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An Alternative Route for Biodiesel Synthesis from Bioethanol

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Abstract

According to the EU 2003/30/EC directive, all members of EU must replace until 1.01.2010, 5.75 wt% from diesel fuel with biodiesel, succeeding to rise to 10% at the beginning of 2020.
The most used method for biodiesel production is the transesterification of the fatty acids from vegetable oils with methanol. A high toxicity, a low flash point, the harmful irreversible effects over the human health, makes that utilization of methanol for biodiesel synthesis to be less desired. In our studies we investigate the possibilities of methanol with ethanol replacing in the transesterification of fatty acids from vegetable oils process and development of the separation method of ethylester from glycerol, as well as modification of the reaction parameters (temperature, pressure, stirring speed, volumetric speed), in order to optimize the process.

Keywords: *biodiesel, bioethanol, transesterification*

Introduction

According to the European directive 2003/30/EC all members of EU must replace at 1.01.2010, 5.75% from the diesel fuel produces by oil with biodiesel. The international standards define that the biodiesel is obtained only by transesterification of vegetable oils and of animal greases with low alcohols (methanol, ethanol, n-propanol, n-butanol) or iso-aliphatics (diols and benzoic), catalyzed by (sodium or potassium hydroxide), acids or enzymes. Nowadays, the best conversions in biodiesel are achieved by triglyceride from vegetable oils transesterification with methanol, catalyzed by potassium hydroxide [1]. Utilization of methanol for transesterification has the result a non ecological biodiesel because the methanol is not produce by renewable raw materials. In order to produce an ecological biodiesel, we propose to replace the classical synthesis method with transesterification of triglyceride from vegetable oils with ethanol produces by renewable raw materials.

Although ethanol forms azeotrope with water, and the separation of glycerol by ethyl ester is very difficult, in our investigations we attempt to eliminate most of the problems that can take place at substitution of methanol with ethanol therefore, we propose a method for breaking the emulsion formed after transesterification by introducing of a demulsify agent. According to our previous studies we observed that by introducing the demulsify agent into the reaction system at temperatures between 50-60°C, under vigorous agitation for 5 hours, the separation of the esters by glycerol become unproblematic [1, 2].

Experimental study

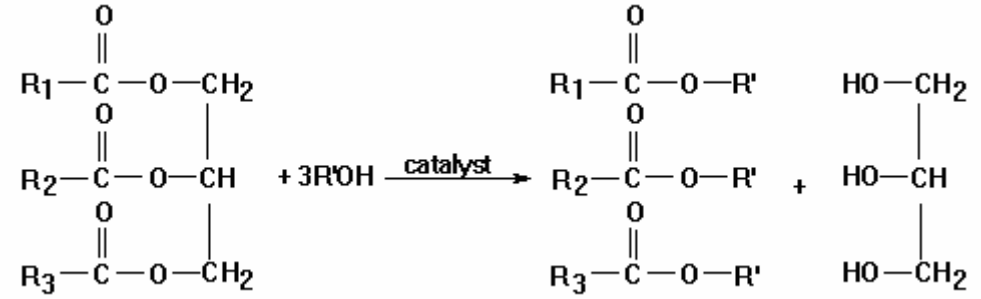
In our study the esters were synthesized by transesterification of triglycerides from sunflower oil. For comparison we prepared methyl ester and ethyl ester according to a method presented below [2].

Fatty acid methyl esters synthesis

Methyl ester

Transesterification of the fatty glycerides existing into the sunflower oil was realized in a batch reactor using potassium hydroxide as catalyst via a method given elsewhere [3-6]. The reaction was carried out at 60°C, atmospheric pressure for 2 hours under vigorous agitation in order to achieve the maximum conversion. In order to obtain the fatty methyl ester by transesterification we used 100% excess methanol, keeping the molar ratio sunflower oil to methanol 1:6 and the catalyst concentration of 1%.

The crude methyl ester was separated by glycerol by gravity and the catalyst was eliminated by hot water washing.



triglyceride alcohol ester glycerol

Ethyl ester

Transesterification of sunflower oil in the presence of ethanol was carried out in similar conditions as methyl ester synthesis. The reaction conditions were 60°C, atmospheric pressure for 5 hours under vigorous agitation, potassium hydroxide catalyst, the ratio between sunflower oil and alcohol was 1:6. In order to improve the separation between the ester and glycerol, 1wt% of a demulsify agent (related to alcohol) was added at the begging of transesterification process into the reaction mixture.

