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UTILIZATION OF PET WASTES AND THE SIDE PRODUCTS OF BIODIESEL PRODUCTION

Engineering

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ABSTRACT

The increased use of polyethylene terephthalate (PET) for packaging and the increase of biodiesel production raised the necessity to utilize both waste PET and glycerol phase which is a side product of the biodiesel production. The present paper describes a possibility for chemical recycling of PET waste from beverage bottles using glycerides of fatty acids (GFA) obtained from the glycerol phase. A great number of depolymerizations were carried out under varied conditions – mass ratio GFA/PET, temperature, process duration and amount of catalyst. The products of the depolymerization were studied by spectral methods of analysis and gel permeation chromatography.

KEYWORDS

Recycling, waste PET, glycerol phase, glycerides

INTRODUCTION

According to the report of Smithers Pira for 2014, the world production of PET packaging had been 16 mln tons and is expected to increase by average 4,6% yearly in the following five years to reach 19.9 mln tons in 2019 [1]. The PET packaging of food products are usually discarded in less than a month. The PET wastes can be recycled which is in accordance with environment protection.

A number of methods for chemical recycling of PET have been reported in the literature – hydrolysis, glycolysis, methanolysis and aminolysis [2]. Glycolysis takes place in presence of various monomer compounds containing two or more OH groups – monoethylene glycol, diethylene glycol, [2] pentaerythritol [3], glycerol [4], etc.

However, no reports were found in the available literature on PET depolymerization with glycerides obtained from the glycerol phase which is a side product of biodiesel production. The utilization of the glycerol phase is of substantial importance for the stimulation of the biodiesel industry.

In our previous work [5] it was announced for the possibility to obtain monoglycerides from the organic components of the glycerol phase. The present paper is a continuation of the previous one. It reveals a possibility to utilize PET wastes by chemical depolymerization with glycerides derived from the side products of biodiesel production.

2. EXPERIMENTAL

2.1. Materials

Polyethylene terephthalate (PET) – obtained from waste beverage bottles.

The glycerol phase (GF) was submitted by Rapid Oil Industry Co. It consisted of glycerol -55,3%; methanol – 4,6; water – 11,5; K_2SO_4 – 2,72 %; soaps – 17,45 %; FAMEs – 7,13 %, glycerides – 0,9 % and other substances – 0,4%.

Ethyl acetate, KOH, H_2SO_4, THF, toluene, methanol were purchased from Sigma Aldrich. Deionized water was obtained by a system for pure/ultrapure water Purelab PRIMA, product of Thermo Scientific.

2.2. Synthesis of glycerides of fatty acids

The fatty acids glycerides were prepared from the glycerol phase. Processes of saponification (with KOH) and neutralization (with H_2SO_4) were carried out by a well-known technique [6]. As a result, three layers were obtained – crude glycerol (CGly), free fatty acids (FFAs) and K_2SO_4. After their separation, CGly and FFAs were used for synthesis of glycerides.

In a round bottomed flask equipped with mechanical stirrer, Dean-Stark apparatus, thermometer and inlet for inert gas, 69 g CGly and 4 g toluene were placed. The stirrer was turned on and the flask is heated to the temperature of boiling until full evaporation of the water contained in the crude glycerol. Then 85 g FFAs and 6 g preliminarily prepared glycerides were added and the temperature was increased to 180°C. The interaction proceeded for 90 min. After turning off the stirrer, three layers were obtained which were hot separated with a separating funnel. Then the upper layer (glycerides) was rapidly cooled down in a water bath to temperature of 75°C. The glycerides were washed several times with water and separated by extraction with methanol.

2.3. Depolymerization of PET

In a round bottomed flask of 500 ml equipped with mechanical stirrer, thermometer and inert gas inlet, certain amount (Table 1) of glycerides and K_2SO_4 were placed and heated to the necessary temperature. Then, PET flakes heated to 200°C were added. Processes of transesterification were carried out with duration from 6 to 8 h. The products obtained were cooled to room temperature and ethyl acetate was added to obtain solution and precipitate. The solution was removed and later it was distilled at low pressure to separate the ethyl acetate for reuse. After evaporating the moisture, the product of depolymerization (PD) was obtained. Hot deionized water was added several times to the precipitate to remove the non-reacted glycerol and K_2SO_4. The non-solved PET was dried, weighed and the conversion was calculated by the formula:

$$C_{PET}, \% = \frac{W_i - W_f}{W_i} . 100$$

where: W_i and W_f – are the initial and final weight of PET

2.4. Analysis and characterization

The UV spectra were registered on a spectrophotometer Evolution 300 UV VIS of Thermo Scientific Co., in a solution in THF in a 1 cm thick cuvette.

The FT IR spectra were taken on a spectrophotometer Nicolet iS 50 FT IR with thin film samples fixed on a KBr pellet.

Gel permeation chromatography was used to determine the molecular mass distribution.

RESULTS AND DISCUSSION

The aim of the work was achieved in two stages. The first one is the preparation of glycerides. CGly, FFAs and K_2SO_4 were obtained from the glycerol phase by the method described in 2.2. CGly were esterified with FFAs at mass ratio Gly/FFA = 0,7 which was considered to be the most suitable one according to our previous studies [5]. To reduce the induction period and improve the compatibility of FFAs, preliminarily prepared glycerides were introduced to the reaction mixture. At the end of the interaction, all the contents was poured in a separating funnel and 3 layers were separated – lower one of K_2SO_4, middle one of non-reacted glycerol and upper one – glycerides of fatty acids. The latter were rapidly cooled to temperature 75 ºC to avoid the transformation of monoglycerides into diglycerides.

