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Research article

Chemistry

**GLYCOLYSIS OF WASTE PET BOTTLES USING ETHYLENE GLYCOL
AS A SOLVENT AND A CALCINED SNAIL SHELL AS A CATALYST****以乙二醇为溶剂、煅烧蜗牛壳为催化剂的废宠物瓶糖醇解**

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Abstract

With the increasingly widespread use of polyethylene terephthalate (PET) bottles due to their cheap and robust nature, there has been an exponential increase in waste from these bottles in landfills, dumpsites, gutters, and roadsides, which has led to a negative effect on the environment, plants, animals, and human population with land and water pollution. Chemical recycling of the waste PET bottles would reduce the menace and recover the starting monomers for PET production. In this research, waste PET bottles were chemically recycled through glycolysis to produce bis-hydroxyethyl terephthalate (BHET) using ethyl glycol (EG) as a solvent and calcined snail shell as a catalyst within the temperature range of 180-200°C at different EG:PET ratios of 5:1, 6:1, and 6.5:1, while a constant catalyst:PET of 1:100 was used. After reaction and crystallization, a yield of the glycolysis product of 39.72% was obtained. This yield recorded is not as good as using oyster shell (68.6%), sodium acetate (72%), and calcium carbonate (69%) as catalysts. TGA and FTIR indicated that the samples were composed mainly of BHET monomers as functional groups. It is recommended that longer reaction time and varying catalyst:PET ratio be used to determine the optimum temperature and reaction.

Keywords: Glycolysis, Bis-Hydroxyethyl Terephthalate, Chemical Recycling, Polyethylene Terephthalate Depolymerization, Snail Shell

摘要

随着聚对苯二甲酸乙二醇酯(宠物)瓶因其廉价和坚固的特性而越来越广泛地使用,这些瓶子在垃圾填埋场、垃圾场、排水沟和路边产生的废物呈指数级增长,这对环境造成了负面影响。环境、植物、动物和人口受到土地和水污染。废宠物瓶的化学回收将减少威胁并回收用于宠物生产的起始单体。在这项研究中,废旧宠物瓶通过糖醇解进行化学回收,以乙二醇(例如)为溶剂,以煅烧蜗牛壳为催化剂,在180-

200摄氏度的不同例如温度范围内生产对苯二甲酸双羟乙酯(BHET):宠物比率为5:1、6:1和6.5:1,

同时使用恒定催化剂：宠物为1:100。反应结晶后糖醇解产物收率为39.72%。该产率记录不如使用牡蛎壳(68.6%)、乙酸钠(72%)和碳酸钙(69%)作为催化剂。TGA和红外光谱表明样品主要由BHET单体作为官能团组成。建议使用更长的反应时间和不同的催化剂：宠物比率来确定最佳温度和反应。

关键词: 糖醇解, 对苯二甲酸双羟乙酯, 化学回收, 聚对苯二甲酸乙二醇酯解聚, 蜗牛壳

I. INTRODUCTION

Polyethylene terephthalate (PET) is a tough and rigid artificial fiber and resin that belongs to the polyester family of polymers. Plastic bottles manufactured out of PET have become increasingly popular because of their excellent resistance to rupture, temperature, and gas passage, and even their reduced cost and weight compared with other packing materials like glass and metals. PET is now being used to manufacture well over half of all synthetic fiber and practically all containers of soda and water [1]. Despite the positive attributes of PET bottles, their disposal is a major challenge. Due to significant adverse environmental impact, economic considerations, and human health, the non-degradability of PET is a major hurdle to dumping this trash using traditional methods such as landfilling and incineration [2-4]. Considering ecological and economic considerations, recycling is considered as one of the most promising ways of addressing the issue of PET waste accumulation.

Plastic waste management procedures include burning, landfilling, and recycling. This portends major strategies for waste PET bottle recycling management and energy recovery as a fallout of their disposal [5, 6]. Plastic recycling is extremely poor globally, and large amounts of plastic are disposed of in landfills, where they remain for hundreds of years without naturally degrading. One ton of recycled plastics saves 5.74 cubic meters of landfill area and collecting and transportation costs. Mechanical recycling includes crushing and grinding to reduce PET particle size, re-extrusion, and reprocessing to create new PET products [7]. At the same time, depolymerization, purification, and repolymerization are the steps in the chemical recycling process. Incineration is the last resort where other management strategies are unavailable due to the high cost or lack of facilities for recycling. Incineration is quite environmentally unfriendly, with the emission of toxic gases [8].

