Triethanolamine as an efficient cosolvent for biodiesel production by CaO-catalyzed sunflower oil ethanolysis: An optimization study

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Abstract

Triethanolamine was applied as an efficient „green“ cosolvent for biodiesel production by CaO-catalyzed ethanolysis of sunflower oil. The reaction was conducted in a batch stirred reactor and optimized with respect to the reaction temperature (61.6-78.4 °C), the ethanol-to-oil molar ratio (7:1-17:1) and the cosolvent loading (3-36 % of the oil weight) by using a rotatable central composite design (RCCD) combined with the response surface methodology (RSM). The optimal reaction conditions were found to be: the ethanol-to-oil molar ratio of 9:1, the reaction temperature of 75 °C and the cosolvent loading of 30 % to oil weight, which resulted in the predicted and actual fatty acid ethyl ester (FAEE) contents of 98.8 % and 97.9±1.3 %, respectively, achieved within only 20 min of the reaction. Also, high FAEE contents were obtained with expired sunflower oil, hempseed oil and waste lard. X-ray diffraction analysis (XRD) was used to understand the changes in the CaO phase. The CaO catalyst can be used without any treatment in two consecutive cycles. Due to the calcium leaching into the product, an additional purification stage must be included in the overall process.

Keywords: biodiesel; heterogeneous catalysis; transesterification; XRD

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1. INTRODUCTION

Biodiesel represents an alternative to petroleum diesel due to its favorable properties (biodegradability, low toxicity, reduced CO_2 and sulfur emissions, *etc.*). Although methanol is the most commonly used alcohol in biodiesel production, its replacement with ethanol is becoming more popular [1]. Ethanol can be produced from bio-wastes and is less toxic and more soluble in oils than methanol. Fatty acid ethyl esters (FAEEs) possess higher heat capacity and cetane number, as well as better cold-flow and lubrication properties than the respective fatty acid methyl esters (FAMEs) [2]. Moreover, FAEEs cause lower exhaust gas emissions and have higher biodegradability in water than FAMEs, while higher ester yields are obtained with ethanol than with methanol [3]. However, ethanol is more expensive and less reactive in transesterification than methanol and forms an azeotrope with water, making its separation more problematic. Ethanolysis requires more energy, it is more sensitive to the presence of water and results in the formation of more stable emulsions, while FAEEs are more viscous and have higher acid value than FAMEs.

Although homogeneous alkaline catalysts are mostly used for the current biodiesel production, research on their replacement with heterogeneous (solid) alkaline catalysts has increased in the last years [4,5]. Some of the benefits of the latter are low corrosion risk, low environmental threats and the possibility of catalyst separation from the final product and repeated use, which lowers the biodiesel production costs. However, they are less catalytically active, prone

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to deactivation and can leach into the product. Among many heterogeneous alkaline catalysts, CaO is one of the most attractive because of its many benefits: low cost, high catalytic activity, simple preparation from natural sources and wastes, easy recovery from the reaction mixture and it is environmentally friendly [6,7]. It is used in both batch [8] and continuous biodiesel production processes [9,10], making its potential industrial application justified [11]. Since CaO is sensitive to CO_2 and moisture from the air, its activation, usually thermal, is needed prior to use.

Low miscibility of vegetable oils and animal fats with short-chain alcohols results in a reduced transesterification rate. In multiphase batch stirred reactors, this problem can be overcome by enhancing the mass transfer rate in two ways: i) by intensive agitation (leading to increased liquid-liquid contact area) or ii) by addition of a cosolvent into the reaction mixture (resulting in improvement of the mutual miscibility of the reactants). Commonly used cosolvents in transesterification reactions are organic solvents [9,12], ionic liquids and deep eutectic solvents [13]; they are applied in both homogeneously- [12] and heterogeneously-catalyzed transesterification reactions [8,12], as well as in supercritical transesterification [14]. One of the commonly used „green“ solvents is triethanolamine (TEOA), an amino alcohol, well known as a surfactant, applied in various cosmetic formulations, polishes, metalworking fluids, paints and printing inks. Since it possesses the properties of both amines and alcohols, it is applied for various chemical reactions [15-17].

In the present work, the sunflower oil ethanolysis catalyzed by calcined CaO in the presence of TEOA was optimized with respect to the reaction temperature, ethanol-to-oil molar ratio and cosolvent loading using a rotatable central composite design (RCCD) combined with the response surface methodology (RSM). The aim was to evaluate the impact of the selected process factors on FAEE content, to correlate FAEE content with the process factors and to define the optimal process conditions ensuring the best FAEE content. The effect of TEOA on the CaO-catalyzed ethanolysis of some other oily feedstocks, such as expired sunflower oil, hempseed oil and waste lard, was also investigated. In addition, reusability of the CaO catalyst and leaching of calcium were evaluated. According to the best of the authors' knowledge, data on statistical optimization of the CaO-catalyzed ethanolysis of vegetable oils in the presence of TEOA as a cosolvent do not exist in literature.

