

Depolymerization of Poly(ethylene terephthalate) Wastes through Glycolysis using Lewis Acidic Bentonite Catalysts

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In the present investigation, the authors explored the depolymerization of waste poly(ethylene terephthalate) (PET) beverage bottles using glycolysis (transesterification) catalyzed by Al^{3+} , Fe^{3+} and Zn^{2+} impregnated bentonite catalysts. Heterogeneous catalysts such as clay, zeolite, alumina *etc.* preferred over homogeneous catalysts, thus we focused on the development of solid acid catalysts based on economically viable clay catalysts. The desired Lewis acidic nature was introduced by wet impregnation method at variable metal ion to clay ratio such as 0.5, 1.0, 2.0, 3.0, 4.0 and 5.0 wt. %. The effect of metal-ion loading on the surface area, pore volume and crystalline nature of the bentonite has been evaluated by nitrogen adsorption and desorption studies and XRD. The PET wastes collected from post-consumer beverage bottles were depolymerized using ethylene glycol as a glycolytic agent afforded *bis*(2-hydroxy ethyl)terephthalate (BHET) in 85-90 % yield under optimized conditions. The yield of BHET was observed to be increasing with increase in Lewis acidic metal ions loading from 0.5 to 4.0 wt. % as well as increase in catalysts to PET ratio. Among the catalysts, Al^{3+} and Zn^{2+} -bentonite catalysts showed higher yield of BHET up to 90 % at 4 and 5 wt. % loading of metal-ion.

Keywords: Bentonite, Catalysis, Depolymerization, Glycolysis, Poly(ethylene terephthalate), Solid waste management.

INTRODUCTION

The conversion of solid polymeric wastes into reusable monomers with potential applications is of great importance from the environmental and economical perspective. Among the multifunctional polymeric materials, poly(ethylene terephthalate) (PET) is widely used for the manufacturing of mineral water bottles, soft-drinks bottles, food packaging, synthetic fibers, and insulation materials [1]. The major contributor for PET production as well as consumption is from China followed by India. Almost, 80 % of the global production of PET is located in Asian countries [2]. As a result, these countries become the victims of highly polluted by the non-degradable PET wastes. However, the growing environmental awareness and the innovations in the solid waste management have led to the development of novel recycling methods of PET wastes. Nearly, 70 % of the post-consumer PET wastes are consumed for production for fibers and 4 % consumed for the chemical recycling process. Among these, chemical recycling methods include glycolysis; methanolysis, aminolysis and acidic/alkaline hydrolysis are

widely used eco-friendly methods to recover the terephthalic acid from PET wastes when compared with conventional land-filling and incineration [3]. Thus, effective recycling of PET wastes through chemical process is elevated as one of the economically viable ways of saving resources and resolving "white pollution" caused by the excessive consumption of PET wastes [4].

The post-consumer PET wastes are glycolyzed using ethylene glycol in the presence of metal salts especially, zinc salts at 190-240 °C for 38 h, which afforded 80 % of BHET as a major product as well as other oligomers. In addition, glycolysis procedures make use of non-recoverable homogeneous Lewis acid catalysts for the depolymerization, which is both environmentally and economically not viable [5]. Because these homogeneous catalysts possess major disadvantages like isolation and recycling of spent catalysts, high reaction temperature, purification of products and removal of dyes from the coloured PET materials. Heterogeneous catalysts based on the microporous and mesoporous materials offers solution to overcome the problems encountered with homogeneous

catalysts. For instance, mesoporous carbon materials supported solid super acid catalysts used to achieve the effective glycolysis of PET wastes.

