ORIGINAL RESEARCH PAPER

Natural Science

Volume : 6 | Issue : 11 | November 2016 | ISSN - 2249-555X | IF : 3.919 | IC Value : 74.50

SYNTHESIS OF GLYCERIDES BY UTILIZATION OF THE GLYCEROL PHASE OBTAINED BY BIODIESEL PRODUCTION

KEYWORDS

biodiesel, glycerol phase, monoglycerides, utilization

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ABSTRACT Biodiesel production generates glycerol phase as by-product. It is brown colored mixture of glycerol, water, soaps, methyl esters of fatty acids, methanol, catalyst residue, free fatty acids, mono, di- and triglycerides, pigments, etc. To support the biodiesel industry, the present work shows the possibility to obtain glycerides from the organic components present in the glycerol phase. For this purpose, its composition is first simplified by saponification and neutralization. Some unwanted components like salts and methanol are removed. As a result, two products were obtained – crude glycerol and fatty acids. Glycerides were synthesized at various ratios between them. The compositions of the initial and end products were determined by standard methods.

Introduction

The glycerol phase /GPh/ is a by-product from the biodiesel production. Due to its complex and unknown (varying) composition, its use is fairly limited and it causes already ecological problems (Hájek and Skopal, 2009). To support the biodiesel industry, methods of utilization of the glycerol phase are sought for. Methods of burning, composting, animal nutrition, thermos-chemical transformation and biological methods have been suggested (Tan et al., 2013).

One ot the methods of transformation is glycerolysis. There are some scares data in the literature about preparation of glycerides from crude glycerol (CGly) and various oils. Noureddini (Noureddini et al., 2004) suggested a continuous process of glycerolysis of soybean oil with pure and crude glycerol. Chetpattananondh and Tongurai (Chetpattananondh and Tongurai, 2008) obtained monoglycerides from CGly and palm stearin. Echeverri et al. (Echeverri et al., 2013) carried out glycerolysis of ricin oil with CGly while Maneechot et al. (Maneechot et al.,2009) – glycerolysis of CGly and methyl esters of fatty acids /FAMEs/.

No data were found in the available literature on the preparation of glycerides from CGly and the organic phase which are then separated from the glycerol phase after neutralization. This determined the aim of the present work – to obtain glycerides from the organic components present in the glycerol phase.

2. EXPERIMENTAL

2.1. Materials

The glycerol phase was supplied by Rapid Oil Industry Co., Ltd., municipality of Lyaskovets, Bulgaria. H_2SO_4 was pure for analysis. Glycerol (99%), KOH and methanol were purchased from Sigma Aldrich. The deionized water was prepared on a system for pure/ultrapure Purelab PRIMA of the firm Thermo Scientific

2.2. Saponification and neutralization of the glycerol phase

In a 1 l flask, 300 ml GPh were placed. Solid KOH is dissolved in methanol (50 g/l) and added under agitation until the saponification process starts. The process was carried out for 60 min at temperature of 40 °C. The flask content was cooled to room temperature and deionized water was added. To the reaction mixture obtained, concentrated H_2SO_4 was slowly added until pH=2 and the mixture was stirred for another 15 min after some time, three layers were formed – two liquid and one solid. The latter was removed by filtering. The filtrate was placed in a rotational vacuum evaporator EV311PLUS-V. VP30 LabTech to remove the methanol and was then poured in a separating funnel. An optimum amount of deionized water was added and the mixture was stored. Two liquid fractions were obtained. The light one contains mainly free fatty acids (FFA). After their separation from the heavier fraction (glycerol), it was neutralized with 50% KOH and then the water was evaporated for 2 hours at temperature of 105°C.

To determine the composition of the GPh, neutralization without saponification was carried out.

2.3. Preparation of glycerides

In a round bottomed flask of 500 ml, equipped with mechanical stirrer, thermometer and inlet for nitrogen, 89 g (0,10 mol) FFAs from these prepared in 2.2 and 89 mg (0,1 %) g KOH were added. The mixture was heated to 180° and the necessary amount of preliminarily heated CGly was added. Samples were taken at 15 min intervals to determine the acid number.

After completion of the glycerolysis, the product was hot filtered.

By this method, the glycerides Gl-1,Gl-2 and Gl-3 were obtained by varying the ratio Gly/ FFAs. The Gl-4 glycerides were obtained from pure glycerol (99%), and oleic acid at ratio Gly/OA=1,5.

2.4. Analysis and characterization

The content of free glycerol was determined by HPLC (Thermo Scientific Dionex Ultimate 3000). The contents of Glycerides, Glycerol, FAMEs and FFAs were determined on a gas chromatograph with flame ionization detector. (Agilen Technologies 7890A) according to standard ASTM D6584-10a. The yields of the fractions after neutralization were calculated as the ratio between the weight of the fraction and the weight of the glycerol phase.

The contents of water and ashes were determined by standard methods ISO 12937:2003 and ISO 3987:1999, respectively while the acid number – according to standard EN 14104:2003.

The conversion of fatty acids was calculated by the following

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equation:

Conversion, % = (Ai – At) x 100 / Ai

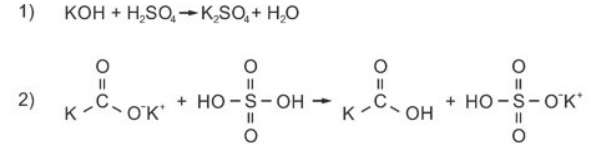
where: Ai – is the initial acid number; At – the acid number at moment t.

