ECO FRIENDLY TECHNOLOGY FOR UTILIZATION OF POLYETHYLENE TEREPHTHALATE WASTES

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The present paper suggests an original laboratory method for utilization of polyethylene terephthalate (PET) wastes. The process involves a sequence of processes in several stages: glycolysis, separation of polyester polyols, purification and drying.

PET pellets were subjected to glycolysis with crude glycerol obtained as side product from biodiesel production. The depolymerization was carried out in a microwave reactor with low energy consumption. The insoluble admixtures (PE, PP, PVC, etc) were removed by filtration. The polyester polyols produced by the glycolysis were removed from the product by cooling to temperature of 4°C.

The technology suggested involves microwave depolymerization which leads to shortening the depolymerization time from 300 to 40 min, saves energy and water and is carried out using crude glycerol without catalyst. The polyester polyols obtained as side product from the depolymerization can be used as initial materials for synthesis of unsaturated polyester, alkyd and polyurethane resins.

Key words: *environmental technology, depolymerization, PET, Crude Glycerol*

INTRODUCTION

Polyethylene terephthalate (PET) consumption is growing every year. It successfully replaced glass bottles and metal cans. It is used for beverage, mineral water, nutritive oils, fruit juices and cosmetics. PET provides a good combination of physical properties and, furthermore, it is easily recyclable. [1].

The amount of waste PET increased with consumption [2-4], as did also the number of technologies for its recycling [5].

Glycolysis as a method for PET depolymerization was first described in Polish and American patents in 1964 and 1965, respectively. Since then, this method for recycling polyester wastes is constantly attracting the attention of the researchers from both scientific and economic point of view. After the mechanical recycling, this is the second most widely used technology. It is cheaper and requires less energy compared to methanolysis, aminolysis and hydrolysis and can be implemented in batch and continuously operated facilities. Pet depolymerization is carried out most often with ethylene glycol [1, 5]. According to the leading scientists in the field, the future of glycolysis is in the purification of the precursor monomer obtained - bis(hydroxyl ethylene terephthalate) and to carry it out with reagents different from ethylene glycol [5].

The present work is responding to the necessity to search for new reagents for conducting glycolysis. With the increase of biodiesel production, the amounts of the side product obtained – crude glycerol also increased. Thus, carrying out glycolysis of PET with crude glycerol is of scientific, application and environmental importance.

2. MATERIALS AND METHODS

2.1. Initial materials

- PET pellets produced by a Bulgarian recycling firm in the town of Gabrovo – RISK 91 Ltd.
- Crude glycerol (CGly) purchased on the market.
- Toluene – produced in Bulgaria and used without further purification.

2.2. Removal of water from the crude glycerol

In a round bottomed flask of 250 (or 500) ml, equipped witj mechanical stirrer, Dean-Stark apparatus, thermometer and in inlet for inert gas, 53.8 g CGly (0.4 mil Gly) and 5.4 g toluene were

placed. The stirrer was switched on and the flask was heated to 120°C until full evaporation of the water contained in it.

2.3. Conducting glycolysis of PET with crude glycerol

In a flat-bottomed one-neck flask of 250 ml, 9.6 g PET frits and the necessary amount of crude glycerol were placed so as to keep the ratio Gly/PET = 8. A heterogeneous mixture of solid PET and liquid depolymerizing reagent is obtained. The mixture is then placed in a microwave reactor DAEWOO KOR 6485. The necessary microwave power was set so as to reach the temperature required - 220°C. The interaction proceeded for 40 min to obtain the glycolysis product.

2.4. Removal of the polyester polyols

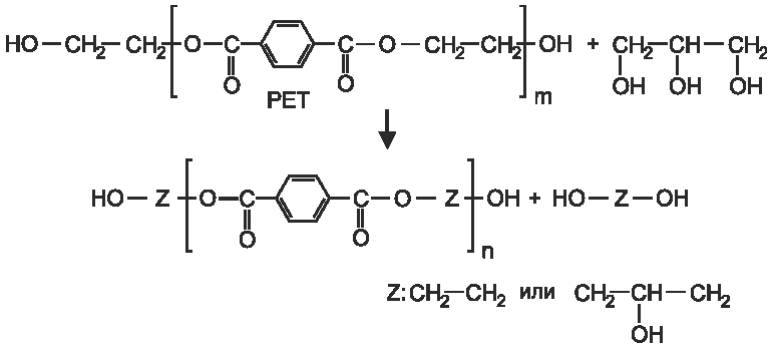
The glycolysis product was hot filtered. Then, water was added, stirred well and the resulting mixture was kept at temperature of 4°C for 24 h. The polyester polyols are contained in the sediment. Finally, processes of filtering, purification and drying at 60ºC were carried out.