Numerous efforts [6-8] have been attempted to develop recoverable heterogeneous catalysts, acidic/basic ionic liquids, binary metal oxides, organic bases and porous materials for the efficient glycolysis of post-consumer PET wastes to replace the conventional catalysts. However, the reports on the use of microporous and mesoporous materials for the catalytic depolymerization are vaguely appeared. Shukla *et al.* [9] investigated glycolysis of PET waste using sodium form of γ - and β -zeolite as catalyst. The glycolyzed product was obtained in 65 % yield at 196 °C using 1 % catalyst. However, the authors were not comprehensively investigated the catalytic activity of zeolite catalyst. Bartolome *et al.* [10] utilized super-paramagnetic γ -iron oxide nanoparticles for the glycolysis of PET polymer wastes. By using this catalyst, the glycolysis reaction was achieved up to 90 % yield at 300 °C and the spent catalyst were recovered by magnetic decantation. Although, the catalyst showed efficiency, removal of dyes or colourants from the glycolyzed PET waste is much difficult and also requires higher reaction temperature. Metal oxides of Zn, Ce and Mn doped over silica nanoparticles have been utilized as recoverable catalysts for the glycolysis reaction. Among all the catalysts, manganese dioxide doped silica nanoparticle afforded 90 % yield [11]. Microwave assisted glycolytic recycling of PET bottles waste have been conducted using ethylene glycol as glycolyting agent in the presence of zinc acetate, sodium carbonate and sodium bicarbonate as catalyst. The reaction time drastically reduced from 8 h to 35 min, and the yield of BHET increased to 65 % using microwave as the heating source [12].

In earlier study, the effect of Al^{3+} , Fe^{3+} and Zn^{2+} containing kaolin on the depolymerization of PET polymer using glycolysis was reported [13]. In the present investigation, the PET wastes from soft drink bottles depolymerized using glycolysis process catalysed by Al^{3+} , Fe^{3+} and Zn^{2+} containing bentonite catalysts. Commercially available bentonite clay catalysts ion exchanged with Al^{3+} , Fe^{3+} and Zn^{2+} ions to bring the Lewis acidic character and characterized using XRD and BET techniques. The optimization of glycolysis reaction parameters such as temperature, PET to catalyst ratio and PET to glycol ratio have been optimized to obtain maximum yield of BHET. The glycolyzed products were identified using ^1H and ^{13}C NMR.

EXPERIMENTAL

Bentonite and aluminum nitrate, ferric nitrate, zinc nitrate and 1, 2-ethylene glycol were of reagent grade purchased from Loba and used for the reaction as such without further purification. The substrate poly(ethylene terephthalate) polymer obtained from waste water bottle. All the glassware's and quick-fits employed in the experimental work were made up of corning/borosil glass thoroughly all the glassware's were washed and dried in hot air oven before use.

Impregnation of Al^{3+} , Fe^{3+} and Zn^{2+} : In the present work, metal ions impregnated at 0.5, 1.0, 2.0, 3.0, 4.0 and 5 wt. % loadings into bentonite catalysts were prepared. Thus, in wet-impregnation process, for various percentage loadings of Al^{3+} , Fe^{3+} and Zn^{2+} ions varied while amount the clay was kept

constant. For instance, preparation of 1.0 wt. % Al^{3+} containing bentonite was prepared by adding 1.44 g of $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (mol. wt: 375.13 g/mol) as a metal-ion source into 100 mL distilled water containing 10 g of bentonite and the mixture stirred well at 100 °C for 12 h. The impregnated catalysts were isolated by filtration. The loaded catalysts were dried in vacuum at 120 °C for 6 h and stored in desiccator. The similar procedure adopted for the preparation of Fe^{3+} and Zn^{2+} containing bentonite catalysts.

Characterization of bentonite catalysts: The synthesized catalysts were characterized using XRD and BET analysis in order to determine the crystalline nature and surface area and pore diameter of the catalyst. The XRD analyses was performed on a PANalytical powder diffractometer model Empyren. The XRD pattern of bentonite catalysts was recorded at 2θ angle between 5 and 80°. The surface area and porous nature was determined using nitrogen adsorption and desorption isotherms which performed on a volumetric gas adsorption apparatus (Micrometrics, Canada, Model: ASAP2420).

