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A Method of Polyethylene Terephthalate Depolymerization by Biodiesel Wastes

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Abstract

In the modern world, the environmental problem is one of the most important. The amount of plastic waste increases sharply every year. The recycling of such waste is complicated by a large number of types of plastic and the difference in their structure. Polyethylene terephthalate (PET) is widely used in everyday life, as well as polyethylene and polypropylene, but in contrast to them, PET contains esters groups. Thus, this plastic can be recycled with various polar reagents, such as water, alcohols, glycols, and so on. This paper describes a method for the depolymerization of PET using the main by-product of biodiesel production-crude glycerol. waste PET and crude glycerol, a raw material containing potassium salts of fatty acids, which were formed during alkaline catalysis of the biodiesel production reaction, were used as raw materials. Complete PET conversion can be achieved in 90 minutes at 190-195° C and at atmospheric pressure. As a result of the recycling of PET and biodiesel wastes, valuable products such as the potassium salt of terephthalic acid, its esters with glycerol and glycol as well as fatty acids glycol esters can be isolated.

***Keywords**: Crude glycerol; Waste utilization; PET; Depolymerization; Recycling; Green chemistry.*

1. Introduction

In the last years, the total production of polymers rapidly increased. Although PET represents only 6% from total polymers amount [1], for 2017, its world production was 75,8 million metric tons [2]. PET is widely used as a feedstock for the production of packing materials, synthetic fiber ("terylen") and nonwoven fabrics. However, the wide use of PET products, especially of bottles, is associated with the formation of a huge amount of wastes, with a decomposition period of up to 200 years. At the same time, the highest index of PET waste was only 77% in 2010 [3]. So developing a reasonable way of recycling PET waste is a vital task.

There are four categories of PET recycling [4]:

1) *Primary recycling* - mixing plastic waste with virgin material for the production of material with requisite properties.

2) *Secondary recycling*:

A) Mechanical recycling by the sorting and separation of the wastes with further melt filtration and reforming of the plastic material.

B) Using PET waste as modifying additive for production of materials with improved properties (cement-based materials with increased strength [5], antistripping additive for bitumen [6]).

Mechanical recycling of PET is relatively simple and requires low investments. It is also flexible in terms of feedstock volume and has a little adverse environmental impact. But there are some problems concerned with a high temperature of melt reprocessing: thermal and hydrolytic degradation, the formation of linear and cyclic oligomers [7]. So it is impossible to use such material at beverage bottles production.

3) *Tertiary recycling* - chemical depolymerization of PET into monomer units or randomly ruptured into larger chain fragments (i.e., random chain scission) with the associated formation of gaseous products.

A) Pyrolysis is thermal plastic degradation, which leads to a mixture of gases and petroleum liquids [8].

B) Solvolysis is polyester depolymerization into the monomer unit by different solvents. There are several types of solvolysis according to solvent class, among them hydrolysis, alcoholysis, aminolysis and glycolysis [8-11]. Glycolysis allows obtaining terephthalic esters with different structures. These esters are valuable feedstock for polyurethane foams, different coatings and resins [12-15]. So a great amount of works is concerned with glycolysis. There is a wide range of glycolysis catalysts from zinc salts to based on cobalt and manganese nanocatalysts and ionic liquids [16-20]. But these processes in sensitive to contaminants and these novel catalysts are quite expensive.

On the other hand, there is another industrial waste - crude glycerol, the main by-product of biodiesel production. Development of biodiesel production (1,8 billion gallons in USA during 2013) [21] and absence of industrial utilization method lead to crude glycerol's price reduction (0,077-0,099 $/kg) [22]. Moreover, it already contains metal salts (potassium soaps) and glycol - glycerol. For it is known that sodium, as well as potassium salts, can be used as a glycolysis catalyst [23-24]. This biodiesel waste can be used as a cheap PET depolymerization agent. That is the reason why the development of a method of PET depolymerization by crude glycerol is the main task of this investigation.

2. Materials and methods

2.1. Materials

In this investigation, flakes of waste PET, polypropylene (PP) from plastic covers, unpurified crude glycerol from biodiesel production, technical pure ethanol and isopropanol were used as a feedstock. PET bottles from the soft drinks with dyes (colored) and without them (clear) were the source of polyether. They were washed with water and then were cut into pieces (average size 25-40 mm × 3-7 mm). Crude glycerol was donated by "AVK-Chem" Ltd and contained 61,4 wt.% of glycerol, 8,5 wt.% of fatty acid methyl esters (FAMEs), 30,1 wt.% of soaps (as potassium stearate) and trace amounts of methanol. Ethanol was used as a solvent at product separation. Isopropanol was used as a solvent at titration.

