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*Original scientific paper*

## Influence of various cosolvents on the calcium oxide-catalyzed ethanolysis of sunflower oil

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**Abstract:** Ten organic solvents (triethanolamine, diethanolamine, ethylene glycol, methyl ethyl ketone, *n*-hexane, triethylamine, ethylene glycol dimethyl ether, glycerol, tetrahydrofuran and dioxane) were applied as cosolvents in the CaO-catalyzed ethanolysis of sunflower oil performed in a batch stirred reactor under the following reaction conditions: temperature 70 °C, ethanol-to-oil mole ratio 12:1, initial catalyst concentration 1.374 mol·L<sup>-1</sup> and amount of cosolvent 20 % based on the oil amount. The main goals were to assess the effect of the used cosolvents on the synthesis of fatty acid ethyl esters (FAEE) and to select the most efficient one with respect to the final FAEE content, reaction duration and safety profile. In the absence of any cosolvent, the reaction was rather slow, providing a FAEE content of only 89.7±1.7 % after 4 h. Of the tested cosolvents, diethanolamine, triethanolamine and ethylene glycol significantly accelerated the ethanolysis reaction, whereby the last two provided a final FAEE content of 93.1±2.1 and 94.1±1.5 %, respectively, within 0.5 h. However, because of its safety profile, triethanolamine was selected as the best cosolvent for the ethanolysis of sunflower oil catalyzed by calcined CaO.

**Keywords:** cosolvents; fatty acid ethyl esters; heterogeneous catalysis; transesterification.

### INTRODUCTION

Biodiesel is usually produced by transesterification (alcoholysis) of vegetable oils or animal fats with methanol or ethanol in the presence of a catalyst. It is a promising alternative to mineral diesel due to its favorable properties, such as

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biodegradability, lower toxicity, and lower CO<sub>2</sub> and sulfur emission, can be used on its own or mixed with diesel for diesel-engine vehicles, *etc.* Besides their numerous advantages, the ethanolysis reactions have been studied much less than the methanolysis reactions. Ethanol is less toxic than methanol, can be obtained from agrarian waste and is more soluble in oils than methanol. By using ethanol obtained from biomaterials for biodiesel production, a completely agrarian fuel is obtained. Compared to fatty acid methyl esters (FAMES), fatty acid ethyl esters (FAEEs) have higher heat capacity, cetane number, cloud point and pour point, as well as better lubricity properties.<sup>1</sup> From the environmental point of view, FAEEs are characterized by less exhaust gas emissions and higher biodegradability in water than FAMES. In addition, higher esters' yields can be obtained with ethanol than with methanol. Ethanolysis has several drawbacks too, such as a higher cost and lower transesterification reactivity (caused by steric hindrance of the longer carbon chain) of ethanol compared to methanol, formation of azeotrope with water (making its separation more difficult), higher energy consumption, greater influence of water in the reaction mixture on the FAEEs yield, formation of more stable emulsions, as well as higher viscosity and the acid value of FAEEs than those of FAMES.

The production of biodiesel is currently based on utilizing homogeneous catalysts, but it is expected that the importance of heterogeneous (solid) catalysts will increase in the near future. Unlike homogeneous catalysts, solid catalysts can easily be separated from the final product and used repeatedly, thus reducing the production costs. The other benefits of solid catalysts are low corrosion risk and low environmental threats. On the other hand, their drawbacks are lower reaction rates, possible deactivation and leaching. One of the most attractive heterogeneous catalysts for transesterification is CaO, since it is cheap, highly alkaline and catalytically active, easy for preparation from natural sources and plant or animal wastes, environmentally friendly and easily recovered from the reaction mixture.<sup>2,3</sup> Moreover, CaO can be used repeatedly in batch processes without significant loss of catalytic activity and for long-term continuous biodiesel production.<sup>4</sup> By using nano CaO-based catalysts, both the specific surface and catalytic activity can be improved, resulting in high biodiesel yields.<sup>5</sup> Therefore, CaO catalyst has a potential to be applied in industrial biodiesel production.<sup>6</sup> After being exposed to the air, CaO adsorbs CO<sub>2</sub> and moisture, forming CaCO<sub>3</sub> and Ca(OH)<sub>2</sub> at the surface of catalyst particles, which lowers its catalytic activity. Therefore, activation of CaO prior to use, usually thermally, is necessary.