Catalytic activity: The catalytic activity of 0.5, 1.0, 2.0, 3.0, 4.0 and 5 wt. % Al^{3+} , Fe^{3+} and Zn^{2+} impregnated bentonite was studied towards glycolysis of PET wastes using ethylene glycol as glycolyting reagent.

General procedure for glycolysis of PET wastes: PET bottle wastes (1.0 g) was melted to thread and crushed. To that 20 mL of ethylene glycol was added and heated to 190-200 °C. After reaching the desired temperature, the reaction mixture stirred for 1 h until the PET was dissolved in ethylene glycol. To a homogenous solution, 200 mg of bentonite catalyst was added. The temperature of the reaction was maintained using a temperature controller. Subsequently after 1 h time interval, 0.25 mL of reaction mixture was withdrawn and diluted by acetone. The progress of the reaction was monitored using pre-coated aluminium TLC plates. The spots were eluted using *n*-hexane and ethyl acetate (50:50) solvent mixture and detected at 356 nm light source. After completion of reaction, the mixture was diluted with acetone followed by filtration to remove clay catalyst. After the removal of catalysts, the reaction mixture was dried to evaporate acetone using rotary evaporator. Then, the reaction mixture was diluted with 100 mL 50 % ethyl acetate-hexane mixture. The glycolyzed products were obtained as precipitate and isolated by filtration and allowed to be dried at 70 °C under vacuum. The yield was calculated from the weight of dried product.

Characterization of glycolyzed products: The glycolyzed products were identified from their characteristic absorption bands in the infrared spectrum and were recorded on Nicolet-AVATOR 360 FT IR on solid sample as KBr pellet. The proton NMR spectra were run on Bruker Ultra shield 400 MHz NMR spectrometer.

RESULTS AND DISCUSSION

The commercially available bentonite clay was purchased from Loba Chem Pvt. Ltd., India and used for the ion exchange with Al^{3+} , Fe^{3+} and Zn^{2+} nitrate salts. The wt. % of metal-ion content in bentonite was kept as 0.5, 1.0, 2.0, 3.0, 4.0 and 5.0 wt. % with respect to bentonite weight in order to evaluate the effect of metal-ion loading on glycolysis reaction. The wet-

impregnation method has been successfully adopted for the preparation of bentonite catalysts. The synthesized catalysts were characterized using wide angle powder XRD and nitrogen adsorption and desorption studies revealed the change in crystalline behaviour, surface area and porous nature.

XRD pattern of bentonite catalysts: The XRD patterns of pure bentonite and ion-exchanged catalysts are presented in Fig. 1. In order to identify the change of crystalline nature, the diffraction pattern of 5 wt. % metal-ion exchanged bentonite catalyst was compared with the pure bentonite. The bentonite mineral is generally composed of kaolinite, montmorillonite, quartz and caritobalite in 7-39 %, 0.4 to 21 %, 30-75 % and 5-20 %, respectively. In bentonite catalyst, montmorillonite was abundantly found as compared to other minerals. Bentonite forms lattice structures which is composed of a single plate located between two alumina and silica plates. Because of the layer structure, the montmorillonite can expand and contract, and have to absorb water and cations. Thus, bentonite could be used as catalyst supports. The cation exchange can be expected to occupy the inter-layer space of montmorillonite which could be reflected by the size of its interlayer space (d_{001} and d_{020}) of montmorillonite [14]. The XRD patterns of metal ion impregnated bentonite indicated a decreased shift in the position of the d_{001} peak from 12.58 to 12.36, 12.23 and 12.28 Å, respectively for Al^{3+} , Fe^{3+} and Zn^{2+} and a slight decreased shift in the position of d_{020} peak from 6.94 to 6.76, 5.88 and 5.66 Å for Al^{3+} , Fe^{3+} and Zn^{2+} , respectively. A decrease in (d_{001} and d_{020}) spacing could be indicative of an increase in the interlayer space due to the impregnation of metal ions [15]. In addition, XRD patterns of pure and Al^{3+} , Fe^{3+} and Zn^{2+} containing bentonite catalysts showed similar crystalline peaks indicating that the metal-ion exchange is not affected the network of bentonite.