2.2. Methods

2.2.1. Experimental method of PET depolymerization

Before the depolymerization process, PET bottles were washed with water, dried and cut into flakes with average size 0.2-0.4x0.2-0.4 cm.

The process was conducted in a 250 mL four-necked round bottom glass reactor equipped with a condenser, a mechanical PTFE blade stirrer, and a thermometer. One neck was empty and closed with a bung. Crude glycerol was heated up to 150-190°C. During heating, all methanol evaporated from the reaction zone and was collected after the condenser. When reaction temperature was attained, PET flakes were added to the reactor through an empty neck in 5-10 minutes. The reaction was carried out at atmospheric pressure and 150-190°C for 1.5 hours. After a specified reaction time, the reactor was cooled in air. For products separating ethanol was added in excess to the reactor and mixture was stirred to the full dissolving of reaction mass. Then obtained suspension was filtrated and the white crystalline compound was dried in air. Then it was dissolved in ethanol again to purify it by removal all liquid products. The filtrate contained ethanol, glycerol, FAMEs and other liquid products. Ethanol was removed from the filtrate by heating in a rotary evaporator at 65-70°C and 50-70 mm Hg for 3 hours.

2.3. Analysis methods

Free glycerol and FAMEs were determined through gas chromatography (GC) of samples using liquid-gas chromatograph “Kristall 4000 Luks” equipped with a flame ionization detector (FID) and a capillary column DB-23 (30 m, 0.25 mm ID, 0.25 μm). Nitrogen was used as a carrier gas at a flow rate of 90 mL min−1. Samples were injected at an injection volume of 1 μL into LGC. Injector, detector, and column temperatures were held constant at 275°C, 250°C and 140°C, respectively.

Soaps were determined by titration on the titrator model "Akvilon" ATP-02. The molecular mass of PET was calculated from its repeating unit (192 g/mole) and was considered for further calculations. Conversion of PET was calculated on weight of PET consumed to the initial weight of PET (Eq. 1):

$$X_{PET} = \frac{m_{PET,0} - m_{PET}}{m_{PET,0}} * 100\% \qquad (1)$$

IR spectra of a solid product were measured on a Nicolet 380 FT-IR spectrograph. Nuclear magnetic resonance (NMR) spectrum of the main product was recorded on Bruker AVANCE-III 200 NMR spectrometer operating at 200 MHz in DMSO-d6.

3. Results and discussion

3.1. Selection of process temperature

The effect of reaction temperature on PET conversion was investigated at PET/soaps molar ratio 0,36 for 1.5 hours. Table 1 shows that PET conversion rapidly enhanced depending upon the temperature. The temperature can't be higher than 200°C because of the beginning of glycerol polycondensation in the presence of alkali metal salts [25]. So, for further investigation, 190-195°C was chosen.

Table 1. Effect of temperature on PET degradation

Temperature, °C	PET conversion, %
150	4.7
170	54.3
190	100

3.2. Determination of solid product structure

The main product of the process is white solid powder, which was analyzed by IR spectrograph and ^{13}C NMR spectrograph. The IR spectrum of the purified compound (Figure 1) corresponds to the IR spectrum of dipotassium terephthalate [26]. It may be clearly seen that the spectrum contains peaks at 886, 975,1105, 1288, 1375, 1562 and 1618 cm^{-1} indicating the presence of the carboxylic group. The peaks for C-C and C-H bonds are observed at 742, 1312, 1352, 1438 and 1497 cm^{-1} and 820, 1013 and 1087 cm^{-1} respectively. Figure 2 gives ^{13}C NMR spectrum for the same compound wherein it may be observed that the peaks at δ 130,4 correspond to core aromatic carbon atoms, at δ 143,2 corresponds to carbon atoms near to carboxylic group and at δ 177,1 corresponds to carboxylic carbon.