Chemical recycling strategies include methanolysis – degradation of the waste PET using ethylene glycol at elevated temperatures to form bis (2-hydroxyethyl) terephthalate (BHET)

[9], aminolysis – degradation of PET using amines or ammonia to obtain BHET [10]; hydrolysis, which occurs in either an acidic, alkaline, or neutral environment to yield monomers of terephthalate acid (TPA) [11]; and glycolysis, where PET is degraded into oligomers and monomers [12].

II. METHODS/MATERIALS

A. Collection and Preparation of the Samples

Waste PET bottles were collected from plastic bins at Covenant University, Ota, Nigeria. The bottle caps, protective rings, and labels were removed from the bottles, then washed and rinsed with water to remove contaminants. Afterwards, the bottles were cut into a small size of 5 mm by 5 mm and air-dried to remove any moisture before being stored in closed containers.

B. Calcination of the Snail Shell

10 g of ground snail shell was heated in a furnace for two hours at 850°C. It was then kept in a desiccator to cool to room temperature, 27°C, then stored in a closed container.

C. Glycolysis of PET Bottles

At a constant mass of 0.1 g of a snail shell catalyst, with 10 g of waste PET, but at EG:PET ratios of 5:1, 6:1, and 6.5:1 at temperatures of 180°C, 190°C, and 200°C, the waste PET and EG were charged into a three-necked round bottom flask, which was connected to the condenser, with a thermometer placed in one of the necks. This was placed on a hot plate and subjected to the reaction at different temperatures with a magnetic stirrer for adequate mixing at 500 rpm. The reaction time was two hours. After two hours, the reaction mixture was allowed to cool to room temperature to stop the reaction.

100 g of boiled distilled water was added (at room temperature) to remove excess ethyl glycol (EG), and the solution was filtered by gravity filtration. The filtrate was heated on a hot plate until it became clear and allowed to cool to room temperature before being placed in the refrigerator at 10°C for 16 h for the crystallization of BHET.

The crystallized solution was then filtered

under vacuum, and the BHET was obtained as the filtrate, weighed, and stored in a small enclosed container in the refrigerator.

The reaction was then repeated at other temperatures and EG:PET ratios (Table 1).

Table 1.
Schedule of the activities

Temp.	EG:PET ratio	EG:PET ratio	EG:PET ratio
180 °C	5:1	6:1	6.5:1
190 °C	5:1	6:1	6.5:1
200 °C	5:1	6:1	6.5:1

Note: The constant catalyst:PET ratio - 1:100.

A schematic representation of the steps involved is presented in Figure 1.

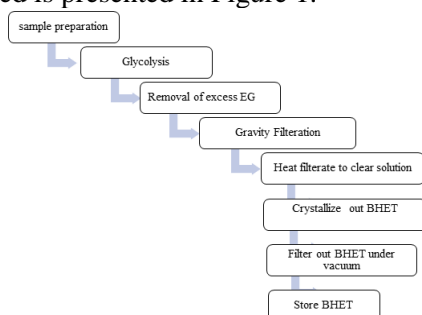


Figure 1. Schematic representation of the glycolysis steps

D. Characterization of BHET

FTIR and thermogravimetric analysis (TGA) were carried out on the reaction product, BHET.

III. RESULTS AND DISCUSSION

The mass of BHET and the computed yields are presented in Tables 1 and 2.

Table 2.
Mass of BHET recovered in grams (g) using the calcined snail shell as a catalyst

Temp. (°C)	EG:PET ratio		
	05:01	06:01	06.5:01
180	1.6785	2.4113	3.022
190	1.6789	2.570	3.728
200	3.182	3.422	3.972

The results of TGA and FTIR are presented in Figures 2-13.