Mixture of esters

1:1 methanol-ethanol molar ratio was used for transesterification of sunflower oil, keeping the ratio between vegetable oil and alcohol at 1:6. The transesterification took place in the same reactor previously used for methyl and ethyl esters synthesis. The alcohol mixture together with sunflower oil was heated up to 60°C at atmospheric pressure under energetic stirring for 5 hours. The separation of glycerol from esters was done as previously mentioned.

The alcohols used in our investigation (anhydrous methanol 99.8% and ethanol 99.9%) were provided by Sigma-Aldrich.

The chemical composition of sunflower oil is given in table 1. After preparation, the methyl ester, ethyl ester and mixture of esters were characterized from viscosity, density, lubricity and refraction index points of view (table 2).

Table 1. The chemical composition of sunflower oil

Fatty acids	**Symbol**	**Sunflower oil, wt %**
Lauric acid	12:0	-
Miristic acid	14:0	-
Palmitic oil	16:0	5.5
Stearic acid	18:0	5.2
Oleic acid	18:1	24.3
Linoleic acid	18:2	64.5
Linolenic acid	18:3	-

Table 2. Physical-chemical characteristics of sunflower oil, methyl ester and ethyl ester

Characteristics	**Sunflower oil**	**Methyl ester**	**Ethyl ester**	**Mixture of esters**
Kinematics Viscosity at 40^{o}C, cSt	32.46	4.67	4.20	4.31
Density, d_4^{20}	0.9176	0.8791	0.8752	0.8771
Lubricity, (HFRR test), μm	117	209	183	198
Refraction index	1.4732	1.4559	1.4542	1.4551

Results

Biodiesel yield investigations

In order to investigate the yield of biodiesel obtained by transesterification of fatty acids in vegetable oils in the presence of different alcohols.
Concerning the ethanol, it is well known that forms azeotrope with water that complicate the recovery process and utilization of the ethanol into the transesterification process leads to an emulsion which makes difficult the separation of ethylic esters by biodiesel.
The previous studies we realized, proved promising results and consists in inserting into the system of a demulsify agent that inhibit the formation of emulsions from ethyl ester and glycerol produced in the process. Therefore, before transesterification, a demulsify agent (1:10 demulsify agent-sunflower oil molar ratio) was introduced into the reaction system in order to increase the solubility of the glycerol produces in transesterification process. The biodiesel yield obtained by transesterification on presence of different alcohols is presented in table 3.

Table 3. Biodiesel yield obtained by transesterification on presence of different alcohols

	Methyl ester	**Mixture of methyl and ethyl esters**	**Ethyl ester**
Biodiesel yield	94.6	66.7	44.20

Unfortunately, first attempts lead us to a much lower ester yield than obtain in transesterification process with methanol.

Conclusions

In this paper, the laboratory experiments were conducted to produce biodiesel by transesterification of sunflower oil in presence of methanol, ethanol and mixtures of methanol and ethanol. The experiments reveal that the rate of sunflower oil transesterification with methanol was faster then the transesterification rate in the presence of ethanol.

The separation of glycerol from biodiesel product was improved by adding a demulsify agent into the reaction system before transesterification process and 1:10 demulsify agent-sunflower oil molar ratio was found to give the faster separation although the ethyl ester yield is much lower than methyl ester yield therefore, additional studies are essential in order to increase the ethyl ester yield.

Acknowledgements

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Metodă alternativă de fabricare a biodieselului din bioetanol

Rezumat

Conform directivei europene EU 2003/30/EC toți membrii Uniunii Europene trebuie să înlocuiască până la 1.01.2010, 5,75 gr% din combustibilul diesel obținut din resurse fosile cu combustibili obținuți din materii prime regenerabile, urmând ca acest procent să crească la începutul anului 2020 până la 10 % gr. In prezent, cea mai utilizată metodă pentru fabricarea biodieselului este transesterificarea acizilor graşi din uleiurile vegetale în prezența metanolului. Din păcate, toxicitatea ridicată, temperatura de inflamabilitate scăzută, efectele ireversibile asupra sănătății umane, fac ca utilizarea metanolului la sinteza biodieselului să fie din ce in ce mai puțin dorită.

In studiile noastre am investigat posibilitatea înlocuirii metanolului cu etanolul în procesul de transesterificare a acizilor graşi din uleiurile vegetale şi am dezvoltat o metoda de separare a etilesterului de glicerina. In vederea optimizării procesului am modificat parametrii de reacție (temperatura, viteza de agitare şi viteza volumară).