

HETEROGENEOUSLY CATALYSED ETHANOLYSIS OF SUNFLOWER OIL IN THE PRESENCE OF PROPYLENE GLYCOL, ETHYL ACETATE AND DIETHYL ETHER AS COSOLVENTS

Dušica R. Đokić-Stojanović^{1*}, Zoran B. Todorović², Dragan Z. Troter², Vanja M. Todorović³, Biljana S. Đorđević², Olivera S. Stamenković², Vlada B. Veljković²

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¹ Zdravlje Actavis, Leskovac, Serbia

² Faculty of Technology, University of Niš, Leskovac, Serbia

³ Faculty of Pharmacy, University of Belgrade, Belgrade, Serbia

A heterogeneous reaction process using propylene glycol (PEG), ethyl acetate and diethyl ether as cosolvents for the transesterification of sunflower oil with ethanol in the presence of calcium oxide as a catalyst has been developed. Significant results were obtained with propylene glycol as a cosolvent. Under determined reaction conditions (CaO concentration, based on the oil weight 1.3736 mol·dm⁻³; temperature 70 °C; and ethanol-to-oil molar ratio 12:1), the conversion of sunflower oil to fatty acid ethyl esters (FAEE) exceeded 98% after 120 min, which was 2 times faster than transesterification of sunflower oil without a cosolvent. After initially enhanced ethanolysis, after 180 min ethyl acetate and diethyl ether negatively influenced the reaction rate and the FAEE yield.

Keywords: biodiesel, ethanolysis, sunflower oil, calcium oxide, catalyst, cosolvents.

Introduction

Biodiesel is a promising alternative energy source with properties similar to diesel. This biofuel is frequently made by alcoholysis of vegetable oils (or animal fats) with a primary aliphatic alcohol, usually methanol or ethanol [1-5]. Catalysts used for this reaction can be homogeneous acidic or basic catalysts, heterogeneous acidic or basic catalysts, or lipases. Homogeneous catalysts are mostly used. The corrosive nature of homogeneous catalysts, their difficult removal from the reaction mixture after the reaction, and water pollution present serious disadvantages [6]. Acid-catalysed reactions are usually slower than base-catalysed [7-8] and may require a large excess of alcohol and high pressure [9]. A greener alternative to chemical transesterification is enzyme-catalysed transesterification [10]. Unfortunately, high cost of enzymes, lipase inactivation caused by methanol and impurities in crude and waste oils represent big disadvantages for this type of transesterification [11]. Heterogeneous (solid) catalysts in the biodiesel production provide a number of benefits. The separation of solid catalysts and purification of products are simpler and cheaper, compared to the same processes when homogeneous catalysts are used. Also, the solid catalysts can be used repeatedly, reducing the operating costs [12]. Biodiesel is a mixture of fatty acid alkyl esters. When ethanol is used as a reactant, the resulting mixture will be fatty acid ethyl esters (FAEE) [13-14], and if methanol is chosen as a reactant, the product will be the mixture of fatty acid methyl esters (FAME) [14-15]. The advantage

of using ethanol for the alcoholysis of vegetable oils is reflected in its lower toxicity and higher solubility in oils than methanol [13]. Since ethanol has one carbon atom more than methanol, FAEE have a higher heat content and cetane number compared to FAME [14]. In addition, ethanol is obtained from biological raw materials, which is why its use in the synthesis of biodiesel fuel is completely agrarian.

Because of its basicity, low solubility and low price, CaO is commonly used as a heterogeneous catalyst for biodiesel synthesis from vegetable oils [16]. CaO attracted the attention because of its high catalytic activity [17] and the possibility of multiple use without significant decrease of its catalytic properties [18-19]. In the previous studies CaO used in the methanolysis of vegetable oils was obtained from different sources [18-23] and from various precursors [24], so the reported optimum reaction conditions are different. Also, quicklime bits represent a very promising catalyst for continuous sunflower oil methanolysis in the continuous flow packed-bed tubular reactor [25].