Vegetable oils and animal fats are not completely miscible with methanol and ethanol, which slows down the transesterification rate. The reaction rate in multiphase batch stirred reactors can be increased by enhancing the mass transfer rate, either by intensive agitation that increases the liquid–liquid contact area or by the addition of a cosolvent (usually an organic solvent) to the reaction mixture

that improves the mutual miscibility of the reactants. The preferable cosolvent should have the boiling point similar or close to that of the employed alcohol, allowing their simultaneous recovery by distillation. Some of the commonly used cosolvents in transesterification reaction are organic solvents, such as tetrahydrofuran, acetone, dioxane, *n*-hexane, methyl esters and various ethers. Specifically, ethyl acetate is used as either a reactant or cosolvent.<sup>7</sup> Recently, some ionic liquids and deep eutectic solvents have been used as cosolvents.<sup>8</sup> Cosolvents can be used in both homogeneously<sup>9,10</sup> and heterogeneously<sup>9,11</sup> catalyzed transesterification reactions, as well as in supercritical transesterifications.<sup>12</sup> Some cosolvents (diethyl ether, dioxane and methyl ethyl ketone), which promote the homogeneous KOH-catalyzed methanolysis of sunflower oil, inhibit heterogeneous CaO-catalyzed methanolysis.<sup>9</sup> It could be expected that different cosolvents affect CaO-based catalysts differently, as observed in the methanolysis of palm oil over a river snail shells-derived CaO catalyst.<sup>13</sup>

In the present work, the ethanolysis of sunflower oil catalyzed by calcined CaO in the presence of various cosolvents (diethanolamine, triethanolamine, ethylene glycol, methyl ethyl ketone, *n*-hexane, triethylamine, ethylene glycol dimethyl ether, glycerol, tetrahydrofuran and dioxane) was investigated. The main goals were to test the efficacy of these cosolvents in promoting CaO activity and to select the cosolvent providing the highest final FAEE content in the shortest reaction time and having a good safety profile. According to the best of our knowledge, there are no available data on the comparison of the influence of different cosolvents in CaO-catalyzed ethanolysis of vegetable oils.

## EXPERIMENTAL

### Materials

Commercial edible sunflower oil (Dijamant, Zrenjanin, Serbia) was used. Physico-chemical characteristics of oil were determined by the standard methods for oils.<sup>14</sup> Acid, saponification and iodine values were 0.29 and 190 mg KOH·g<sup>-1</sup> and 1.39 g I<sub>2</sub>·g<sup>-1</sup> oil, respectively. The density (918.4 kg·m<sup>-3</sup>) and the dynamic viscosity (77.1 mPa·s) were measured at 20 °C using a pycnometer and a rotational viscometer (Visco Basic Plus v. 0.8, Fungilab S.A., Barcelona, Spain), respectively. CaO (extra pure) was provided by Sigma-Aldrich (St. Louis, USA) and was activated by calcination at 550 °C for 2 h.<sup>15</sup> The activated CaO was cooled and then stored in well closed, glass bottles in a desiccator containing CaCl<sub>2</sub> and KOH pellets. The cosolvents used were: diethanolamine, triethanolamine, ethylene glycol, triethylamine, tetrahydrofuran (all 99.0 %, Sigma-Aldrich, St. Louis, USA), methyl ethyl ketone (HPLC grade 99.5 %, JT Baker, Center Valley, Pennsylvania, USA), *n*-hexane (99 %, LGC Promochem, Wesel, Germany), ethylene glycol dimethyl ether (99.0 %, Acros Organic, Geel, Belgium), glycerol (Ph Eur grade, MeiLab, Belgrade, Serbia) and dioxane (p.a., Merck-Millipore, Darmstadt, Germany). Some properties of the used cosolvents and ethanol are listed in Table S-I of the Supplementary material to this paper. Ethyl acetate (99.5 %, Merck-Millipore, Darmstadt, Germany) and glacial acetic acid (Zorka, Šabac, Serbia) were employed as solvents. HPLC grade methanol, 2-propanol and *n*-hexane were provided from Lab-Scan (Dublin, Ireland). Hydrochloric acid (36.0 %) was purchased from Centrohem (Stara Pazova, Serbia). The standards

containing ethyl esters of palmitic, stearic, oleic, linolenic and linoleic acids (20.0 % of each ester), as well as the standards of triolein, diolein and monoolein, were purchased from Sigma-Aldrich (St. Louis, CA, USA).