2. EXPERIMENTAL

2. 1. Materials

Commercial edible sunflower oil (Dijamant, Zrenjanin, Serbia) was used. Physico-chemical characteristics of the oil were determined by standard methods for oils [18]. The acid, saponification and iodine values were 0.29 mg $KOH \cdot g^{-1}$, 190 mg $KOH \cdot g^{-1}$ and 1.39 g $I_2 \cdot g^{-1}$, respectively. The density (918.4 $kg \cdot m^{-3}$) and the dynamic viscosity (77.1 mPa·s) were measured by a pycnometer and a rotational viscosimeter (Visco Basic Plus v. 0.8, Fungilab S.A., Barcelona, Spain), respectively at 20 °C. Expired commercial sunflower oil (Dijamant, Zrenjanin, Serbia) was donated from a local shopping store. Hempseed oil was obtained by the Soxhlet extraction from the seed purchased from a local market; prior to the extraction, the hempseed was grounded in an electric mill (SF-2818, Alpina, Switzerland) for 1 min. The waste lard collected from a local roasted pork meet shop was melted, filtered through a cotton cloth and dried at 100 °C for 1 h. Acid values of the expired sunflower oil, hempseed oil and waste lard were 0.64, 2.89 and 0.78 mg $KOH \cdot g^{-1}$, respectively. CaO (extra pure) was provided by Sigma Aldrich (St. Louis, USA) and activated by calcination at 550 °C for 2 h [19]. The activated CaO was cooled and then stored in well-closed, glass bottles in a desiccator containing $CaCl_2$ and KOH pellets. TEOA (99.0 %) was provided from Sigma Aldrich (St. Louis, USA). 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 wt%) was purchased from Centrohem (Stara Pazova, Serbia). The standards containing ethyl esters of palmitic, stearic, oleic, linolenic and linoleic acids (20.0 wt% of each ester), as well as the standards of triolein, diolein and monoolein, were purchased from Sigma Aldrich (St. Louis, USA).

2. 2. Equipment and experimental procedure

The ethanolysis reaction was performed in a batch reactor (500 cm^3 three-necked glass flask), immersed in a glass thermostated chamber, equipped with a reflux condenser and a magnetic stirrer. Temperature in the chamber was kept constant at the desired value by circulating water from a water bath by a pump. Desired amounts of ethanol, TEOA and calcined CaO were added to the reactor and stirred for 30 min at the desired temperature. The CaO concentration was 1.374 mol·dm^{-3} and held constant for all experiments. After turning off the magnetic stirrer, the corresponding amount of sunflower oil (preheated in advance at the same temperature in a stirred glass beaker) was added to the reaction flask. When the stirrer was switched on again, the reaction time was measured for 20 min. During the ethanolysis reaction, samples (1 cm^3) were removed from the reaction mixture, neutralized by adding a required amount of the aqueous 5 mol·dm^{-3} HCl solution and centrifuged (Sigma 2-6E, Sigma Laborzentrifugen GmbH, Germany; 3500 rpm, 15 min). The upper layer (ester/oil fraction) was withdrawn, dissolved in the 2-propanol/*n*-hexane (5:4 v/v) mixture in an appropriate ratio (1:10 or 1:200 for qualitative thin layer or quantitative high performance liquid chromatography analysis, TLC and HPLC, respectively) and filtered through a 0.45 µm Millipore filter (Merck KGaA, Germany). The resulting filtrate was used for TLC and HPLC analyses. After the reaction, the ester, alcohol and bottom (precipitated CaO) phases of the final reaction mixture were separated in a separation funnel. Samples of the separated ester phase were taken for calcium determination analysis. In order to get more insight into the catalytically active phase(s), the precipitated CaO catalyst after the reaction without or with TEOA was separated from the reaction mixture after 20 min of the reaction under the optimal reaction conditions, washed with ethanol, filtered, dried for 2 h at 110 °C and analyzed by the X-ray powder diffraction (XRD) method.

Moreover, the CaO-catalyzed ethanolysis of several other oily feedstocks (expired sunflower and hempseed oils and waste lard) in the presence of TEOA was also conducted at the following reaction conditions: the reaction temperature 75 °C, the same ethanol amount as in the reaction where sunflower oil was used, the amount of cosolvent 30 % based on the oily feedstock amount and CaO concentration of 1.374 mol·dm^{-3}.