Based on literature reviews [12,19] it was concluded that the main catalyst in CaO-catalysed ethanolysis is actually basic ethoxide anion which is formed directly and indirectly: (a) O²⁻ from CaO extracts H⁺ from the hydroxyl group of ethanol, and (b) O²⁻ from CaO extracts H⁺ from water to form OH⁻, which further extracts H⁺ from ethanol, thus generating ethoxide anion and water, respectively. In step II, the transesterification mechanism of acyl glycerols takes place in

*Author address: Dušica R. Đokić-Stojanović, Zdravlje Actavis, Vrljkova 199, 16000 Leskovac, Serbia
E-mail: 777dusica@gmail.com
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the presence of ethoxide anions. First, the ethoxide anion attaches to a carbonyl carbon atom of the triacylglycerol (TAG) molecule to form the tetrahedral intermediate. Second, the intermediate picks up an H^+ ion from CaO and reacts with ethanol to produce ethoxide anion. Finally, the reallocation of the tetrahedral intermediate results in the production of both biodiesel and glycerol. Lisboa et al. [26] reported that the calcium diglycerolate was stable up to the third reuse cycle. This is not a big problem because the compounds formed after decomposition ($CaCO_3$ and $Ca(OH)_2$) could be calcinated to form the calcium oxide (CaO), and the glycerol synthesized as a by-product in soybean oil methanolysis can be used to react with calcium oxide to obtain a new batch of calcium diglycerolate. Since the work of Boocock et al. [27], many studies have been performed with the use of various cosolvents in transesterification reactions. Homogeneously catalysed methanolyses are preferred in most of the previous works [16,27-30]. Tetrahydrofuran (THF) has been mainly used as a cosolvent [27, 28, 31], because of its low price, non-reactivity and easy separation from the reaction mixture after completion of the reaction, since methanol and THF have close boiling points ($65^\circ C$ and $67^\circ C$, respectively). THF increases the rate constant of transesterification reactions [28,31], but possesses a tendency to form peroxide during the storage [30], which is a major disadvantage.

Guan et al. [29] suggested dimethyl ether, an environmentally friendly solvent, as a cosolvent for the transesterification process. The same research team [30] tested several cosolvents (THF, dimethyl ether, diethyl ether and *tert*-butyl methyl ether), and dimethyl ether proved to be the most efficient. Park et al. [32] used fatty acid methyl ester (FAME) as a cosolvent. According to Encinar et al. [33] *tert*-butyl methyl ether and diethyl ether showed the best potential as cosolvents, compared with various cosolvents (dibutyl ether, diisopropyl ether, tetrahydrofuran, and acetone). Pena et al. [34] studied *n*-hexane as a cosolvent for castor oil transesterification with three alkaline catalysts (CH_3ONa , NaOH and KOH). Hancsóok et al. [35] studied the production of fatty acid methyl esters (FAME) from frying oil with acid/base-catalysed transesterification with THF and dioxane as cosolvents. Hernando et al. [36] studied the transesterification of rapeseed and soybean oils combining the use of *tert*-butyl methyl ether and microwave irradiation to reduce the mass transfer limitation in the first reaction stage. Todorović et al. [37] studied both homogeneously and heterogeneously base-catalysed sunflower oil methanolysis with and without the presence of cosolvents. In the former case, KOH and THF were used as a catalyst and a cosolvent, respectively. In the latter case, CaO and various organic solvents such as THF, *n*-hexane, dioxane, diethyl ether, triethanolamine, ethyl acetate and methyl ethyl ketone were employed as a solid catalyst and a cosolvent, respectively. The rate of KOH-catalysed sunflower oil methanolysis increased with increasing the THF concentration up to 50% of the oil mass. No effect of THF present at the concentration of 20% on the rate of CaO-catalysed methanolysis was observed,