#### *Equipment and experimental procedure*

The reaction was performed in a 500 mL, three-necked glass flask, equipped with a reflux condenser and a magnetic stirrer, at the atmospheric pressure. The flask was placed in a glass vessel, through which heating water circulated from a thermostated bath. The desired amounts of ethanol, cosolvent and calcined CaO were added to the flask and stirred at 70 °C for 30 min. The CaO concentration was 1.374 mol·L<sup>-1</sup> in all experiments. The stirrer was turned off and the corresponding amount of sunflower oil, heated separately to the same temperature, was added to the reaction flask. Then, the stirrer was switched on again and the reaction was timed. During the reaction, samples were taken from the reaction mixture and immediately quenched by adding the required amount of aqueous hydrochloric acid solution (5 mol·L<sup>-1</sup>) to neutralize the catalyst. After centrifugation (Sigma 2-6E, Germany) at 3500 rpm for 15 min, the upper layer (ester/oil fraction) was withdrawn, dissolved in a 2-propanol/*n*-hexane (5:4 volume ratio) mixture in the appropriate ratio (1:10 or 1:200 for qualitative thin layer or quantitative liquid chromatography analysis, TLC and HPLC, respectively) and filtered through a 0.45 µm Millipore filter. The resulting filtrate was used for TLC and HPLC analyses. At the end of the reaction, the CaO catalyst was separated from the reaction mixture by centrifugation, washed with ethanol, filtered, dried for 2 h at 110 °C and analyzed by the X-ray powder diffraction (XRD) method.

#### *Analytical methods*

The chemical composition of each sample from the reaction mixture was first estimated qualitatively by TLC and then quantitatively by the HPLC method described elsewhere.<sup>15,16</sup> Calibration curves were prepared using standard mixtures of FAEE and acylglycerols, which were used for the quantification of the FAEE and acylglycerols present in samples of the reaction mixtures. Calcium was determined in the upper (FAEE) and middle (alcohol) layers by ICP/AES (inductively coupled plasma atomic emission spectrometry; iCAP-6500 Duo, Thermo Scientific, UK) analysis. The XRD measurements were performed on a Philips PW 1050 X-ray powder diffractometer using Ni-filtered Cu K $\alpha_{1,2}$  ( $\lambda = 1.54178 \text{ \AA}$ ) radiation and the Bragg–Brentano focusing geometry. The measurements were realized at room temperature over a  $2\theta$  range of 7–70° with a scanning step width of 0.05° and a counting time of 3 s per step.

## RESULTS AND DISCUSSION

### *Impact of different cosolvents on the CaO-catalyzed ethanolysis of sunflower oil*

The influence of the tested cosolvents on the CaO-catalyzed ethanolysis of sunflower oil was investigated under the same reaction conditions (ethanol-to-oil molar ratio of 12:1, catalyst concentration of 1.374 mol·L<sup>-1</sup> and cosolvent amount of 20 % of the oil mass) applied in a previous study of the calcined CaO-catalyzed methanolysis of sunflower oil.<sup>9</sup> The FAEE contents during the calcined CaO-catalyzed ethanolysis of sunflower oil, compared to the control reaction in the absence of any cosolvent, are shown in Fig. 1.

The control reaction was slow and hence, quite time-consuming, as was previously observed.<sup>17</sup> Under the control reaction conditions, an FAEE content of

89.7±1.7 % was achieved in 4 h, while further prolongation of the reaction negligibly increased the FAEE content. Another observance characterizing the control reaction system was slow separation of the two liquid phases of the final reaction mixture (more than 24 h). No reaction between the oil and ethanol occurred in the presence of cosolvents in the absence of CaO, implying that the tested cosolvents had no catalytic activity. After 6 h, the FAEE contents were less than 0.5 % in these reactions (not shown in Fig. 1).