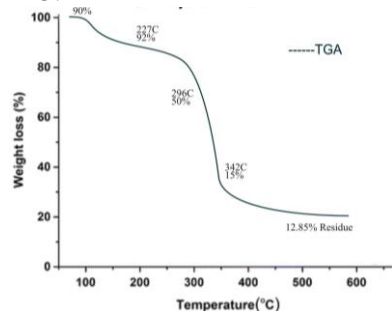


Figure 2. TGA at 5:1 (EG:PET ratio) at 190°C using a calcined snail shell as a catalyst

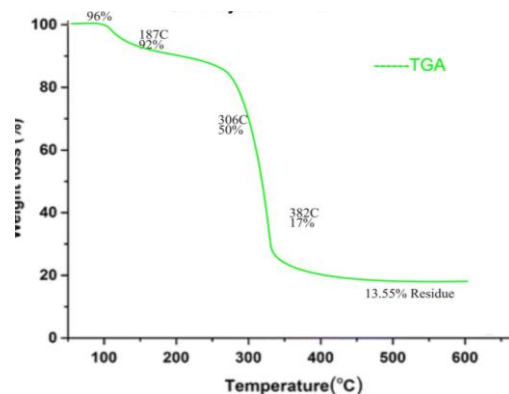


Figure 3. TGA at 6.5:1 (EG:PET ratio) at 180°C using a calcined snail shell as a catalyst

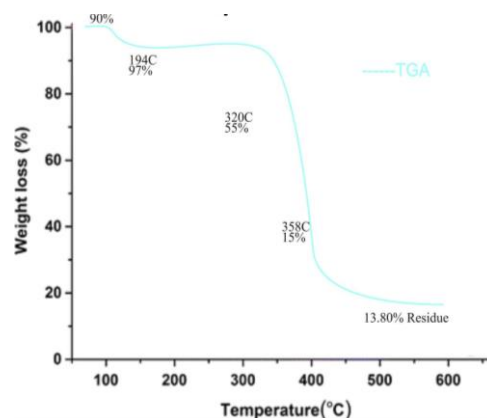


Figure 4. TGA at 6.5:1 (EG:PET ratio) at 190°C using a calcined snail shell as a catalyst

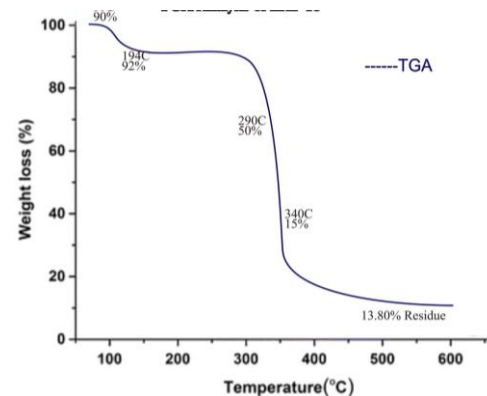


Figure 5. TGA at 5:1 (EG:PET ratio) at 190°C using a calcined snail shell as a catalyst

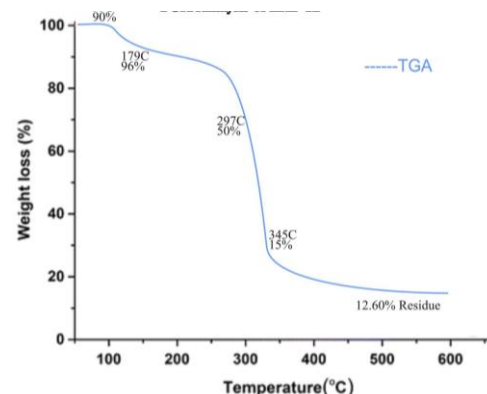


Figure 6. TGA at 6:1 (EG:PET ratio) at 190°C using a calcined snail shell as a catalyst

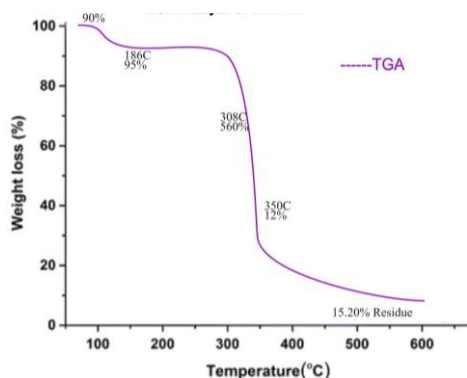


Figure 7. TGA at 6.5:1 (EG:PET ratio) at 200°C using a calcined snail shell as a catalyst