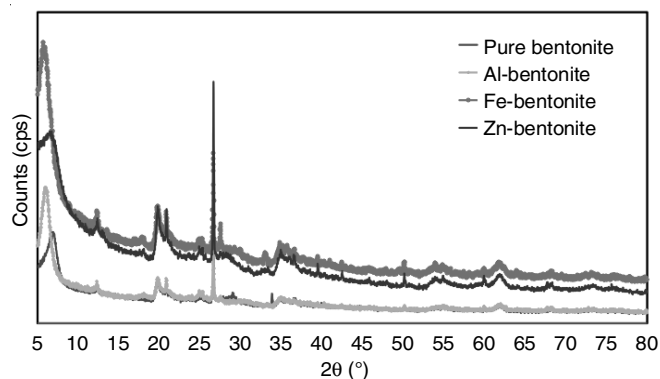


Fig. 1. Powder XRD patterns of pure bentonite and 5 wt % of Al^{3+} , Fe^{3+} and Zn^{2+} catalysts

Surface area analysis: Fig. 2 shows the results of nitrogen adsorption and desorption isotherms of bentonite and Al^{3+} ion-exchanged bentonite catalysts. In the present study, pure bentonite (Fig. 2a) showed BET surface area 42.18 m^2/g with

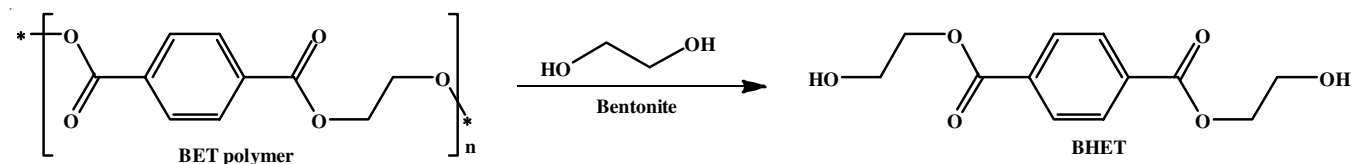
pore volume 0.03509 cm^3/g and pore diameter 6.01 nm. However, it is interesting to note that ion-exchange with Al^{3+} , Fe^{3+} and Zn^{2+} showed notable changes in the surface area and porosity. For instance, increase wt. % loading of metal ions from 1 to 5 wt. % increased the surface area from 42.18 to 126.80, 345.44 and 78.52 m^2/g , pore volume from 0.03509 to 0.06239, 0.3618 and 0.09907 cm^3/g for Al^{3+} , Fe^{3+} and Zn^{2+} , respectively. In contrast, pore diameter decreased from 6.01 to 4.87, 4.57 and 5.58 for Al^{3+} and Zn^{2+} ion-exchanged bentonite catalysts (Table-1). As compared to pure bentonite Fe^{3+} -bentonite showed tremendous increase in the surface area and pore volume and marginal variation was observed in surface area and porosity for Al^{3+} and Zn^{2+} -exchanged bentonite. Increase in surface area and pore volume may be attributed by interlayer widening of bentonite by metal ions. The similar phenomenon also supported from the powder XRD analysis.