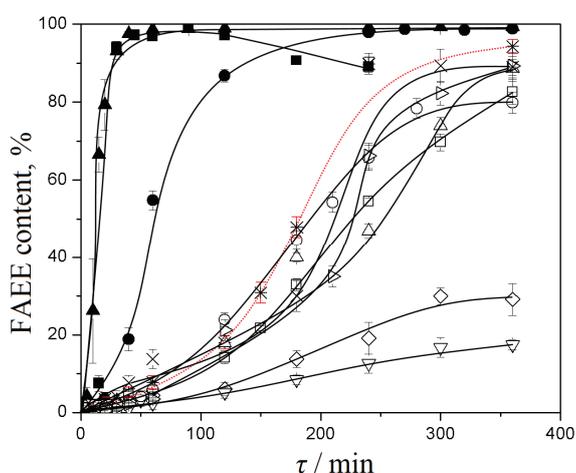


Fig. 1. FAEE synthesis by the calcined CaO-catalyzed ethanolysis of sunflower oil in the presence of different cosolvents: diethanolamine (●), triethanolamine (▲), ethylene glycol (■), dioxane (×), glycerol (○), methyl ethyl ketone (△), *n*-hexane (□), triethylamine (◇), ethylene glycol dimethyl ether (▽) and tetrahydrofuran (▷), compared to the control reaction with no cosolvent (\*, dotted line). Reaction conditions: temperature 70 °C, ethanol-to-oil mole ratio 12:1, CaO concentration of 1.374 mol·L<sup>-1</sup> and amount of cosolvent 20 % based on the oil amount.

Based on their effects on the reaction performance, the cosolvents were classified as stimulative and inhibitory (represented in Fig. 1 by the black and open symbols, respectively). The first group included diethanolamine, triethanolamine and ethylene glycol, while the second group consisted of methyl ethyl ketone, *n*-hexane, triethylamine, tetrahydrofuran, ethylene glycol dimethyl ether and glycerol. All curves were more or less sigmoidal, indicating a slow reaction in the initial induction stage of the reaction, an accelerated stage in the middle of the reaction and a decelerated stage approaching the final equilibrium. These effects were ascribed to mass transfer limitations (both liquid–liquid and liquid–solid) and the kinetics of the reactions occurring on the surface of the solid catalyst particles,<sup>15</sup> as well as the improved miscibility of the reactants that influenced the equilibrium of partition.<sup>18</sup> The formed esters could also act as a cosolvent,<sup>19</sup> thus contributing further to the mutual miscibility of the reactants. The slow reaction in the final stage was due to the reduced concentrations of the reactants.

The curves corresponding to the stimulative cosolvents (diethanolamine, triethanolamine and ethylene glycol) are located above the curve corresponding to the control reaction (dotted curve, Fig. 1). Obviously, these cosolvents positively

affected the ethanolysis reaction from its start by improving the mutual miscibility of the reactants (equilibrium of partition), as they shortened the initial induction period, accelerated the reaction and provided a higher final FAEE content in a shorter time, compared to the control reaction. These results highlighted the kinetic effects, leading to the highest yields for a significantly reduced operating time. The efficiency of these cosolvents was in the following order: triethanolamine > ethylene glycol > diethanolamine. Moreover, deep eutectic solvents (DESS) might be formed from these cosolvents and hydrogen bond donors, such as glycerol and water,<sup>20</sup> shifting the reaction to the right, thus increasing the FAEE content. Due to their strong water affinity, these cosolvents limited the availability of water molecules for triacylglycerols' hydrolysis and soap formation. Since ethylene glycol is moderately toxic for humans and animals, triethanolamine may be recommended as an optimal cosolvent for the CaO-catalyzed ethanolysis sunflower oil. With this cosolvent, an FAEE content of  $79.3 \pm 6.54$  % was achieved in 20 min, which was much higher compared to the control reaction ( $2.3 \pm 1.6$  %). In addition, an FAEE content of  $93.1 \pm 2.07$  % was achieved after 0.5 h, while the same content in the control reaction system was obtained after 6 h.

Some cosolvents from the second group, such as triethylamine and ethylene glycol dimethyl ether, inhibited the ethanolysis reaction from its beginning, while the others (glycerol, methyl ethyl ketone, *n*-hexane, triethylamine and tetrahydrofuran) did not affect the ethanolysis reaction up to its middle stage, compared to the control reaction system (no cosolvent present), as indicated by the gathering of their curves around the control curve (Fig. 1). Thereafter, the reaction rate decelerated and the FAEE content decreased, so the curves corresponding to these hydrophobic cosolvents were, more or less, far from the control curve. Dioxane, as an exception, seemed not to affect the catalyst activity, compared to the control reaction, as its curve overlapped with the control curve (dotted line). For the CaO-catalyzed methanolysis, Todorović *et al.*<sup>9</sup> reported that triethanolamine and ethyl acetate had no effect while dioxane, methyl ethyl ketone and diethyl ether had a negative influence on both the reaction rate and FAME content. Glycerol accelerated the reaction until 2 h; after which, the FAEE content was lower, compared to the content achieved in the control reaction. This means that the excess glycerol (amount not used for Ca-diglyceroxide synthesis plus amount produced during the ethanolysis) retarded the reaction. This glycerol-induced loss of the Ca-diglyceroxide catalytic activity was also observed in the methanolysis of soybean oil.<sup>21</sup> The excess glycerol also favored the reverse reaction, hence reducing the FAEE content. Unlike the hydrophilic cosolvents, the hydrophobic cosolvents did not react intensively with water and glycerol in the presence of a solid catalyst, thus having a low influence on the initial ethanolysis reaction rate. A possible inhibitory effect of the hydrophobic cosolvents might be ascribed to their multiple actions in the ethanolysis reaction. The hydrophobic