2.5. Study of the polyester polyols by gel-permeation chromatography /GPH/

The measurements were taken on a system WATERS consisting of M510 pump, U6K injector, refractometric detector M410 and UV detector M484. A number of columns produced by PHENOMENEX – PHENOGEL were used: 50A, 100A and 10000A, at flow rate of 1.0 ml/min, temperature 40°C, solvent THF. The molecular mass characteristics (MMX) were determined using polystyrene standards of known molecular mass (MM) and narrow molecular mass distribution, using the CLARITY software. The analysis was carried out by double detection – refractometric and UV.

RESULTS AND DISCUSSION

The process of PET glycolysis with crude glycerol can be generally described by the following reaction:



Scheme 1. Glycolysis of polyethylene terephthalate with crude glycerol

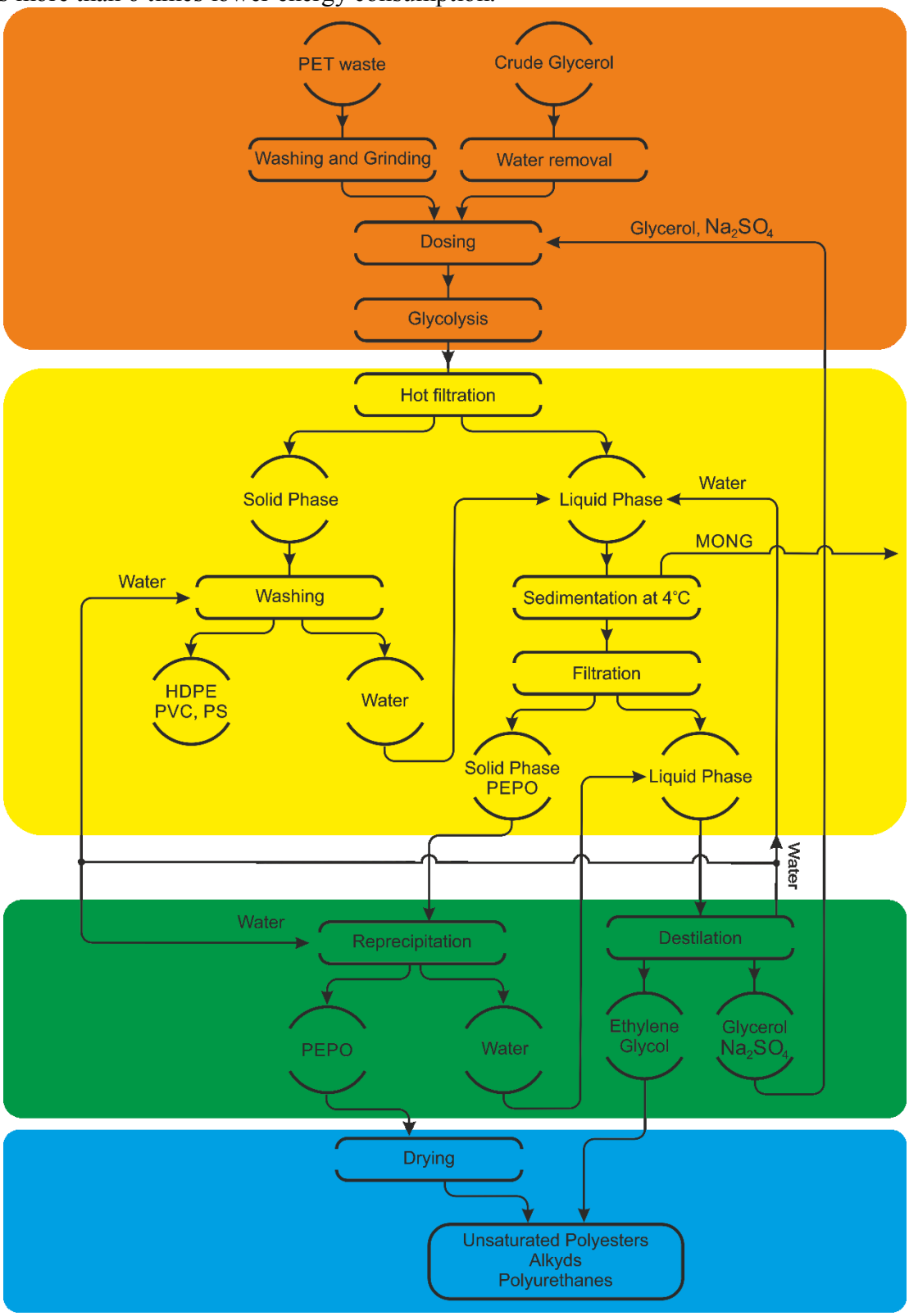
As can be seen from Scheme 1, polyester polyols are obtained as a result from the reaction. The preparation, separation and purification of the polyester polyols consists of a series of processes and operations which is illustrated in Scheme 2.