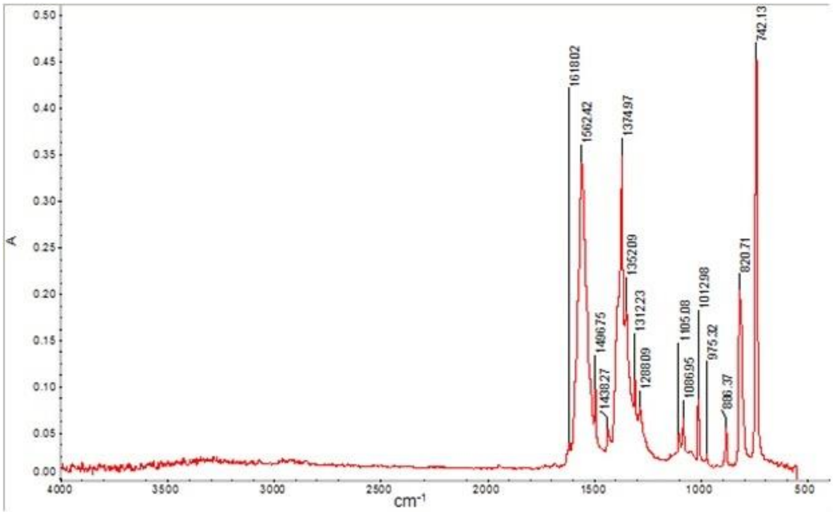


Figure 1. IR spectrum of obtained dipotassium terephthalate

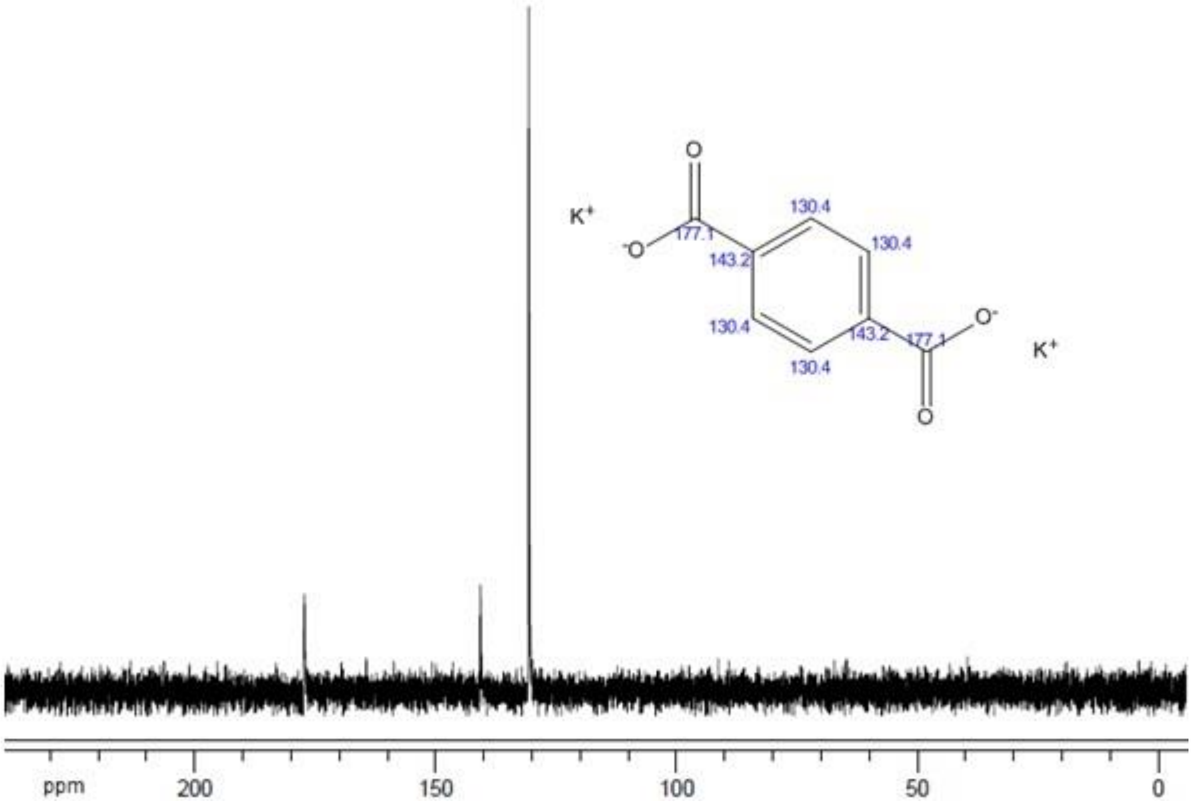


Figure 2. ^{13}C-NMR spectrum of obtained dipotassium terephthalate

3.3. Influence of polymeric feedstock on the process parameters

As far as one of the goals of this study was to evaluate the affinity of complex polymeric wastes for depolymerization by crude glycerol, different types of PET and PET-PP mixture were used as a feedstock. For full conversion of PET experiments were carried out at 190°C and PET/soaps molar ratio 0,36 for 1.5 hours. It could be noticed in Table 2 that within experimental errors, the yield of DPT to soaps doesn't depend on the type of used PET. The presence of other plastic also has no influence on the yield of DPT (Table 3). PP didn't react during the process and it was filtered out at the separation of the product. This method is absolutely insensitive to main contaminants contained in PET wastes and can be used for plastic mixture separation.

