

STUDIES ON PROCESS OPTIMIZATION FOR CATALYTIC GLYCOLYSIS OF POST-CONSUMER PET WASTES

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Abstract

Glycolysis has been the subject of increased interest as a valuable feedstock recycling for poly(ethylene terephthalate). However, there are no reports on the technical literature that deal with the design and optimization of the global process. In this study, the global glycolysis process was optimized in terms of recycling of the unconverted residue, recovery of EG, the amount of water required for crystallization and eventual glycolysis of complex PET wastes. The conversion into BHET (monomer) of the non-glycolyzed solid was feasible and could be carried out in the presence or absence of fresh PET. The yield varied between (63-80%). The monomer could be recovered by extraction with hot water followed by crystallization at 4 °C and the optimized water:BHET ratio was 6.7 mL g⁻¹. The ethylene glycol/water was effectively separated by vacuum distillation and ethylene glycol of 99.6% v/v purity was recovered. Thus, it could be used in a new glycolysis process. Finally, the highly active catalytic role of sodium carbonate salt for glycolysis was evident not only for transparent PET wastes but also for complex wastes. The global glycolysis process was designed and optimized in order to increase the global efficiency thereby improving the economical viability of the recycling technology.

Keywords: PET wastes, recycling, glycolysis, process optimization, bis(2-hydroxyethyl) terephthalate

1. Introduction

The principle of chemical recycling is to convert high molecular weight polymers into low molecular weight substances via chemical reaction. PET can be depolymerised into the monomer, bis(hydroxyethyl) terephthalate (BHET), via glycolysis reaction in excess ethylene glycol (EG) [1]. The aim of this study was to optimize the global ecofriendly recycling process of PET extending our previous studies on the chemical valorization of post-consumer PET wastes by glycolysis [2,3], with the specific objectives of minimizing the mass and energy requirements of the reaction and separation processes and reducing the generated solid and liquid wastes.

2. Results and Discussion

In this work, glycolysis experiments were carried out in a four-necked double-walled reaction vessel, equipped with a stirrer, a thermometer and a reflux condenser operated at atmospheric pressure. Sodium carbonate was selected as transesterification catalyst. The following operation conditions were used: 196 °C, PET:EG molar ratio 1:7.6, PET:Na₂CO₃ molar ratio 100:1 and 1 h. The obtained monomer was separated by means of two consecutive steps (extraction with hot water followed by crystallization), quantified by gel permeation chromatography (GPC) and characterized by elemental analysis, differential scanning calorimetry, infrared spectroscopy, hydroxyl group determination, and nuclear

magnetic resonance. All these techniques revealed that the recovered product was highly pure [2].

Afterwards, the global glycolysis process was optimized in terms of recycling of the unconverted residue, recovery of EG, the amount of water required for crystallization and eventual glycolysis of complex PET wastes (Figure 1).

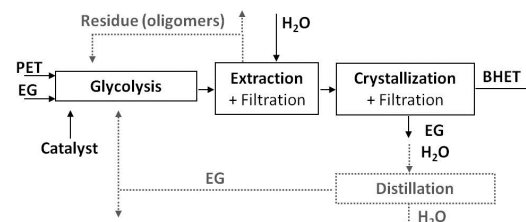


Figure 1. Scheme of the global recycling process.

When the equilibrium conversion was achieved at 196 °C (80%) the solid residue obtained after the first filtration step was composed by the dimer along with small amounts of oligomers ($n < 6$), as revealed by GPC [3]. This was reasonably expected to be a good raw material for glycolysis. On one hand, it was found the reaction rate was higher with increasing amount of partially glycolyzed residue in the reactor mixture, thereby suggesting a higher reactivity of the feed. On the other hand, the maximum equilibrium conversion decreased (from 80 to 64%) probably due to an accumulation of impurities present in the fed residue. These results regarding the optimized use and exploitation of PET

wastes gave valuable information about the way of reintroducing unconverted PET into the reaction process. In all the cases a purge would be necessary in order to avoid the accumulation of impurities in the global system.

The filtrate obtained from the BHET crystallization mainly contained unreacted EG and water. Since a high yield to BHET requires an excess of EG, it is of great importance to recover EG and re-use it for glycolysis. The EG was separated by vacuum distillation. Hence, ethylene glycol of 99.6% v/v purity was recovered and fed again in the reactor. The global cycle (glycolysis, extraction, and distillation) was repeated eleven times. It was found that conversion was virtually constant, around 80%. Although this observation could lead to assume that recovered EG is as reactive as fresh EG, it has to be pointed out that these results may be affected to an increased catalyst concentration during the consecutive reactions. In this sense, some additional experiments to clarify the intrinsic reactivity of recovered EG were performed. These experiments were focused on an eventual thermal degradation of the glycol during extended time on reaction at high temperatures. It was observed that the reaction rate was negatively affected when aged EG was used. However, in view of the yield reached after 1.5 h all the reactions carried out showed the same value (equilibrium conversion), probably owing to the excess of glycol used in all these experiments. These results therefore evidenced the recyclability of the EG in the glycolysis reaction.

The Na content in different streams of the global process was measured by ICP-AES. It must be pointed out that the presence of organic compounds in the sample interfered in the analysis and did not allow an accurate quantification of the sodium concentration. Therefore, the obtained values of sodium concentration were taken as a qualitative approximation. It was found that the catalyst used in the reaction was mainly present in the filtrate from extraction and crystallization and in the EG solution after distillation.

Next, experiments were focused on the BHET/H₂O separation process, more specifically on the crystallization step. The scope was to minimize the quantity of water required for the complete extraction of the obtained BHET. The degree of recovery by extraction notably increased up to a H₂O:BHET ratio close to 6.7 mL g⁻¹. Above this value it remained constant (99%), while the global degree of recovery also increased up to this value but decreased for higher quantities of water.

As the last step of this study, the glycolysis of complex (highly colored and multi-layered) PET wastes was performed. This task is of great relevance given the increased presence of this type of wastes in recycling plants. These fractions are not appropriate for a mechanical recycling and up to now their management can be only focused on incineration or landfill. The scope of this study was to evaluate the affinity of complex PET wastes for glycolysis in order to extend the versatility of the proposed recycling process. A set of glycolysis runs

was carried out with these complex wastes. Within experimental error, yields were between 70 and 80%, very close to the yield obtained with clear PET. Apparently the coloring compounds did not play any chemical role in the process and the recovered monomer was highly pure as determined by various analytical techniques (GPC, DSC and FTIR). However, they tended to discolor the glycolyzed products and a further purification process of the BHET would be necessary to extract the pigments.

3. Conclusions

Glycolysis can be described as a molecular depolymerization process by transesterification between PET ester groups and a diol (ethylene glycol) to obtain the monomer bis(2-hydroxyethyl) terephthalate (BHET). The monomer was separated by means of two consecutive steps, extraction with hot water followed by crystallization.

The global glycolysis process was optimized in terms of recycling of the unconverted residue, recovery of EG, the amount of water required for crystallization and eventual glycolysis of complex PET wastes.

The recirculation of the solid residue from extraction, the separation of the ethylene glycol and water mixture from the crystallization and the subsequent refeeding of the organic reactant in the depolymerization reaction, the minimization of the water amount used to recover all the monomer obtained in the glycolysis reaction and the suitability of the chemical recycling of PET of a more complex nature, are operational aspects which significantly increased the global efficiency and therefore improve the economical viability of the recycling process.

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