cosolvents did not effectively homogenize the alcohol and oil phases, thus not influencing the rates of mono- and diacylglycerol formation, as already reported for THF and *n*-hexane.<sup>22</sup> The blockage of the active sites on the catalyst surface by these cosolvents was also possible, which resulted in prevention of the formation of the catalytically active calcium alkoxide.<sup>9</sup> The positive action of the hydrophilic cosolvents was related to the dramatic reduction in the viscosity of the reaction mixture. Diethanolamine and triethanolamine could be also transesterified with sunflower oil using the CaO catalysts to produce esteramines, known as cationic surfactants, which increased the homogenization of the alcohol and oil phases.<sup>23</sup> Moreover, because of their polarity, the hydrophilic cosolvents were well soluble in the alcohol, but not in sunflower oil, which aggravated the ethanolysis, thus leading to a decreased FAEE content.<sup>13</sup>

In an attempt to explain the impact of different cosolvents on the CaO-catalyzed ethanolysis of sunflower oil, the FAEE content achieved after 1 h was correlated with the hydrophobicity of the cosolvents measured by  $\log P$  (Fig. 2), where  $P$  stands for the partition coefficient ( $\log P$  values are listed in Table S-I of the Supplementary material). It was indicative that a slight change in the cosolvent hydrophobicity had a major effect on the ethanolysis reaction rate. The characteristic examples were the reactions with triethanolamine and ethylene glycol (improvers), as well as triethylamine and ethylene glycol dimethyl ether (inhibitors). Generally, the activity of the cosolvents increased gradually with decreasing  $\log P$  value, thus suggesting that the organic solvents with a negative  $\log P$  value might improve the mass transfer rate and increase the mutual miscibility of methanol and oil. The group of hydrophilic cosolvents with a positive effect on the ethanolysis reaction, such as diethanolamine, triethanolamine and ethylene glycol, gather at lower  $\log P$  values ( $<-1.5$ ). The others (hydrophobic)

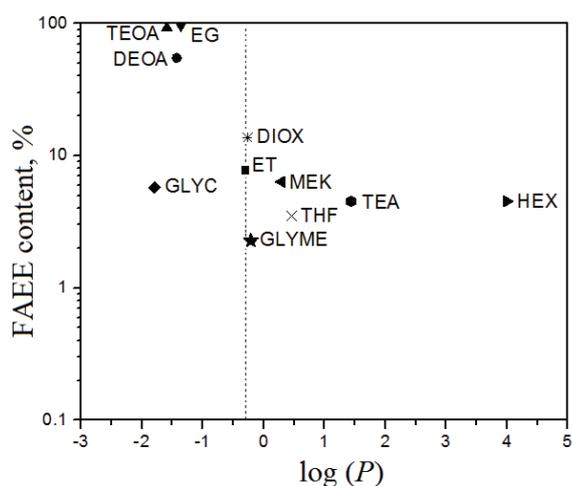


Fig. 2. Correlation of FAEE content achieved after 1 h with the  $\log P$  of the cosolvents (ET – no cosolvent present, TEOA – triethanolamine, DEOA – diethanolamine, EG – ethylene glycol, MEK – methyl ethyl ketone, HEX – *n*-hexane, TEA – triethylamine, GLYME – ethylene glycol dimethyl ether, GLYC – glycerol, THF – tetrahydrofuran and DIOX – dioxane).

cosolvents that inhibited the ethanolysis reaction had a log  $P$  value higher than  $-0.5$ . Although dioxane and ethylene glycol dimethyl ether have similar log  $P$  values to ethanol (Table S-I), they affected the ethanolysis reaction differently, indicating that specific functional groups might also affect the reaction. However, it appeared that the polarity of the cosolvents was not the only factor with a decisive influence on the ethanolysis reaction rate and FAEE content.