Table 2. DPT yield to soaps in the depolymerization of highly colored PET

PET type	DPT yield, %
Clear	75.0
Green	74.9
Brown	75.4

Table 3. DPT yield to soaps in the depolymerization of PET/PP mixture

PP/PET mass ratio	DPT yield, %	PP conversion, %
0,23	58.96	0.5
0,53	58.72	0.1
1,03	59.53	0.3

3.4. Influence of PET/soaps molar ratio on the process parameters

These experiments were carried out at 190°C for 1.5 hours. Figure 3 shows that at lack of PET (due to stoichiometry of saponification reaction (Figure 4-A)), only one reaction takes place, and selectivity of DPT to PET is 100%. But with the increasing amount of PET, this parameter decreases to 63.4%. At the same time, glycerol conversion rapidly increases with increasing PET amount in the reaction mixture. In work [11] authors claim that glycerol is much less active in the glycolysis process than ethylene glycol.

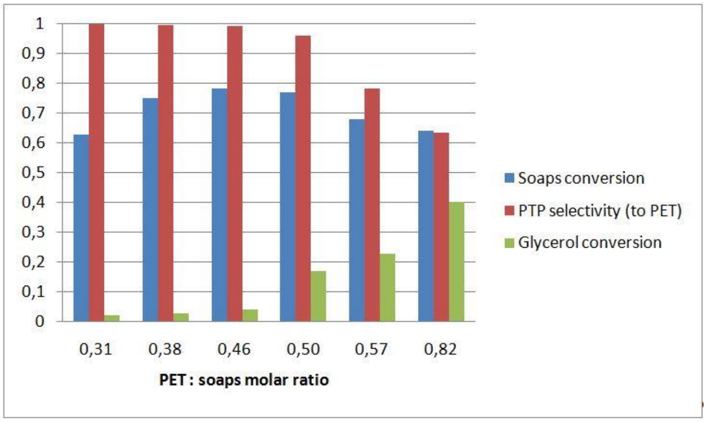


Figure 3. Influence of PET: soaps molar ratio on parameters of the process

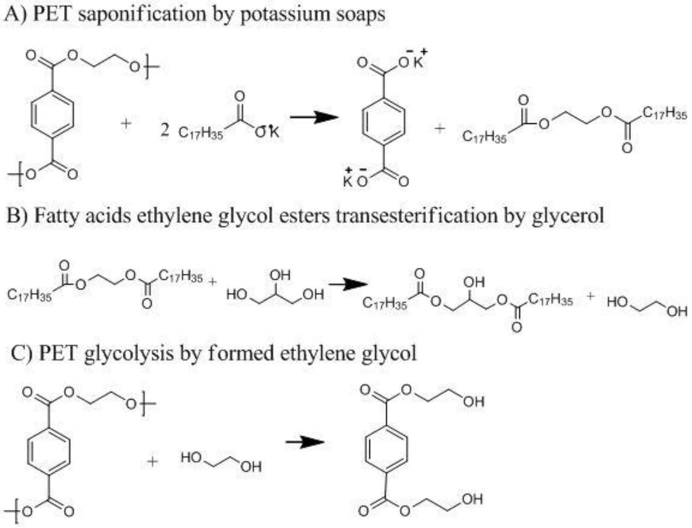
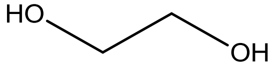
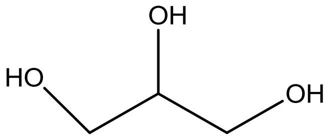
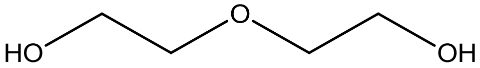
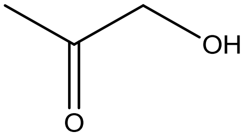


Figure 4. Scheme of the process PET depolymerization

So, according to all these facts, it was proposed that in the process, there are three main reactions (Figure 4). This scheme of the process is also confirmed by the presence of ethylene glycol in the liquid product mixture. For ethylene glycol presence determination liquid products were separated be vacuum distillation at 150-180°C and 10-15 mm Hg. And then obtained distillate was analyzed by GC-MS method using chromatographic system "Chromatek-Crystal 5000.1" with MSD (mass spectrometric detector) Trace DSQand quartz capillary column THERMO TR-5MS (50m-0.25 ID-1.0 um). It is clearly seen from Table 4 that glycerol and ethylene glycol are the main substances in the distillate.