but at higher THF concentrations, the reaction was delayed and the final fatty acid methyl esters (FAME) yield was decreased. Of all the tested cosolvents, only *n*-hexane and THF slightly improved the methanolysis reaction in its initial period, triethanolamine and ethyl acetate had no effect, while diethyl ether, dioxane and methyl ethyl ketone negatively influenced the reaction rate and the FAME yield [37]. Sakthivel et al. [38] investigated the effects of residence time and reaction temperature on the yield of fatty acid methyl ester (biodiesel) with and without the presence of biodiesel as a cosolvent. The results showed that the yield of fatty acid methyl esters obtained was almost 20% higher than the cosolvent free process. The KOH-catalysed sunflower oil methanolysis in the absence and presence of THF as a cosolvent was investigated by Banković-Ilić et al. [39] in a continuous cocurrent upflow reciprocating plate reactor. In this study, the positive effects of this cosolvent on the Sauter-mean diameter of the dispersed phase, the drop size distribution and the TAG conversion degree in both reactive (methanol/KOH/oil) and non-reactive (methanol/oil) systems were reported.

Despite above mentioned benefits, the use of cosolvents in heterogeneously catalysed methanolysis has been reported in a few papers [21,40-42]. Gryglewicz [21] and Yang and Xie [42] described the positive impact of THF on heterogeneously catalysed methanolysis, while Ilgen et al. [40] and Kim et al. [41] observed an inhibitory effect of THF. Kim et al. [41] also found that methanolysis reaction can be improved in the presence of *n*-hexane, while Ilgen et al. [40] and Yang and Xie [42] reported a negative effect of *n*-hexane. The observed disagreement on the effect of cosolvents on heterogeneously catalysed transesterification should be investigated in order to be clarified [37].

The present work deals with the ethanolysis of sunflower oil catalysed by the calcinated CaO ($550^\circ C$, 2 h) in the presence of various cosolvents. The heterogeneously catalysed ethanolysis of sunflower oil is a three-phase reaction system (oil, alcohol and solid catalyst), where mass transfer limitations, due to immiscibility of the reactants, determine the overall reaction rate. An organic solvent added as a cosolvent reduces immiscibility of the reactants and increases the transesterification reaction rate. Calcium oxide and various organic solvents such as propylene glycol (PEG), ethyl acetate and diethyl ether were employed as a solid catalyst and cosolvents, respectively, and the reactions were carried out at the $70^\circ C$ with ethanol-oil molar ratio of 12:1. The impact of PEG, ethyl acetate and diethyl ether as a cosolvent on the heterogeneously CaO catalysed ethanolysis have been discussed in detail.

Experimental

Materials

Commercial edible sunflower oil (Dijamant, Serbia) was used. Ethanol (99.8%) was purchased from La-

chema (Czech Republic). CaO (extra pure) was from Centrohem (Serbia). CaO was activated before use by calcination at 550 °C for 2 h [20]. In order to avoid the adsorption of water and carbon dioxide from the air on catalytic active sites on the catalyst surface, the activated CaO was cooled and then stored in a well closed glass bottles in a desiccator containing CaCl₂. Also, the following solvents were used: propylene glycol (PEG) (Ph Eur, Meilab, Belgrade, Serbia), ethyl acetate (99.5%, Merck), diethyl ether (Lachner). The properties of the used cosolvents and ethanol are presented in Table 1.

Table 1. The properties of used cosolvents and ethanol

Cosolvent	ETAC ^a	DEE ^b	PEG ^c
Density (g·cm ⁻³)	0.894	0.713	1.036
Viscosity at 20 °C (mPa·s)	0.45	0.24	56
Partition coefficients at 25 °C (log P)	0.73	0.89	0.92
Dipole moment, D	1.78	1.15	3.6
Dielectric constant at 40 °C	6.02	4.33	32

^aETAC - ethyl acetate; ^bDEE - diethyl ether; ^cPEG - propylene glycol.