#### *Characterization of the used CaO*

In order to gain more insight into the catalytically active phase(s), the used CaO was separated from the reaction mixtures and analyzed by XRD. For comparison, commercial calcined CaO was also analyzed. The XRD patterns of the samples of freshly calcined CaO, calcined CaO taken after 2 and 6 h from the control ethanolysis reaction, CaO taken after 2 h from the ethanolysis reaction performed in the presence of different cosolvents, as well as CaO taken after 6 h from the ethanolysis reaction realized in the presence of TEOA are shown in Fig. 3.

The XRD analysis of the fresh calcined CaO sample revealed almost a single well-crystallized CaO phase. Its characteristic peaks at  $2\theta$  32.4, 37.55, 54.05, 64.35 and 67.55° were in a good agreement with the reported values (JCPDS Card 43-1001). In addition, the weak peaks at  $2\theta$  18.15, 34.25 and 47.3° and the small peak at  $2\theta$  29.5° indicated the presence of small amounts of Ca(OH)<sub>2</sub> (JCPDS Card 84-1263) and CaCO<sub>3</sub> (JCPDS Card 81-2027), respectively. This verified the successful activation of CaO by calcination.

Substantial changes of the fresh CaO were observed during the first 6 h of the ethanolysis conducted in the presence and absence of cosolvents. In all the samples, Ca(OH)<sub>2</sub> was a dominant phase (the peaks at  $2\theta$  about 18.2, 28.8, 34.2, 47.2, 50.8 and 54.5°), along with an amorphous phase characterized by a broad peak (amorphous hump) with a maximum at  $2\theta$  about 20°. A small peak at  $2\theta$  about 29.5° indicated the presence of a CaCO<sub>3</sub> phase. No XRD peak of a CaO phase could be identified in these samples because of CaO hydration during the collection step, which resulted in the formation of Ca(OH)<sub>2</sub>.<sup>20,24</sup> The amorphous phase probably corresponded to Ca-ethoxide, produced in the catalyst preparation step when the calcined CaO/ethanol mixture was stirred with or without the chosen cosolvent at 70 °C for 30 min. Rodriguez-Navarro *et al.*<sup>25</sup> reported that after transformation of the Ca(OH)<sub>2</sub> particles into Ca-ethoxide, the newly formed Ca-ethoxide was amorphous and no XRD peaks assignable to crystalline alkoxide were noticed. Amorphization occurred because of desolvation during oven-drying of a Ca-ethoxide sample. The appearance of Ca-diglyceroxide in the samples of calcined CaO with glycerol (after 2 h), ethylene glycol (after 2 h) and triethanolamine (after 6 h) might only be speculated based on the weak peaks at  $2\theta$  8.05 and 10.15° (JCPDS Card 21-1544). The presence of Ca-diglyceroxide was explained by the reaction between glycerol and CaO that produced Ca-digly-

