

CHEMICAL DEPOLYMERIZATION OF PET COMPLEX WASTES: HYDROLYSIS vs. GLYCOLYSIS

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Abstract

The huge increase in the generation of post-consumer plastic wastes has produced a growing interest about eco-efficient strategies and technologies for their appropriate management and recycling. In response to this PROQUIPOL Project is focused on developing, optimizing and adapting feedstock recycling technologies as an alternative of management for the treatment of complex plastic wastes. Among the different plastic wastes studied, PROQUIPOL Project is working on providing a suitable treatment to the highly colored and complex multilayered post-consumer waste fractions of PET by chemical depolymerization methods. Glycolysis and alkali hydrolysis processes have been studied with the aim of promoting the transformation of PET into bis (2-hydroxyethyl) terephthalate (BHET) monomer and terephthalic acid (TPA) respectively. In both cases operational conditions such as temperature, reaction time, catalyst to PET rate and solvent to PET rate have been considered to optimize product yield, achieving values nearly to 90% and monomer purities over 95% in both processes. This paper presents results obtained for each treatment as well as a simplified comparison of technical, economic and environmental issues.

Keywords: depolymerization, alkali hydrolysis, glycolysis, PET waste

1. Introduction

Needs of content preservation have been responsible for the development of barrier materials and marketing strategies favored the introduction of high colored materials associated to brands and quality perception. Currently, one emerging challenge associated to PET recycling, is to provide a suitable treatment to the highly colored and complex multilayered post-consumer waste fractions of PET. These fractions are not appropriate for mechanical recycling because derived products present limitations either in color, transparency or intrinsic viscosity, restricting their applications and value. In accordance with this, PROQUIPOL project is assessing the glycolysis (degradation of PET with ethylene glycol by a catalytic reaction to promote the formation of BHET [1]) and alkaline hydrolysis (degradation of PET by an aqueous solution of NaOH to promote the formation of TPA [2]) as alternatives of management for these non-mechanically recoverable fractions.

2. Materials and Methods

2.1. Materials

During this research work virgin PET supplied by NOVAPET and samples of highly colored and complex multilayered post-consumer PET wastes provided by ECOEMBES, the Spanish integrated management system for the light packaging waste, have been used. The caustic soda used in hydrolysis runs has been purchased from PANREAC. Meanwhile, glycolysis runs have employed EG

purchased from JABER and $Zn(Ac)_2 \cdot 2H_2O$ as catalyst (zinc acetate dihydrate 99.5%) from SCHARLAU.

2.2. Glycolysis process

Glycolysis experiments have been carried out in a 2 L stainless steel reactor. It has an electrical resistance to heat and control the temperature in the reactor, and a stirrer to ensure good mixing properties. The system can operate at a pressure of 6 bar. In a first step, a factorial design of experiments has been carried out with virgin PET to establish the better conditions for the process. Then, optimum experiment has been repeated with post-consumer PET. Factors under study in the factorial design of experiments have been process temperature (195, 208 and 220°C), reaction time (150, 180 and 210 min), EG/PET ratio (2, 4 and 6 w/w) and ZnAc/PET (0.2, 0.6 and 1.0 %w/w). After glycolysis reaction, boiling water has been added in excess to the reaction mixture under vigorous agitation. Then, the mixture has been filtrated obtaining a solid subproduct above the filter and a liquid phase. This recovered liquid has been refrigerated to ensure the crystallization of the BHET. A second filtration has been performed to separate BHET crystals from EG. BHET has been dried at 65°C until constant weight.

2.3. Alkaline hydrolysis process

Hydrolysis experiments have been carried out in a 1.8 L batch operated stainless steel reactor with a maximum operating pressure and temperature of 250 bar and 500°C, respectively. Reaction system included automated control, real time parameter monitoring, gas feeding lines and

manual sampling for liquids, vapours and gases. In all runs, 40 g of PET have been charged to the reaction system. Firstly, a set of reactions with virgin PET have been carried out to assess the influences of temperature, particle size and PET:NaOH ratio. Finished the reaction, the mixture has been filtered to remove non-reacted PET. After filtration, HCl has been added to promote the formation and precipitation of TPA. The solution has been filtered again where the solid phase, composed of TPA, has been cleaned with water to remove possible solid elements and dried at 80 °C during 2 hours for later analysis.