Heterogeneously catalysed ethanolysis

The apparatus for heterogeneously-catalysed ethanolysis consisted of 500 ml three-neck round-bottomed flask, placed in a glass chamber and equipped with a magnetic stirrer and a condenser. Water was circulated through the chamber from a thermostated bath (70 ± 1 °C). In these series of experiments, where the effect of different cosolvents (20%, based on the mass oil) was studied, the amount of CaO was corresponding to the concentration of 1.3736 mol·dm⁻³. In all experiments, the catalyst was suspended into ethanol (28.76 g; ethanol-to oil molar ratio 12:1) in the reaction flask. The amount of a cosolvent (9.19 g) was added to the mixture of ethanol and the catalyst, and the reaction flask was shaken for 30 minute. Sunflower oil (45.96 g, at temperature 70 ± 1 °C) was added in the reaction flask, and the measurements of the reaction time began. The samples (750 µL) were removed from the reaction mixture during the ethanolysis reaction, immediately quenched by adding the solution of hydrochloric acid (5 mol·dm⁻³) to stop the reaction and centrifuged (3500 rpm, 10 min). The upper layer (named FAEE fraction) was withdrawn, dissolved in 2-propanol/n-hexane (5:4 v/v) in an appropriate ratio and filtered through a 0.45 µm Millipore filter. The resulting filtrate was used for a high performance liquid chromatography (HPLC) analysis.

Analytical methods

Thin layer chromatography (TLC) analysis

In order to perform the qualitative analysis, the composition of each sample of the reaction mixture was estimated by TLC. Solutions and standards were spotted onto a 20 x 10 cm plate (Silica gel 60 F254; Merck, Darmstadt, Germany) with a 10 µL HP microsyringe in amounts of 5 µL of solution per spot. The plates were

developed in a glass chambers with an organic mixture of n-hexane/ethyl acetate/acetic acid (90:10:1 v/v/v) [43] and air-dried thoroughly. In order to visualise the spots that developed, iodine vapor was used [44].

High performance liquid chromatography (HPLC) analysis

For quantitative determination, the composition of the FAEE fraction (both glycerides and FAEE) of the selected samples of the reaction mixture was determined by the modified HPLC method by Holčapek et al. [45]. An HPLC chromatograph (Agilent 1100 Series) equipped with a micro vacuum degasser, a binary gradient system, a thermostated column compartment and a variable wavelength detector was employed. For separation, a Zorbax Eclipse XDB-C₁₈ column (4.6 X 150 mm with 5 µm particle size) was used. The column temperature was constant at 40 °C. In all experiments, the injection volume of 20 µL and flow rate of 1 mL/min were applied. The mobile phase was methanol (reservoir A) and 2-propanol/n-hexane (5:4 v/v; reservoir B). A linear gradient from 100% A to 40% A + 60% B in 15 min was employed, and the components were detected at 205 nm. By using the standard mixture of FAEE and the standard glycerides, the calibration curves were prepared and used for the quantification of the FAEE and the glycerides present in the selected samples.

Results and discussion

In order to investigate the impacts of some cosolvents on the CaO-catalysed ethanolysis of sunflower oil, in all experiments the amount of cosolvent was 20% of the mass oil and the amount of the catalyst corresponded to the concentration of 1.3736 mol·dm⁻³.

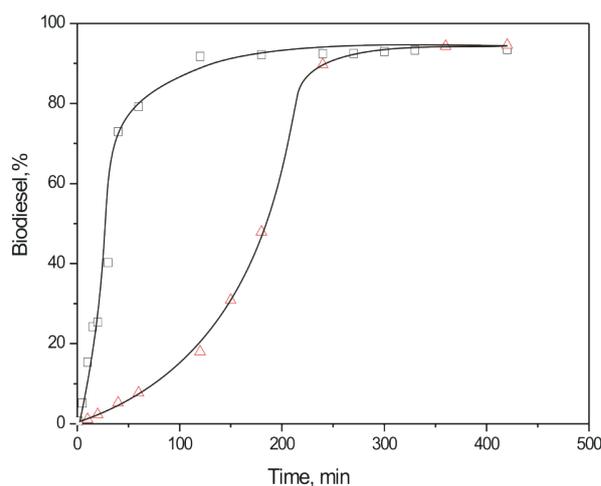


Figure 1. The variations of the FAEE yield with the progress of sunflower oils ethanolysis catalysed by CaO (20%, based on the oil weight): no cosolvent - ○; with propylene glycol (PEG) as cosolvent - □. Reaction conditions: catalyst concentration, based on the oil weight 1.3736 mol·dm⁻³; temperature 70 °C; and ethanol-to-oil molar ratio 12:1.