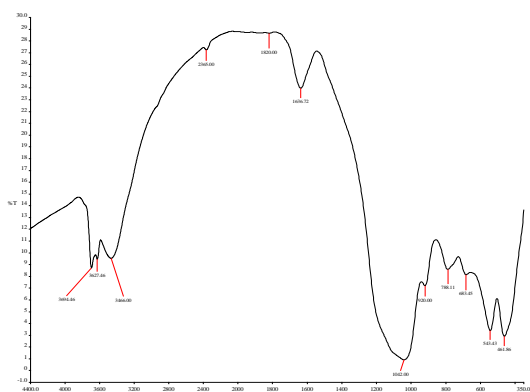


Figure 8. FTIR at 6:1 (EG:PET ratio) at 190°C using a calcined snail shell as a catalyst

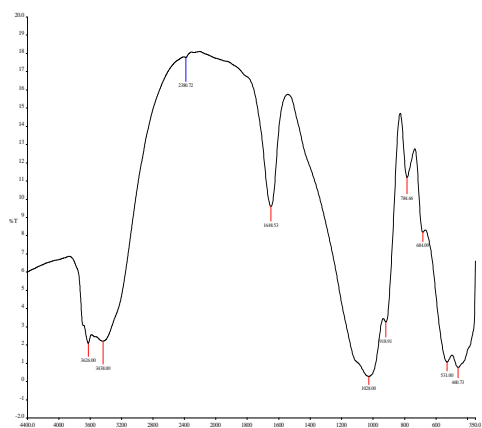


Figure 9. FTIR at 6.5:1 (EG:PET ratio) at 200°C using a calcined snail shell as a catalyst

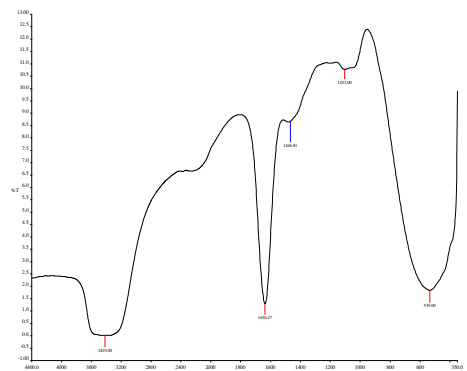


Figure 10. FTIR at 6.5:1 (EG:PET ratio) at 190°C using a calcined snail shell as a catalyst

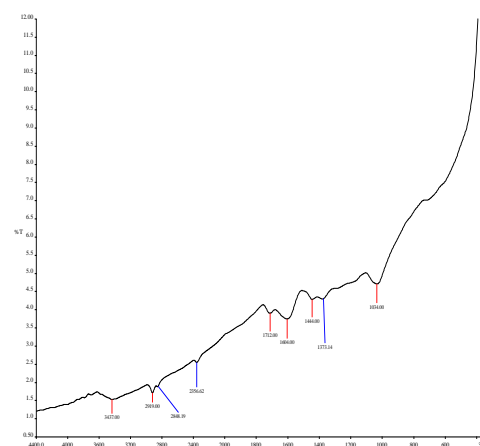


Figure 11. FTIR at 6.5:1 (EG:PET ratio) at 180°C using a calcined snail shell as a catalyst

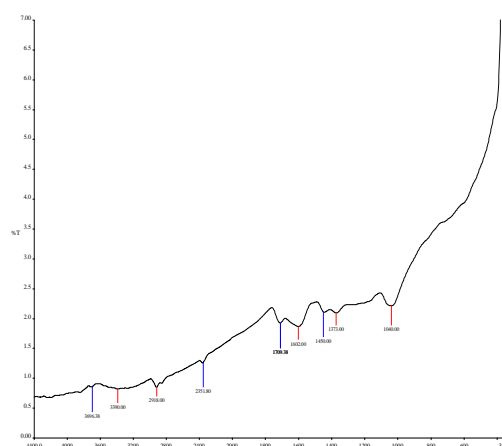


Figure 12. FTIR at 5:1 (EG:PET ratio) at 190°C using a calcined snail shell as a catalyst

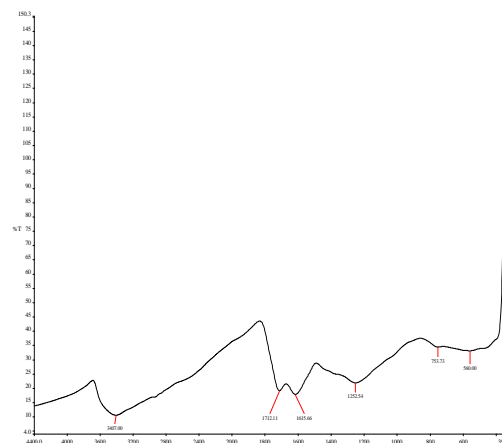


Figure 13. FTIR at 5:1 (EG:PET ratio) at 180°C using a calcined snail shell as a catalyst

A. Effect of Temperature

It was observed from Tables 2 and 3 that the increase in temperature at constant mass of PET bottles and catalyst increased the BHET yield when using a calcined snail shell as a catalyst. Compared to the results by Lopez-Fonseca et al. [13], it is similarly observed that an increase in the reaction temperature will increase the efficiency of the reaction.