TABLE-1
BET SURFACE AREA, PORE VOLUME AND
PORE DIAMETER OF BENTONITE CATALYSTS

| Catalyst | BET surface area (m^2/g) | Pore volume (cm^3/g) | BJH average pore diameter (nm) |
|-----------------------|--------------------------------------------|----------------------------------------|--------------------------------|
| Bentonite | 42.18 | 0.03509 | 6.01 |
| Al-bentonite (1 wt %) | 7.95 | 0.02679 | 13.12 |
| Al-bentonite (5 wt %) | 126.80 | 0.06239 | 4.87 |
| Fe-bentonite (1 wt %) | 3.68 | 0.02493 | 26.30 |
| Fe-bentonite (5 wt %) | 345.44 | 0.36180 | 4.57 |
| Zn-bentonite (1 wt %) | 5.73 | 0.02615 | 18.26 |
| Zn-bentonite (5 wt %) | 78.52 | 0.09907 | 5.58 |

Glycolysis of PET wastes and optimization of parameters: The waste beverage bottles were thoroughly washed with hot water to remove the dirt's and labels. After drying, bottles were cut into small pieces and heavy-duty laboratory blender was used to crush the PET chips. The coarse PET powder used for the glycolysis reaction. The glycolysis of PET polymer has been carried out using ethylene glycol as a transesterification agent in the presence of bentonite catalysts (Scheme- I). The catalytic efficiency was calculated based on the yield of bis(hydroxyl ethyl)terephthalate derivative (BHET). The effect of metal loading, PET to ethylene glycol ratio and catalysts to PET ratio have been optimized. The results are summarized in Fig. 3.

Effect of metal ion loading, 1 g (20 wt. % with respect to catalyst) of PET wastes were glycolyzed with 200 mg (1:5 catalyst to PET ratio) of Al^{3+} , Fe^{3+} and Zn^{3+} loaded bentonite catalysts at 190-210 °C in ethylene glycol medium (Fig. 3a). The reaction progress was monitored by TLC method. The reaction mixture stirred for 12 h. The TLC plates showed the presence of BHET oligomers in trace amounts along with major product. Among the metal ion loading 0.5, 1, 2 and 3 wt. % loaded catalyst showed low yield of BHET irrespective of the metal ion. However, 4