Figure 1 shows the variations of the FAEE yield during the ethanolysis reaction catalysed by CaO without a cosolvent and in the presence of propylene glycol propylene glycol (PEG) as a cosolvent. PEG significantly accelerates the ethanolysis reaction. The FAEE yield in the presence of PEG as a cosolvent in 20 minutes was 25.3%, which is 10.83 times more than in the reaction without a cosolvent. After 40 minutes, the FAEE yield was 72.9%, which was 14 times more than in the reaction without a cosolvent, and after 180 minutes the FAEE yield was 92.2%, which was 2 times more than in the reaction without a cosolvent. This means that the ethanolysis reaction is almost complete after 180 minutes from the reaction start. It was 3 hours less for the same FAEE yield if the reaction which was carried out without a cosolvent.

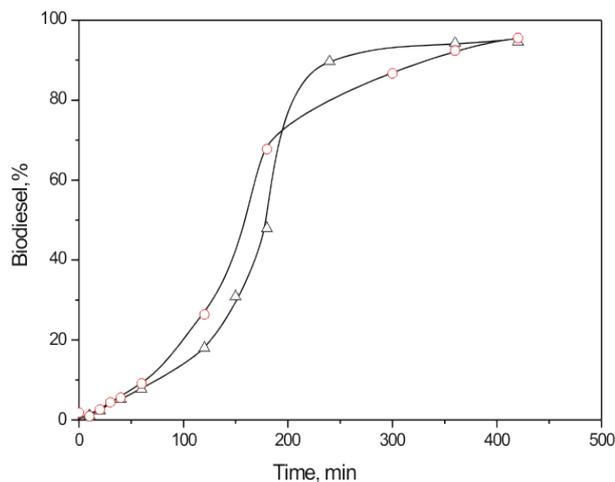


Figure 2. The variations of the FAEE yield with the progress of sunflower oils ethanolysis catalysed by CaO (20%, based on the oil weight): no cosolvent - ○; with ethyl acetate as cosolvent - □. Reaction conditions: catalyst concentration, based on the oil weight $1.3736 \text{ mol}\cdot\text{dm}^{-3}$; temperature $70 \text{ }^\circ\text{C}$; and ethanol-to-oil molar ratio 12:1

As seen from Figure 2, the ethyl acetate has no significant effect on the ethanolysis reaction rate. In the first 180 min the FAEE yield is a little bit higher than the FAEE yield in the ethanolysis without cosolvent. After 180 minutes, the ethanolysis reaction with ethyl acetate as a cosolvent was delayed and the final FAEE yield was decreased. The assumption was that ethyl acetate provided an extra ethyl group due to its degradation, so the same reaction was carried out in the absence of ethanol. After 6 hours, the quantity of the oil was the same as at the beginning, meaning that the reaction was unsuccessful, proving that the dissociation of ethyl acetate does not occur, and ethyl group which reacts with triglycerides in order to form FAEE originates only from ethanol. As it can be seen from Figure 2, the ethyl acetate has no significant impact on the ethanolysis reaction rate. Up

to 180 minutes from the reaction start, the FAEE yields are a little larger than the FAEE yields in the ethanolysis without a cosolvent. After 180 minutes, the ethanolysis reaction with ethyl acetate as a cosolvent was delayed and the final FAEE yields were decreased.