It is important in this case to consider the effect of the impurities present in CGly. These are water (7,1%), MONG (2,5%) and K_2SO_4 (4,9%). Water is easily removed before the synthesis. The main

components of MONG are fatty acids, methyl esters of fatty acids (FAMEs), mono-, di- and triglycerides. Under the conditions of the esterification, all the components can react with glycerol which results in formation of monoglycerides (or diglycerides). Simultaneously, low molecular weight products are released (water or methanol) which are blown off by the inert gas. The last impurity is K_2SO_4 which is insoluble in glycerides and can easily be separated.

The second stage is the depolymerization of flakes from waste PET beverage bottles using the glycerides of fatty acids (GFA), obtained in stage one. A great number of transesterifications were carried out at varied conditions – temperature (T), mass ratio (GFA /PET), process duration and amount of catalyst /Table 1/.

Table 1. Conversion of PET at various conditions

Denotation	mass ratio GFA/PET	T, ºC	Process duration, h	Catalyst, %	Conversion of PET, %
D-1	2	200	7	1	50
D-2	3	200	7	1	77
D-3	4	200	7	1	91
D-4	5	200	7	1	91
D-5	4	180	7	1	35
D-6	4	190	7	1	56
D-7	4	210	7	1	91
D-8	4	200	6	1	68
D-9	4	200	8	1	91
D-10	4	200	9	1	91
D-11	4	200	7	-	58
D-12	4	200	7	2	92

In all depolymerization processes, the catalyst used is K_2SO_4, which precipitates upon neutralization of the glycerol phase. As can be seen from the table, the optimal conditions for the process were: temperature 200ºC, mass ratio 4, catalyst content 1% with respect to PET and process duration of 7 hours.

The depolymerized products were separated and studied. They were wax-like substances of light-brown color. It indicated that the polymer molecules of the PET flakes were transformed into oligomer ones. At sufficiently low molecular weight of the oligomers, they become soluble in solvents like ethyl acetate and THF.

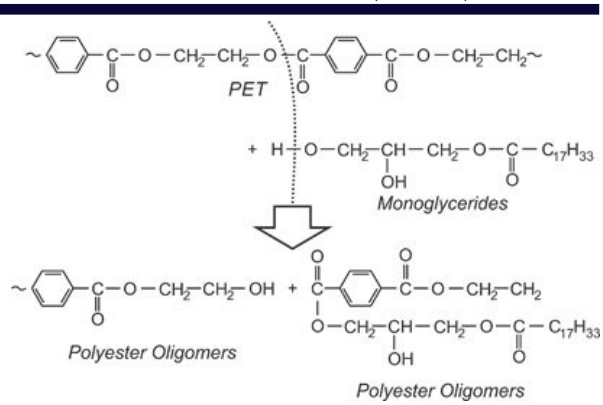
The chemical bonds in the oligomers were studied by spectral methods of analysis.

The UV spectra of the products dissolved in THF showed absorption in the interval 240-300 nm with maximum at 292 nm which corresponds to the terephthalate units.

The following characteristic frequencies were found in the IR spectrum of the purified products:

- 3447 -broad band for intermolecular OH groups;
- 3100-3000 cm^{-1} – stretch vibrations of the =C-H bond;
- 2926 and 2855 cm^{-1} – stretch (asymmetric and symmetric, resp.) vibrations of the CH_2-groups;
- 2956 and 2878 cm^{-1} – stretch (asymmetric and symmetric, resp.) vibrations of the CH_3-groups;
- 1727 cm^{-1} – stretch vibrations of the C=O bonds;
- 1505 and 1595 cm^{-1} – stretch vibrations of aromatic rings;
- 1462 cm^{-1} – bending vibrations of the CH_2-groups;
- 1410 cm^{-1} – bending vibrations of the C-H bond in the CH_2-O groups;
- 1378 cm^{-1} – bending vibrations of the CH_3-groups;
- 1271 and 1174 cm^{-1} – Stretch vibrations of the C-O-C bonds;
- 1117 and 1049 cm^{-1} – Stretch vibrations of the C-O bonds in the C-OH groups;
- 1019 and 896 cm^{-1} – p-substituted aromatic rings;
- 732 – ρ (CH_2).

The presence of characteristic Absorption Frequencies for both terephthalate units and glyceride units suggests that the depolymerization of PET with monoglycerides proceeded along the following scheme:



Scheme 1. Depolimerization of PET with monoglycerides

The extent to which the depolymerization process had reached can be estimated using the results from the molecular mass distribution (Table 2).

Table 2. Results obtained from the molecular mass distribution of some of the depolymerization products

Denotation	Mn	Mw	Mw/Mn
D - 1	2831	5158	1,822
D - 2	2180	3790	1,738
D - 12	1095	1413	1,290

It can be seen that D-1 and D-2 had higher molecular weight and higher polydispersity. This can be explained with the formation of comparatively bigger molecules and branches. The molecular weight of the product D-12 corresponded to the precursor dimers.

The precursor dimers and oligomers obtained were successfully used for synthesis of alkyd resins.

CONCLUSION

The present paper describes one possibility for utilization of two waste materials – PET wastes from beverage bottles and the glycerol phase which is a side product of the biodiesel production. After certain treatments of the organic components present in the glycerol phase, glycerides of fatty acids were obtained. It was found that they can successfully be used as PET depolymerizing agent. By varying the conditions, it was established that the best conditions for the transesterification are: temperature 200ºC, mass ratio GFA/PET = 4, process duration 7 h and catalyst content 1 %. Using gel-permeation chromatography, FT IR and UV-VIS spectroscopy, it was proved that precursor dimers and higher oligomers were obtained.

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