Table 3.
BHET yield in percentage (%) using the calcined snail shell as a catalyst

Temp. (°C)	EG:PET ratio		
	05:01	06:01	06.5:01
180	16.785	24.113	30.220
190	16.789	25.700	37.280
200	31.820	34.220	39.720

Also, trends by Yunita et al. [14] show that as the temperature increased above 180°C, the yield increased sharply. Furthermore, the investigation states that the thermal effect on the reaction efficiency is stronger compared with the catalytic effect concentration [15].

The calcined snail shell used as a catalyst for PET glycolysis depolymerization has shown a performance that is less superior to the oyster shell-derived catalyst [16], which attained 68.6% conversion at 195°C. Also, Kumawat et al. [17], using sodium acetate and calcium carbonate as catalysts, recorded yields of 72% and 69%, respectively, at 190°C.

B. Effect of the Solvent:PET Ratio

The amount of solvent used was observed to significantly impact the final yield. Other glycols, such as ethylene glycol (EG), neopentyl glycol (NPG), propyl diethylene (PG), and diethylene glycol (DEG), can be used in glycolysis reactions. However, EG is more suitable and gives remarkable results in PET depolymerization [18].

The results in Table 2 indicate that higher amount of solvent with the same mass of PET recorded a much higher yield of BHET. It was observed that the most significant factor affecting the reaction is the EG/PET ratio. From the increasing ratio, the decomposition rate is increased, producing lower-weight oligomers. However, this solvent/PET ratio reaches a peak value, the balance between EG, oligomers, and BHET is established, and the degradation rate reaches a constant value [14].

Comparing the trend in Table 2 with previous works from Yunita [14] and Chandel [19], a similarity is observed as the increase in the solvent:PET ratio results in an increased final product.

C. Thermal Analysis

TGA curves of the glycolysis product are shown in Figures 2-8. The first decomposition occurs averagely in the temperature range of 110-140°C, and the second occurs between 300°C and 320°C. The samples were thermally stable up to 110°C before beginning to break down at 120°C.

The rapid mass loss occurred during the initial stage of decomposition in the temperature range of 120-140°C, with 19% of the component decomposing. The second mass loss happened between 300°C and 320°C, and a higher percentage of components, 56%, disintegrated.

The first mass loss occurred during the thermogravimetric analysis due to the temperature degradation of the BHET monomer. In contrast, the second mass loss is a result of the temperature degradation of the high chain oligomers or PET, which are created by the thermal polymerization of the BHET monomer. The result agrees with previous research by Wang et al. [18] in determining the thermal properties of glycolysis products.

D. FTIR (Fourier-Transform Infrared Spectroscopy)

Three FTIR spectra of the glycolysis product are shown, and some samples show similar spectra, which also agrees with the BHET control spectrum in a previous report by Syarriffudeen et al. [20].

When comparing the functional groups in the BHET molecule with the samples, it was observed that the BHET functional groups were present. The spectrum showed differences in the molecules. However, the varying sharpness of the peak can account for the variable sample purity. It is assumed that the highest purity was at 180°C with 1:6.5 (PET:EG ratio) using calcined snail shell as the catalyst because of a more substantial peak in Figures 8-13.

IV. CONCLUSION

This research has shown that snail shells can be effectively used as catalysts in glycolysis of PET in ethylene glycol but with a yield of 39.72%. This yield is less than 68.6% when oyster shells are used as catalysts. This may be attributed to higher presence of CaO (the active reaction ingredient) in oyster shells than in snail shells. Also, environmentally friendly sodium acetate and calcium carbonate used as catalysts have given 72% and 69% yields, respectively. In previous works, longer reaction times (8 hours) have been observed to provide higher yields with other catalysts. Therefore, longer than 2-hour reaction time and varying catalyst:PET ratio are recommended for further research.

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