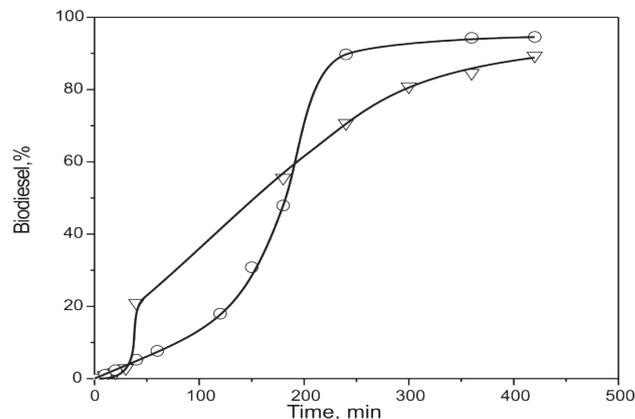


Figure 3. The variations of the FAEE yield with the progress of sunflower oils ethanolysis catalysed by CaO (20%, based on the oil weight): no cosolvent - ○; with diethyl ether as cosolvent - □. Reaction conditions: catalyst concentration, based on the oil weight $1.3736 \text{ mol}\cdot\text{dm}^{-3}$; temperature $70 \text{ }^\circ\text{C}$; and ethanol-to-oil molar ratio 12:1.

Figure 3 represents the variations of the FAEE yield during the ethanolysis reaction catalysed by CaO without a cosolvent and in the presence of diethyl ether as a cosolvent. After 40 minutes, the FAEE yield in the presence of diethyl ether was 20.9%, which was 4 times more than the yield from the reaction without a cosolvent. After 180 minutes from the ethanolysis reaction start with diethyl ether as a cosolvent, the final FAEE yield was less than the FAEE yield in the ethanolysis reaction catalysed by CaO without a cosolvent. Because the diethyl ether has a lower density than the reaction medium, its addition increased the reaction rate at the beginning of the reaction due to the easier mass transfer. But, as the ethanolysis reaction progressed, the final FAEE yield with diethyl ether as a cosolvent decreased due to a dilution effect of the reactants.

It is obvious from Figure 4 that the activity of all tested cosolvents in the ethanolysis reaction catalysed by CaO act according to the following order: PEG > ethyl acetate > diethyl ether. PEG strongly accelerates the ethanolysis reaction. Under the same reaction condition, the reaction time was 3 hours shorter, compared to the reaction carried out in the absence of PEG. After 20 min from the beginning of the reaction, the ethanolysis catalysed by CaO and with PEG as a cosolvent provided FAEE yield of 25.3%, which was higher than the FAEE yield reported when ethanolysis was carried out without PEG (2.3%).

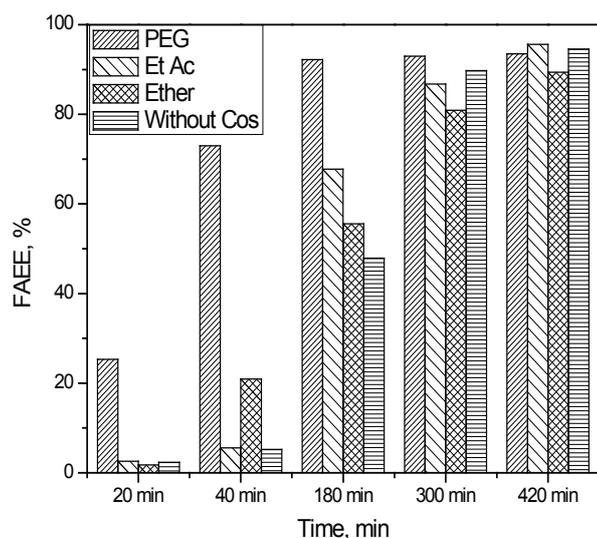


Figure 4. The FAEE yield obtained by catalytic reaction with CaO as catalyst without cosolvents and in catalytic reactions with CaO as a catalyst with the following cosolvents: propylene glycol, ethyl acetate and diethyl ether. Reaction conditions: catalyst concentration, based on the oil weight 1.3736 mol·dm⁻³; temperature 70 °C; and ethanol-to-oil molar ratio 12:1.