The technology suggested comprises four main stages – glycolysis, separation of the polyester polyols generated by the glycolysis, purification and drying.

The first stage is glycolysis. Only two components take part – PET frits and crude glycerol. Crude glycerol was purchased on the market. It was found to have the following composition: glycerol content – 85,5 wt %; water content – 7,1 wt %; matter organic non-glycerol (MONG) – 2,5 wt % and Na_2SO_4 content – 4,9 wt %. Since water reduces glycolysis rate, it was preliminarily removed by the method described in section 2.2.

In our earlier studies [6], results on the optimization of the depolymerization conditions were reported. It was found that the optimal temperature is 220 °C and the optimal ratio Gly/PET is 8.

By the present technology, the heating is carried out by microwave irradiation. As a result, glycolysis time was shortened to 35 min (compared to 180 min by conventional heating). This means more than 6 times lower energy consumption.



Scheme 2. Block diagram of the technology for utilization of waste PET by glycolysis with crude glycerol.

The second stage is separation of the polyester polyols from glycolysis product. To facilitate the depolymerization, it was carried out with excess of glycerol. The product of the glycolysis is a complex mixture of liquid phase (polyester polyols, glycerol, ethylene glycol Na_2SO_4, MONG) and solid phase (PET and other polymers present here as impurities). To remove the solid phase from the liquid one, first hot filtering was carried out followed by washing with water which is then added to the liquid phase of the glycolysis product. Then more water is added to make the ratio glycolysis product/water = 1/7. The mixture obtained is kept at 4°C for 24 h. under these conditions, only the polyester polyols generated by the glycolysis process are precipitated as white sediment. MONG remained as thin film on the surface and can be removed with a separating funnel. All the other substances – glycerol, sodium sulfate and ethylene glycol remained dissolved in the water. The sediment was removed by filtration and the filtrate was distilled. Water distills at 100°C and ethylene glycol – at 197°C. Water is reused for the purification of the polyester polyols while EG – for preparation of polyesters. The residue after the distillation was a solution consisting of glycerol and sodium sulfate. The Na_2SO_4 solubility in glycerol is 8.1%. At higher concentration and in absence of water, Na_2SO_4 precipitates and can be removed from the system.

The third stage is purification. The polyester polyols were purified by super precipitation in water. They were dissolved in water under heating and left to precipitate at 4°C. They were then dried at 60°C and analyzed.

The method of gel permeation chromatography was used to find the molecular mass distribution (Table 1). It was determined from the data that more than 60% of the product corresponds to the molecular mass of precursor monomers (n=1 in Scheme 1), ~ 20% - to precursor dimers (n=2 in Scheme 1) and ~10 % - to precursor oligomers (n≥3 in Scheme 1).

Table 1. Results for the molecular mass distribution obtained by gel permeation chromatography

	Max.RT	Mp	Mn	Mw	PD	Area, µRI.s	Area, %
1	24,32	916	944	960	1,02	2470	9,5
2	25,28	590	595	604	1,01	5304	20,6
3	26,72	326	322	331	1,03	15696	60,2
4	29,60	114	111	112	1,00	1098	4,3
5	30,40	85	66	71	1,07	1586	6,2

The technology suggested is both innovative and environmentally friendly. Crude glycerol does not smell bad and it is non-toxic. No hazardous gasses are released by the depolymerization and the preparatory works on the separation and purification of polyester polyols. This is a no-waste technology. No substances or products are thrown off. The glycolysis temperature is reached through microwave technology which shortens the depolymerization time from 300 min to 40 min and saves energy and water. The impurities in the crude glycerol – sodium sulfate and matter organic non-glycerol accelerate the glycolysis process so it is not necessary to use catalyst which usually contains heavy metal. From the comparison to the conventional technology illustrated in Table 2, it can be seen that the technology suggested is inferior only by the yield of precursor monomers. Nevertheless, the polyester polyols obtained can successfully be used as initial products for manufacturing alkyd, unsaturated polyester and polyurethane resins [7].

Table 2. Comparison between the conventional technology of PET glycolysis with ethylene glycol and the technology suggested in the present paper

	Conventional technology – PET glycolysis with ethylene glycol [1]	PET glycolysis with crude glycerol and microwave irradiation
Toxicity of the depolymerisation agent	toxic	Non-toxic
Temperature, °C	180-200	220
Glycolysis duration, min	180-480	35
Use of catalyst	Zn acetate or Pb acetate	no
Yield of precursor monomers, %	77-91	60
Price of the depolymerizing agent, BGN	7-20	0,5-1

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