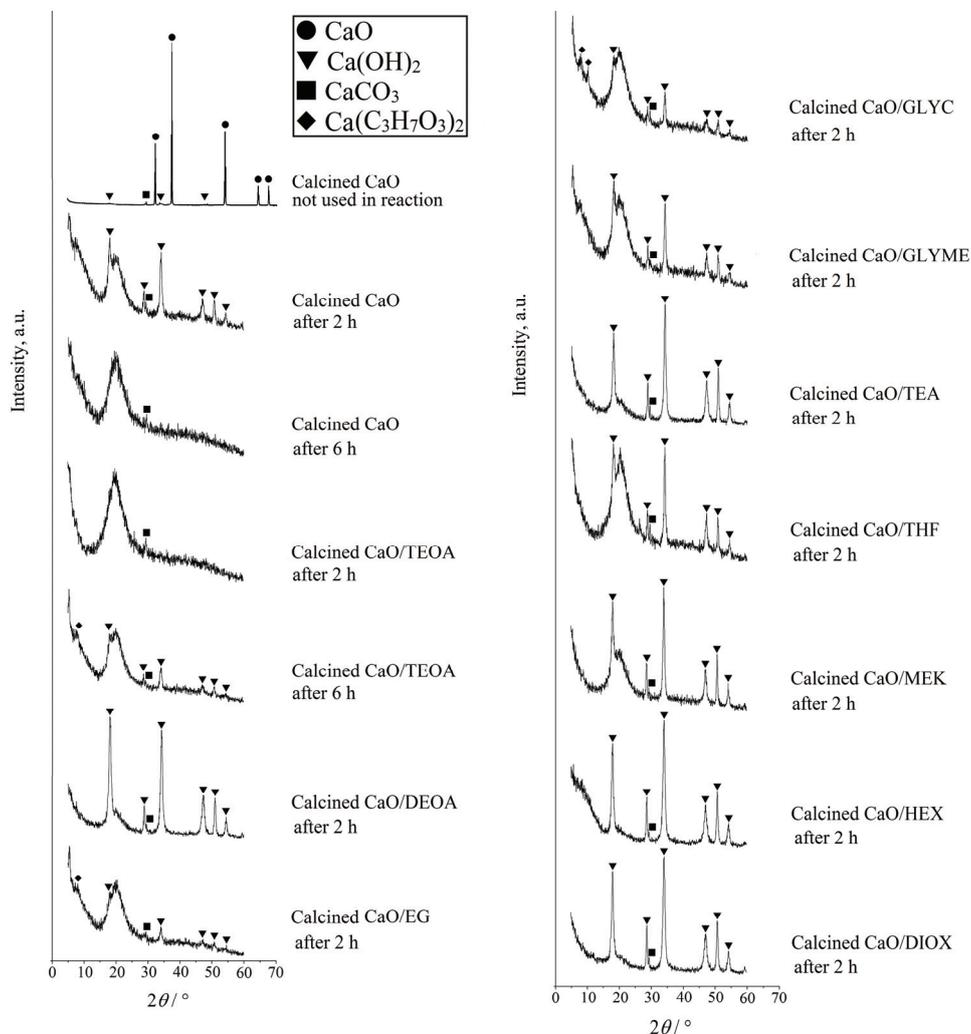


Fig. 3. The XRD patterns of the samples of freshly calcined CaO, calcined CaO taken after 2 and 6 h from the control ethanolysis reaction, calcined CaO taken after 2 h from the ethanolysis reaction carried out in the presence of different cosolvents, as well as calcined CaO taken after 6 h from the ethanolysis reaction carried out in the presence of TEOA (TEOA – triethanolamine, DEOA – diethanolamine, EG – ethylene glycol, MEK – methyl ethyl ketone, HEX – *n*-hexane, TEA – triethylamine, GLYME – ethylene glycol dimethyl ether, GLYC – glycerol, THF – tetrahydrofuran and DIOX – dioxane).

ceroxide before the start of ethanolysis. Moreover, when triethanolamine, diethanolamine or ethylene glycol were present in the reaction medium, they could interact with the produced glycerol, forming DESs (first in 1:1 and later in 1:2 mole ratio). These DESs could have a positive influence on the reaction.<sup>20</sup> It

should be mentioned that, in the methanolysis of castor oil, only  $\text{Ca}(\text{OH})_2$  and  $\text{CaCO}_3$  were identified by XRD analysis of the catalyst after the first use, ascribable to the easy dissolution of Ca-diglyceroxide crystalline phase.<sup>26</sup> This was confirmed by Granados *et al.*<sup>27</sup>, who explained it by the lixiviation of the active phase, which deactivated the catalyst. During the ethanolysis, a partial solubilization of Ca-diglyceroxide in ethanol could occur, resulting in a soluble precursor, which was transformed into the final solid base catalyst, as seen in the methanolysis of oil performed at 60 °C.<sup>21</sup> Finally, the amount of Ca-diglyceroxide crystals could be below the detection limit of the XRD apparatus, but were active in ethanolysis.<sup>26</sup>

### Calcium leaching

The well-known drawback of CaO as a catalyst is its leaching during the reaction, leading to contamination of the reaction products and the hampering of commercialization. Calcium contents in the FAEE and alcohol phases for the reactions performed with or without different cosolvents are summarized in Table I. As the used sunflower oil had a calcium content of only  $0.24 \pm 0.03$  ppm, the increased calcium amount in both the FAEE and alcohol phases was ascribed to CaO leaching.