The other investigated cosolvents are less effective. Ethyl acetate and diethyl ether increased the reaction rate only at the start of the reaction, mostly because their presence in the reaction medium reduced immiscibility of the reactants (oil and alcohol), thus producing nearly homogeneous solution. In addition, their presence in the reaction medium diminishes the density of the reaction mixture, so that the mass transfer is easier. After 20 minutes from the reaction start the ethanolsis catalysed by CaO and with ethyl acetate as a cosolvent provided FAEE yield of 2.6%, which was just slightly more than the FAEE yield obtained when the ethanolsis reaction was carried out without a cosolvent (2.3%). For the same time duration, the FAEE yield of 1.7% was reported for the reaction with CaO as a catalyst and diethyl ether as a cosolvent. It is interesting that, after 40 minutes from the reaction start, the FAEE yield with diethyl ether as a cosolvent was 20.9%, which was 8 times higher than the reported FAEE yield for the reaction when ethyl acetate was chosen as a cosolvent (2.6%). The possible cause for this effect are the density and viscosity of the diethyl ether, which have a dominant impact on the mass transfer of the reactants. As the reactions continued, after 180 minutes both ethyl acetate and diethyl ether inhibited the reactions. This can be explained by their possible blockage of the active sites of CaO crystals' surface, which results in preventing the formation of calcium ethoxide that catalyses the reaction. In addition, the dilution effect of the reactants occurs.

Conclusion

The CaO-catalysed ethanolsis of sunflower oil was investigated with and without different cosolvents in order to determine whether cosolvents can influence the final FAEE yield and the reaction rate. This study confirmed the positive effect of the tested propylene glycol as a cosolvent on the CaO-catalysed sunflower oil ethanolsis. This reaction was completed beyond 3 hours prior to the original CaO-catalysed reaction without a cosolvent. Both ethyl acetate and diethyl ether increased the initial reaction rate, but as the ethanolsis progressed, after 180 min. cosolvents inhibited the ethanolsis. However, further studies are needed in order to optimize the operation conditions for CaO-catalysed ethanolsis of sunflower oil with propylene glycol as a cosolvent which strongly accelerated the reaction.

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Izvod

HETEROGENO KATALIZOVANA ETANOLIZA SUNCOKRETOVOG ULJA U PRISUSTVU POLIETILEN GLIKOLA, ETIL ACETATA I DIETIL ETRA KAO KOSOLVENATA

Dušica R. Đokić-Stojanović¹, Zoran B. Todorović², Dragan Z. Troter²,
Vanja M. Todorović³, Biljana S. Đorđević², Olivera S. Stamenković², Vlada B. Veljković²

(ORIGINALNI NAUČNI RAD)
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¹ Zdravlje Actavis, Leskovac, Srbija

² Tehnološki fakultet, Univerzitet u Nišu, Leskovac, Srbija

³ Farmaceutski fakultet, Univerzitet u Beogradu, Beograd, Srbija

U radu je opisana heterogena transesterifikacija suncokretovog ulja sa etanolom i kalcijum oksidom kao katalizatorom u prisustvu polietilen glikola (PEG), etil acetata i dietil etra kao kosolvenata. Najpovoljniji rezultati su dobijeni sa polietilen glikolom kao kosolventom gde je, pod određenim reakcionim uslovima (koncentracija CaO, računata u odnosu na masu ulja $1.3736 \text{ mol} \cdot \text{dm}^{-3}$, temperatura $70 \text{ }^\circ\text{C}$ i molarni odnos etanol:ulje 12:1), konverzija suncokretovog ulja u etil estre masnih kiselina (FAEE) dostigla vrednost od 98% nakon 120 minuta, što je 2 puta brže od transesterifikacije suncokretovog ulja bez prisustva kosolventa. Etil acetat i dietil etar poboljšavaju reakciju etanolize na početku, ali, kako reakcija napreduje, posle 180 minuta, njihovo prisustvo u reakcionoj smeši negativno utiče na brzinu reakcije i prinos etil estrara masnih kiselina (FAEE).

Ključne reči: biodizel, etanoliza, suncokretovo ulje, kalcijum-oksidi, katalizator, kosolventi.