium are found to be capable of depolymerizing PET fiber waste through glycolysis. Although the BHET yields are little less compared to the conventional catalysts such as zinc acetate, considering the environmental safety factors, the chemicals used stand better acceptance for the depolymerization reaction. Thus, glycolysis has been made possible with cheap, ecofriendly, and almost equally effective catalysts without the requirement of a pressure reaction[5, 10]. (See Table 2)

Table 2: Effect of various catalysts on glycolysis of PET

Catalyst	BHET yield for 0.5 % conc. of catalyst	BHET yield for 1.0 % conc. of catalyst
Zinc acetate	67.63	61.31
Sodium bicarbonate	66.22	63.78
Lead acetate	65.91	62.18
Sodium sulphate	65.72	60
Sodium carbonate	65.43	62.18
Potassium sulphate	64.42	60
Lithium hydroxide	63.5	54.07
Acetic acid	62.42	57
β- zeolite	60	66
Y- zeolite	58	65

*from reference no. 4,5,10

3.1 Disadvantages of conventional catalyst:

1. Zinc and lead both are heavy metal cations that cause pollution due to their nonbiodegradable and toxic nature.
2. The heavy metals possess a tendency to accumulate in the living organisms over a period of time.
3. High exposure level affects the central nervous system.
4. Affects the aquatic animals.
5. The permissible limits of Pb and Zn cations in the effluent discharged to the Surface water are 0.1 and 5 ppm, respectively and Separation of catalyst is difficult.

To overcome these disadvantages of conventional catalysts simple chemicals such as glacial acetic acid or salts of simple metal cations lithium, sodium, and potassium can be used.

But these catalysts also have some disadvantages such as

1. Separation of catalyst is difficult.
2. Little low yield of BHET as compared to conventional catalysts.

3.2 Disadvantages of catalyst recovery techniques:

1. The cost of these techniques is very high.
2. The amount of catalyst used in the reaction is very small in proportion **but the recovery or recycling of it is very expensive as compared to the cost of the catalyst**.

3.3 Various separation techniques for the Water and EG mixture:

1. Vacuum distillation to separate water from the mixture.
2. Liquid-liquid extraction to separate EG by using solvents like Hexane, DMC etc.
3. Reverse osmosis.

To get rid of these conventional as well as simple chemical catalysts **zeolites as a catalyst** can be used.

4. Glycolysis using Zeolites as catalyst:

The **mechanism** we are proposing is the **Solvent Free Reaction for the glycolysis of waste PET.** In this reaction, EG itself acts as a solvent as well as take part in the reaction.

A solvent-free or solid state reaction may be carried out using the reactants alone or incorporating them in clays, zeolites,

silica, alumina or other matrices. Thermal process or irradiation with UV, microwave or ultrasound can be employed to bring about the reaction.

Initially, the reaction mixture is biphasic, one solid phase (PET) and a liquid phase (EG). When the chemical structure of polyesters (molecular weight and compositions) allows their solubilization, they pass into solution due to the presence of terephthalic moieties and lowering the EG concentration, due to the introduction of polyesters. The solubilization of polyesters is maximum at 196^0C. The PET weight (%) loss is higher at higher temperatures.

4.1 Advantages of solvent free reaction:

1. These reactions occur more efficiently and with more selectivity compared to reactions carried out in solvents.
2. Such reactions are simple to handle, reduce pollution, comparatively cheaper to operate and are especially important in industry.
3. It is believed that solvent free organic synthesis and transformations are industrially useful and largely green.
4. Ease of purification.
5. High reaction rate (due to high concentration of reactant).
6. Bring down handling costs due to simplification of experimental procedure, work up technique and saving in labour. These would be especially important during industrial production.

4.2 Zeolites (as a catalyst):

Zeolites are naturally occurring crystalline alumino-silicates wherein Si^{4+} and Al^{3+} atoms are tetra coordinated, shared with oxide ions. This feature develops a negative charge on the aluminum atom and demands the existence of counter-ion to reach neutrality of crystalline structure outside the framework when protons (H^+) are used; these materials act as Bronstead acids. Such zwitter ionic character is responsible for the unique chemistry of these materials. Zeolites have the ability to act as catalysts for chemical reactions which take place within the internal cavities. Zeolites find major uses in petroleum cracking, ion-exchange (water softening and purification), and in the separation and removal of gases and solvents. They are often referred to as molecular sieves. (see Figure 4)