Scheme-I: Glycolysis of PET wastes

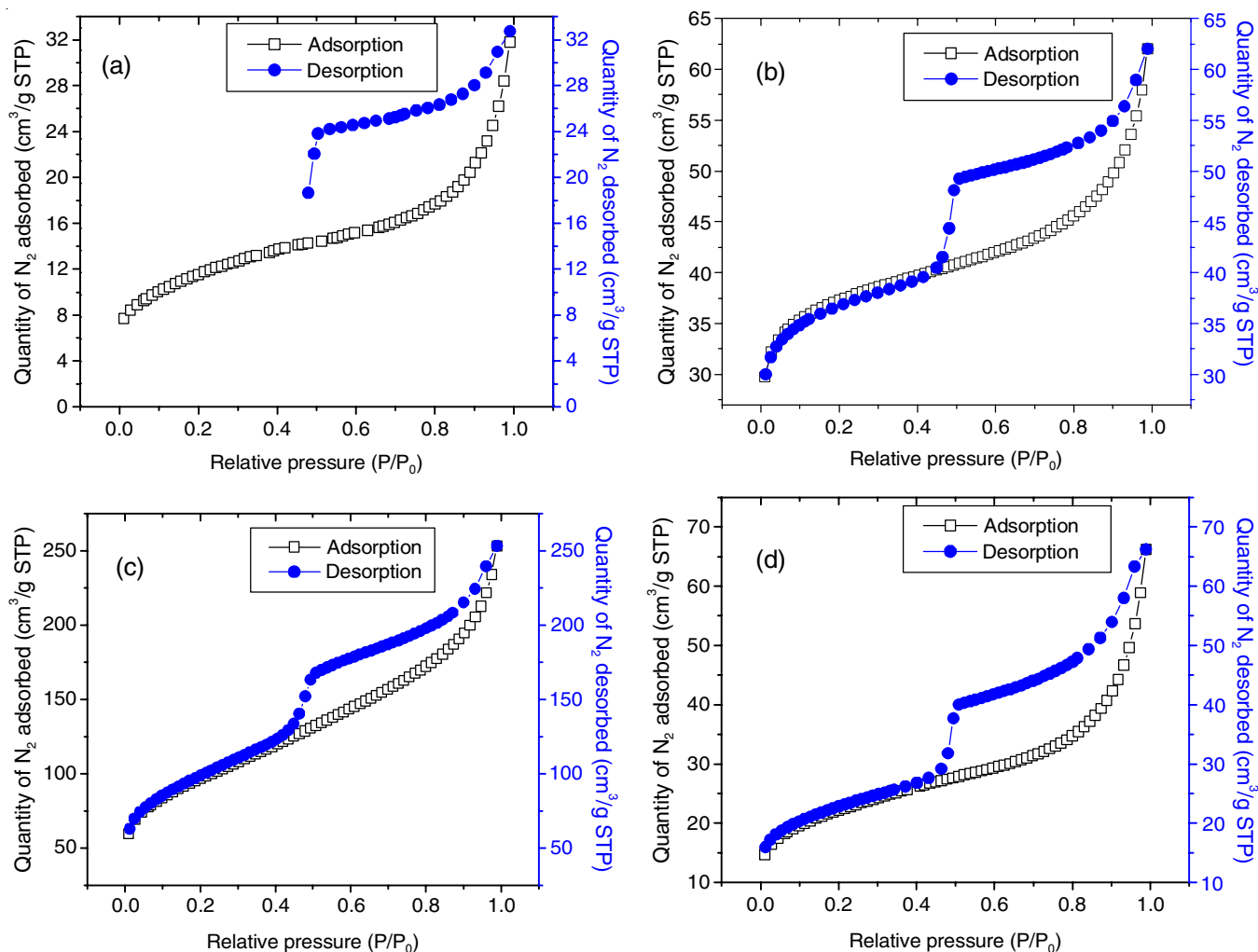


Fig. 2. Nitrogen adsorption-desorption isotherm of (a) pure bentonite, (b) Al^{3+} -bentonite (5 wt %), (c) Fe^{3+} -bentonite (5 wt %), (d) Zn^{2+} -bentonite (5 wt %)

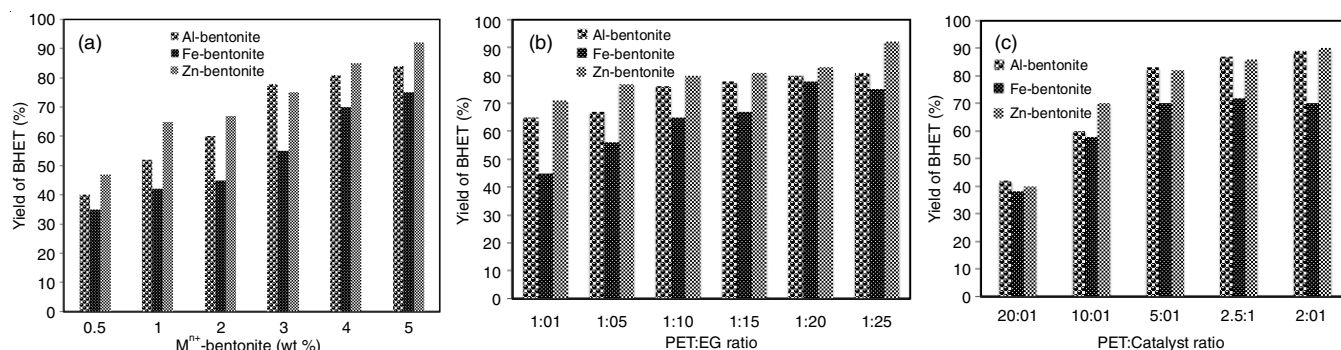


Fig. 3. (a) M^{n+} -Bentonite catalyst (b) PET:EG ratio (g:mL) (c) catalyst: PET ratio (wt %)