RESULTS AND DISCUSSION

The composition of the initial glycerol phase was determined. For this analysis, the GPh was neutralized with sulfuric acid without saponification. For higher purity after the neutralization, the glycerol fraction was extracted twice with petroleum ether. Using chromatographic methods of analysis, the following composition was determined: glycerol 55,3%; methanol – 4,6; water – 11,5; soaps – 17,45 %; FAMEs – 7,13 %, glycerides – 0,9 % and other substances – 0,4%. The complex and varying composition of the glycerol phase depending on the type of the oil used and the production process makes it hard to utilize.

Employing two easy chemical processes, the composition can be substantially simplified. The first one is saponification. It is carried out with alcoholic solution of KOH. For proper completion of the process, it is necessary to keep the mole ratio KOH/(FAMEs + glycerides) = 1,2:1. As a result from the saponification, FAMEs and the glycerides are converted to soaps.

The second process is neutralization. Sulfuric acid was used for the present work since it is cheap and often used in biodiesel production. This process transforms the soaps into free fatty acids while KOH reacts to give K2SO4 (Scheme 1).



Scheme 1. Interaction of potassium hydroxide and soaps with sulfuric acid

As a result, from the processes taking place in the liquid phase, a solid phase of salts is formed. They are the main contaminants in the reaction mixture. They were removed by storing the solution (for about 10 h) so the salts precipitate and can be removed by filtering. The salts can be used as fertilizers. The second major contaminant is methanol. It was removed by distillation and can be used again in the process. Thus, the liquid phase obtained contained aqueous solution of glycerol and FFAs**.** They are mutually insoluble and quite different by relative weight. If stored for an hour, they easily form layers. The process is facilitated by adding an optimal amount of deionized water**.**

Two fractions were obtained – light one containing FFAs and heavy one **(**glycerol**).** The glycerol fraction was neutralized with KOH and then the water was evaporated to obtain the so called crude glycerol**.** Some basic characteristics of the two fractions were determined (Table 1).

Table 1. Some basic characteristics of the crude glycerol and fatty acids obtained from the glycerol phase

Basic characteristics			
CGly		FFAs	
Glycerol content, %	85,9	Acid number, mgKOH/g	195
Ash content, %	2,7	Fatty acids, %	98,5
Water content, %	9,2	Esters, %	1,1
Matter organic non-glycerol /MONG/, %	2,2	Others, %	0,4
Density, g/cm3	1,21	Density, g/cm3	0,88
Color	Light brown	Color	dark brown

It can be seen that the fatty acids obtained were comparatively pure but full removal of MONG and K2SO4 from the glycerol cannot be achieved.

The present work shoes the possibility to utilize these two main by-products by carrying out a process of esterification. The glycerides Gl-1, Gl-2 and Gl-3 were synthesized at ratio CGly / FFAs = 1,0; 1,5 and 2,0, respectively. For comparison, the fourth kind of glycerides was also prepared – Gl-4.

The reaction was monitored by the changes in the acid number. Samples were taken at 15 min to determine the acid number and calculate the conversion /Fig.1./.

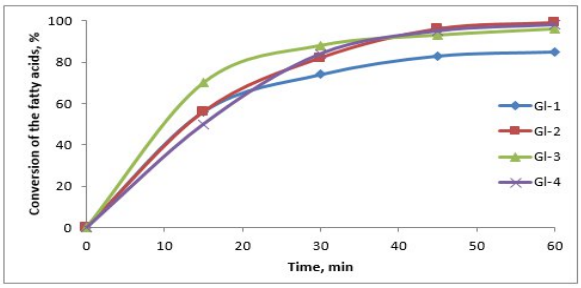


Fig.1. Conversion of the fatty acids with time for Gl-1, Gl-2, Gl-3 and Gl-4.

It can be seen from Fig.1 that the process began fast at ratio CGly/fatty acids = 1:1 bu full conversion was not reached. In presence of more glycerol, the process of esterification proceeded faster and reached equilibrium after 60 min.

Using the method of GC, it was proved that the different samples contained from 52,3 to 61,2 % monoglycerides, from 23,5 to 25,2 % diglycerides, from 3,5 to 5,6 % triglycerides while in Gl-4 the monoglycerides were only 4,8% more than these in Gl-2. In samples Gl-2 and Gl-3 remained 12,5 % and 20,3 % unreacted glycerol, respectively, which can be easily separated by decantation due to the big difference between the relative weights of glycerides and glycerol. The glycerides obtained were successfully used as initial product for preparation of alkyd resins.

Conclusion

The glycerol phase is a by-product of the biodiesel production. For the first time, a method for utilization of the organic component in the glycerol phase for synthesis of glycerides was suggested.

Employing two easy chemical processes – saponification and neutralization, significant simplification of its composition was achieved. After removal of the precipitated salts (which can be used as fertilizer) and distillation of the methanol (which can be reused), two products were obtained: crude glycerol (purity of 84%) and fatty acids (purity of 99%). The possibility to utilize these two main by-products of biodiesel production by carrying out a process of esterification was shown. Using the method of gas chromatography, the content of monoglycerides was found to be from 52,3 to 61,2 % and that of diglycerides – from 23,5 to 25,2 %. The glycerides synthesized were successfully used as initial product for synthesis of alkyd resins. The suggested

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method for preparation of glycerides is environment friendly. Beside the utilization of by-products, the utilization process does not lead to contamination of the environment and any stage.

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