Changing of the IR spectrum of solid participation (Figure 5), which was obtained at high PET/soaps mass ration, is another argument for the proposed process scheme. Despite peaks of terephthalic fragments (peaks at 885, 925, 1105, 1285, 1374, 1562, 1618, 1715 cm^{-1} indicating the presence of carboxylic group; peaks for aromatic C-C and C-H bonds are observed at 740, 1312, 1374, 1439, and 1497 cm^{-1} and 819, 1012, and 1086 cm^{-1} respectively) this spectrum contains peaks at 3284 cm^{-1} and 2854, 2923 cm^{-1} indicating presence of OH-groups and aliphatic C-H bonds. This changing approves the presence of bis(2-hydroxyethyl) terephthalate in solid products. Unfortunately, there is no method of this solid mixture separation for now.

Table 4. Composition of distillate from glycerol containing layer

Compound	Compound's structure	Content, weight %
Ethylene glycol		51.85
Glycerol		35.3
Diethylene glycol		5.45
1-hydroxy-2-propanal		3.35
Others	-	4.05

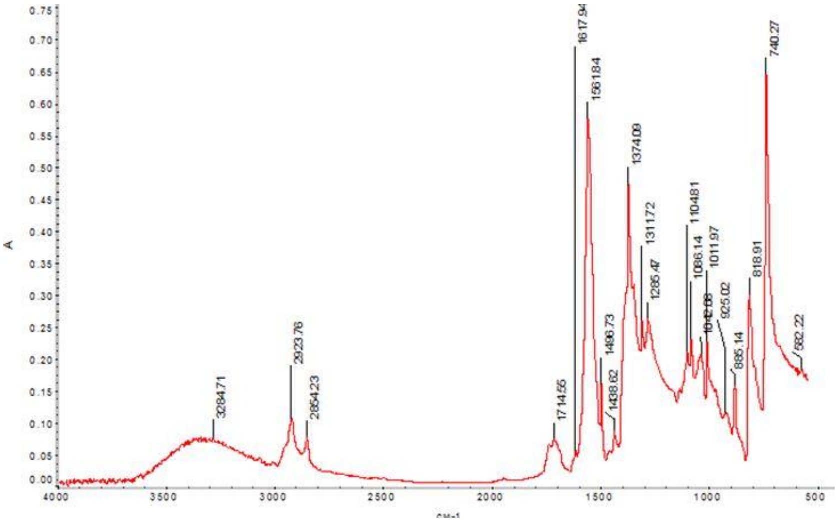


Figure 5. IR spectrum of precipitate obtained at PET/soaps molar ratio 0.8

4. Conclusions

Results of performed work show that crude glycerol can be used as a cheap PET depolymerizing agent. At low PET content in the reaction mixture, the main products of this process are DPT, fatty acids ethylene glycol esters (FAEGEs) and fatty acids glycerol acids (FAGEs). At the same time at high PET content esters of different structures can be obtained. Full conversion of waste polyester can be achieved in mild conditions for 1.5 hours. The highest soaps conversion, the selectivity of DPT to PET and glycerol conversion was 78.5%, 99.9% and 39.8% respectively. This method also is absolutely insensitive to the presence of polyolefin plastic and dyed PET in the polymeric feedstock so it can be used for complex waste mixture recycling and for this mixture reactive separation. Obtained DPT is a feedstock for producing terephthalic acid from this compound by acidification with mineral acids. It also looks promising to use obtained liquid mixture as a source of fatty acids ethylene glycol esters and fatty acids glycerol acids for biodiesel production. This will be investigated in future.

Abbreviations

PET - Polyethylene terephthalate, FAMEs - fatty acids methyl esters, DPT - dipotassium terephthalate, PP - polypropylene; FAEGEs - fatty acids ethylene glycol esters, FAGEs - fatty acids glycerol acids.

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