2.4. Analysis of products

A FTIR spectrophotometer and a DSC thermal analysis have been used to identify chemical structure and to determine purity of reaction products, BHET and TPA.

3. Results and Discussion

3.1. Glycolysis process results

As a result of the factorial design of experiments (DOE), the influences of temperature, reaction time, EG:PET and ZnAc:PET weight ratios have been achieved. Considering optimal operational conditions (195 °C, 150 min, 6:1 and 1.0 %w/w of catalyst), runs with post-consumer PET and recycled EG have been carried out. The results prove the effect of PET nature and reutilization of solvent over BHET yield, decreasing from 90%w to nearly 82%w in both cases (see Figure 1).

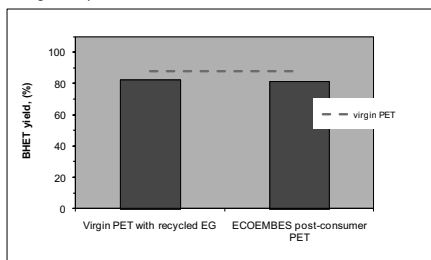


Figure 1. BHET yield in PET glycolysis process.

FTIR and DSC analysis of obtained BHET have been compared with the derived from commercial BHET. Results verify that chemical structures match up with the commercial one and that purity reaches values near to 96% in all cases.

3.2. Alkaline hydrolysis process results

After a set of reactions with virgin PET, the influences of temperature, PET: NaOH molar ratio and particle size have been assessed to select later the appropriate operation conditions. According to results obtained for the alkaline hydrolysis of post-consumer highly colored and complex multilayered PET in optimum conditions (150 °C, 1-0.5 mm, 2.4:1), PET nature doesn't show a remarkable influence on TPA yield, achieving in all cases yields similar or higher than 90% (see Figure 2).

Characterization of alkaline hydrolysis products has been analogous to that made in glycolysis. FTIR and DSC results confirm that chemical structures are identical to commercial one and purity values are over 95% in all cases.

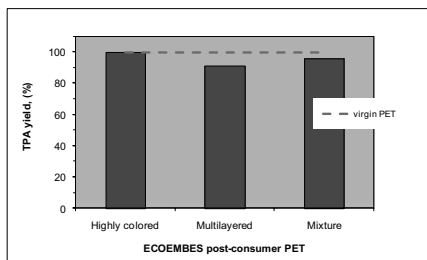


Figure 2. TPA yield in PET hydrolysis process.

4. Conclusions

A technical comparison between the two chemical recycling techniques shows that both achieved similar yields and purities to respective products (TPA and BHET). Regarding economic and environmental aspects, energy consumption in the glycolysis process can be slightly higher due to boiling water addition and EG recovery, although raw material cost is highly reduced. On the other hand, alkaline hydrolysis implies the use of HCl with the subsequently cost and environmental issues in the waste management.

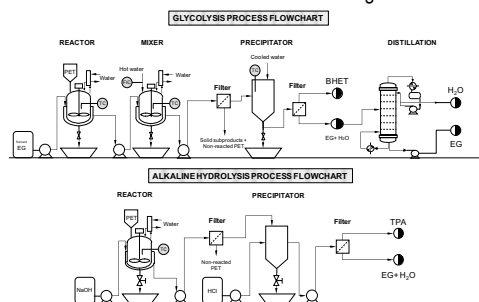


Figure 3. Industrial flowcharts of studied processes.

Finally, despite all, it can be concluded that economic feasibility of both processes will be established by socioeconomic factors such as PET consumption, the most consumed PET, virgin and recycled PET price or even mechanical recycling situation.

References

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