TABLE I. Calcium contents (ppm) in the FAEE and alcohol phases after 2 h for reactions performed under the following reaction conditions: temperature 70 °C, ethanol-to-oil mole ratio 12:1, CaO concentration  $1.374 \text{ mol}\cdot\text{L}^{-1}$  and amount of cosolvent 20 % based on the oil amount

Cosolvent	Phase	
	FAEE	Alcohol
None	50.3±0.5	470±7
None <sup>a</sup>	17.1±0.2	–
Triethanolamine	35.4±0.3	34.2±0.2
Triethanolamine <sup>a</sup>	47.7±0.1	–
Diethanolamine	236±3	250±2
Ethylene glycol	44.4±0.1	–
Methyl ethyl ketone	13.9±0.1	23.2±0.1
<i>n</i> -Hexane	124±1	354±4
Triethylamine	442±5	–
Ethylene glycol dimethyl ether	13.17±0.03	–
Glycerol	36.9±0.1	33.0±0.3
Tetrahydrofuran	56.9±0.2	130.4±2.0
Dioxane	106.8±0.1	335±3

<sup>a</sup>After 6 h

The liquid fraction of the reaction system in the presence of triethanolamine, diethanolamine, methyl ethyl ketone, *n*-hexane, glycerol, tetrahydrofuran and dioxane after 2 h of reaction consisted of two-phases while it was single-phased

in the presence of ethylene glycol, trimethylamine and ethylene glycol dimethyl ether after 2 h of reaction, as well as in the case of triethanolamine after 6 h of reaction. A higher calcium leaching, compared to the reaction without the cosolvents, was observed for the reactions performed in the presence of diethanolamine, *n*-hexane, triethylamine, tetrahydrofuran or dioxane.

The majority of the leached calcium in the two-phase liquid systems was present in the alcohol phase, which was attributed to the change in polarity of the reaction mixture. CaO was more soluble in the glycerol/ethanol mixtures than in FAEE/glycerol/ethanol mixtures, and hence, the alcohol phase had a higher calcium content than did the ester phase, as already observed for methanolysis reactions.<sup>19,27,28</sup> It was interesting to notice that, after 2 h of the reaction in the presence of glycerol, an insufficient amount of Ca-diglyceroxide was produced, leading to a lower amount of leached calcium species, despite the higher solubility of Ca-diglyceroxide compared to that of CaO.<sup>27</sup>

#### CONCLUSION

Among different cosolvents applied in the CaO-catalyzed ethanolysis of sunflower oil performed in a batch stirred reactor, triethanolamine was selected as the best one for a temperature of 70 °C, ethanol-to-oil mole ratio 12:1, CaO concentration of 1.374 mol·L<sup>-1</sup> and amount of cosolvent 20 % based on the oil amount. Triethanolamine is recommended as the optimal cosolvent for the CaO-catalyzed ethanolysis of sunflower oil, as this reaction was fast and significantly improved at atmospheric pressure and a moderate temperature.

#### NOMENCLATURE

DIOX – Dioxane	EG – Ethylene glycol
ET – Ethanol	FAEE – Fatty acid ethyl ester
GLYC – Glycerol	GLYME – Ethylene glycol dimethyl ether
HEX – <i>n</i> -Hexane	HPLC – High performance liquid chromatography
MEK – Methyl ethyl ketone	TEA – Triethylamine
TEOA – Triethanolamine	TAG – Triacylglycerol
THF – Tetrahydrofuran	TLC – Thin layer chromatography

#### SUPPLEMENTARY MATERIAL

Additional data are available electronically from <http://www.shd.org.rs/JSCS/>, or from the corresponding author on request.

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## ИЗВОД

УТИЦАЈ РАЗЛИЧИТИХ КОСОЛВЕНАТА НА ЕТАНОЛИЗУ СУНЦОКРЕТОВОГ УЉА  
КАТАЛИЗОВАНУ КАЛЦИЈУМ-ОКСИДОМ

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Анализиран је утицај десет органских растварача (триетаноламина, диетаноламина, етилен гликола, метил етил кетона, *n*-хексана, триетиламина, етиленгликол-диметилетра, глицерола, тетраhydroфурана и диоксана) на принос етил-естара масних киселина (FAEE) у етанолу сунцокретовог уља у присуству СаО као катализатора изведеној у шаржном реактору. Услови реакције су били: температура 70 °С, молски однос етанол:уље 12:1, концентрација катализатора 1,374 mol·L<sup>-1</sup> и количина косолвента 20 % у односу на количину уља. Без косолвента, реакција је релативно спора, јер се добија садржај FAEE од 89,7±1,73 % тек после 4 h. Од коришћених косолвената само су диетаноламин, триетанол-амин и етиленгликол побољшали реакцију, при чему су последња два значајно убрзала реакцију уз садржаје FAEE од 93,1±2,1 и 94,1±1,5 %, редом, после 0,5 h. На основу експерименталних резултата и безбедносног профила, триетаноламин је одабран као најбољи косолвент за реакцију етанолузе са СаО катализатором.

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