and 5 wt. % loaded Al^{3+} and Zn^{2+} containing bentonite catalysts afforded 80-85 % of BHET. The expected glycolized product, *bis*(hydroxy ethyl)terephthalate (BHET) was obtained by diluting the reaction mixture with 50 mL of acetone. Then, the reaction mixture was filtered through a Whatman filter paper No. 1 to remove the clay catalyst. After filtration, acetone solvent evaporated and 50 % ethyl acetate:*n*-hexane mixture added. The resultant precipitate dried and yield was calculated. The metal ion loading at 4 and 5 wt. % Al^{3+} and Zn^{2+} -bentonite showed yield above 80 % as compared to Fe^{3+} -bentonite. The effect of metal loading showed significant changes in the yield

when increase the loading from 1 wt. % to 5 wt. %. For instance, the yield of BHET was observed 49 % for 0.5 wt. % loaded Zn^{2+} -bentonite reached 85 and 90 % for 4 and 5 wt. % metal loading, respectively. Thus, 4 and 5 wt. % of Al^{3+} and Zn^{2+} loaded catalyst might be viable catalysts for glycolysis.

Fig. 3b summarize the effect of PET to ethylene glycol ratio on the yield of BHET. For the optimization process, PET:EG ratio was taken from 1:1 to 1:25 w/v. The conversion of PET to BHET was found to be 60-70 % at 1:1 and 1:5 w/v ratio and reaction mixture was difficult to stir as well as non-homogeneity of the reaction mixture may be attributed to the lower

conversion. At PET:EG ratio 1:10 and 1:15 the reaction mixture become homogeneous at 190-210 °C. But the reaction afforded the yield of BHET 78, 67 and 81 % for Al-bentonite, Fe-bentonite and Zn-bentonite. But 1:20 and 1:25 ratio yielded more than 90 % of BHET. Optimization of catalysts to PET ratio is summarized in Fig. 3c. The optimized catalyst to PET ratio was achieved by taking 5 wt. % Al³⁺, Fe³⁺ and Zn²⁺ loaded bentonite catalyst with respect to weight of PET polymer. The result showed that 1:5 ratio of catalyst to PET is the optimization studies, 5 wt. % of Al³⁺ and Zn²⁺-bentonite catalyst at 1:5 ratio of catalyst to PET using 1:20 ratio of PET to ethylene glycol afforded good yield of BHET.

The spectral characterization of depolymerized product, BHET have been made to confirm the expected derivative using ¹H and ¹³C NMR and FT-IR as reported earlier [13]. The aromatic protons are appeared at 8.10 ppm as a singlet and aromatic carbons showed two peaks at 133.8 and 129.70 ppm confirmed the formation of BHET. The ester carbonyl appeared 166.1 ppm in ¹³C NMR spectra. The methylene (-CH₂-OC=O) protons attached ester carbonyl oxygen appeared as triplet 4.47 ppm and respective methylene carbon appeared at 67.0 ppm. Another, methylene protons appeared at 3.97 ppm and respective carbon observed at 61.1 ppm. The hydroxyl group appeared as broad peak at 3.70 ppm. Thus, based on ¹H and ¹³C NMR results, the formation of depolymerized product, BHET confirmed.

Conclusion

The present study explored that depolymerization of poly(ethylene terephthalate) (PET) polymer wastes could be effectively catalyzed by Lewis acidic metals containing bentonite catalysts using glycolysis (transesterification) reaction using ethylene glycol as glycolyting agent at 190-210 °C. Bentonite catalysts have been obtained by wet-impregnation method at 0.5, 1.0, 2.0, 3.0, 4.0 and 5.0 wt. % of Al³⁺, Fe³⁺ and Zn²⁺ using corresponding metal nitrate as a source. The present study showed that Al³⁺ and Zn²⁺ exchanged bentonite catalysts have found to efficient catalysts as compared to Fe³⁺ containing catalyst. The yield of depolymerized product, BHET is clearly depends upon weight percentage loading of metal ion on the bentonite. In addition, chemical structure of BHET was confirmed with ¹H and ¹³C NMR and FT-IR analysis.

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CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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