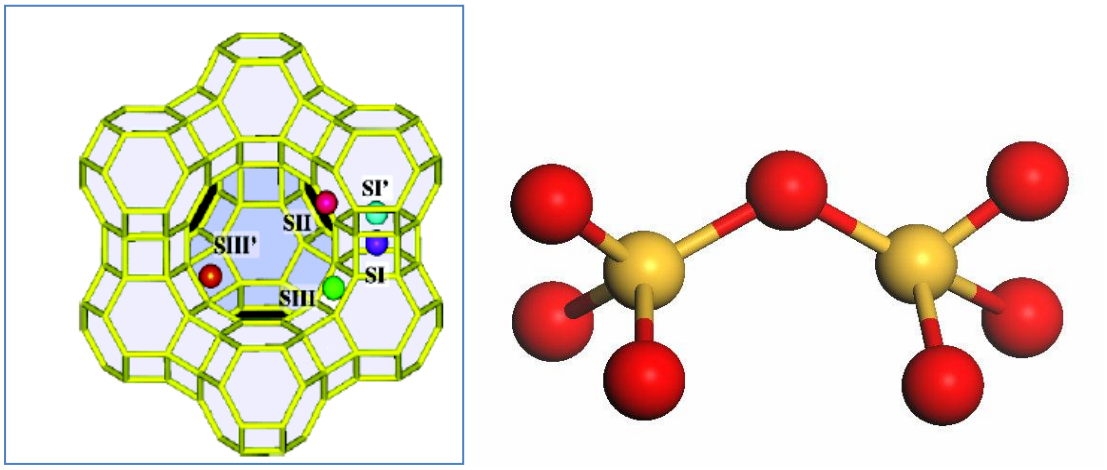

Fig. 4: Molecular structure of Zeolites. (*from internet google images)

For each Al, a negative charge is created. The negative charge is compensated by cation.

- Highly porous (high surface area)
- Cations are exchangeable.
- The zeolite has cages.
- Sharply defined pore structures:
    - Shape selective
    - Molecular sieves
- The aluminum sites are very acidic.

The Zeolites which we are considering are,

1. **β-zeolite:**
    - Na form, SiO_2/AlO_2 ratio= 1:5 powder.
    - It has lower Si/Al ratio and less active sites, hence it cannot solubilize PET as fast as Y-zeolite.
2. **Y- zeolite:**
    - H form, SiO_2/AlO_2 ratio= 4:5.
    - Y-zeolites have high Si/Al ratio and large mesopore surface since it has high hydrothermal stability and suitable acidic and porous properties for catalytic reactions.
    - This directly affects the ion exchange equilibrium providing major part of the surface area and the active sites.

- The number and strength of active sites present in Y-zeolite are the crucial parameters for solubilization of PET and thus it helps in depolymerization of PET in a shorter time.

At the very initial stage (2 hr), glycolysis proceeds at a high rate for the Y-zeolite giving 58% yield of BHET, whereas in the case of β-zeolite, the yield of BHET even after 7 hr is 65% using 1% (w/w) concentration of β-zeolite and 1:6 PET: EG ratio[4].(see Table 3)

Table 3: Material analysis for the reaction

Basis: Given weight of PET is 10.00g.

Chemicals	Given Weight	Molar ratio	Number of moles	Final Weight
PET	10.00g	1	0.052	-
EG	19.31g	6(excess)	0.312	-
BHET	-	-	-	6.5g
Water	700.00g(excess)	Excess	Excess	-
Oligomers	-	-	-	3.5g
Catalyst(Zeolites)	0.1g	1% of PET	-	As per separation

*from reference no.4

4.3 Advantages of zeolites:

1. Zeolites are naturally occurring crystalline alumino-silicates.
2. They act as Bronstead acids.
3. It plays a significant role in reducing toxic impact of conventional catalysts on the environment.
4. Zeolites contribute to a cleaner, safer environment in a number of ways.

4.4 Separation of zeolite catalyst:

1. Melting point of zeolite is much greater than oligomer. So the oligomer + zeolite mixture can be separated by heating it to the melting point of oligomer. At this temperature oligomer will melt and can be separated by solid liquid separation i.e. filtration. Zeolite can be recovered after separation.
2. But the energy requirement for this separation is very high. So this process of separation is very expensive as compared to the cost of zeolite and the activity of the zeolite will decrease by the repetitive use.

5. Uses of BHET and Oligomers:

1. The purified BHET is converted to different fatty amide derivatives to obtain quaternary ammonium compounds that have a potential for use as softener in the textile finishing process. Application of these synthesized compounds is carried out on cotton fabric; they are evaluated for performance and are found to give good results. The chemicals used during depolymerization and reuse of PET are inexpensive and comparatively less harmful to the environment, and thus offer advantages in the chemical recycling of polyester waste fibers.
2. BHET produced in this way may be used alone or together with other monomers for the production of PET or aromatic copolyesters. BHET obtained from industrial PET waste can be used for various products.
3. Oligomer fractions can be used to prepare PET by adding TA to it.

6. CONCLUSION:

The most advantageous method for the recycling of PET is the Glycolysis. Zeolites used as a catalyst can give good yield as well as good recovery. It is

ecofriendly process as well as economical. This process will serve the purpose of future need of recycling of waste PET. This process will reduce the hazards of conventional catalyst.

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