2. 3. Analytical methods

Chemical composition of each ester/oil fraction samples was first estimated qualitatively by TLC and then quantitatively by using an HPLC chromatograph (Agilent 1100 Series, Agilent Technologies, Germany) with a diode array detector as described elsewhere [19,20]. The calibration curves were prepared by using a standard mixture of FAEEs and standard acylglycerols and applied for quantifying FAEEs and acylglycerols present in the ester/oil fraction of the reaction mixture. ICP/AES (inductively coupled plasma atomic emission spectrometry; iCAP-6500 Duo, Thermo Scientific, UK) was used for determination of calcium in the upper (FAEE) layer. A Philips PW 1050 X-ray powder diffractometer (Philips, The Netherlands) using Ni-filtered Cu K$\alpha_{1,2}$ (λ = 0.154178 nm) radiation and the Bragg–Brentano focusing geometry was used for the XRD measurements. Measurements were performed at room temperature over the 2θ range of 7–70° with a scanning step width of 0.05° and a counting time of 3 s per step.

2. 4. Statistical modeling and optimization of the ethanolysis reaction

The ethanolysis of sunflower oil over CaO in the presence of TEOA was statistically modeled and optimized by combining the RSM with a RCCD that included three factors (amount of cosolvent, reaction temperature and ethanol-to-oil molar ratio) at five levels each. The experiments were carried out in a randomized order. The levels of the factors were coded as low (-1), central (0) and high (+1) while axial points were coded as -1.68 (-α) and +1.68 (+α). The complete experimental matrix with coded and uncoded levels of the process factors as well as FAEE content achieved in 20 min are shown in Table 1.

The FAEE content was correlated with the process factors by the reduced third-order polynomial equation:

$$Y = b_0 + b_1X_1 + b_2X_2 + b_3X_3 + b_{12}X_1X_2 + b_{13}X_1X_3 + b_{23}X_2X_3 + b_{123}X_1X_2X_3 + b_{11}X_1^2 + b_{22}X_2^2 + b_{33}X_3^2 \quad (1)$$

where Y is the FAEE content, b_0, b_i, b_{ii}, b_{ij} and $b_{ijk}b_o$, b_i... are the regression coefficients (i=1, 2, 3, j > i and k > j), and X_1, X_2 and X_3 are the independent variables (amount of cosolvent, % of the oil weight; reaction temperature, °C and ethanol-to-oil molar ratio, respectively). The regression coefficients were determined by multiple nonlinear regressions. Impacts of the process factors and their interactions on the FAEE content and the model fit quality were evaluated by the analysis of variance (ANOVA). Optimal reaction conditions for achieving the maximal FAEE content were determined by solving the model equation. The R-Project software (open-source, [21] was used for statistical modeling, assessment and optimization.

Table 1. Experimental matrix for RCCD

Run No.	Factors						Response		Error, %
	Coded values			Actual (uncoded) values					
	X_1	X_2	X_3	X_1	X_2	X_3	FAEE$_{exp}$ (Y), %	FAEE$_{cal}$ (Y), %	
1	-1	-1	-1	10.00	65.00	9.00	19.06	20.31	-6.6
2	1	-1	-1	30.00	65.00	9.00	79.83	81.79	-2.5
3	-1	1	-1	10.00	75.00	9.00	80.42	81.03	-0.8
4	1	1	-1	30.00	75.00	9.00	97.43	98.75	-1.4
5	-1	-1	1	10.00	65.00	15.00	59.32	58.21	1.9
6	1	-1	1	30.00	65.00	15.00	78.98	78.58	0.5
7	-1	1	1	10.00	75.00	15.00	70.51	68.77	2.5
8	1	1	1	30.00	75.00	15.00	93.98	92.95	1.1
9	-1.68	0	0	3.18	70.00	12.00	24.90	25.59	-2.8
10	1.68	0	0	36.82	70.00	12.00	78.61	77.62	1.3
11	0	-1.68	0	20.00	61.59	12.00	56.41	55.50	1.6
12	0	1.68	0	20.00	78.41	12.00	98.04	98.64	-0.6
13	0	0	-1.68	20.00	70.00	6.95	89.62	86.67	3.3
14	0	0	1.68	20.00	70.00	17.05	91.01	93.66	-2.9
15	0	0	0	20.00	70.00	12.00	80.69	79.51	1.5
16	0	0	0	20.00	70.00	12.00	87.27	79.51	8.9
17	0	0	0	20.00	70.00	12.00	80.61	79.51	1.4
18	0	0	0	20.00	70.00	12.00	80.20	79.51	0.9
19	0	0	0	20.00	70.00	12.00	74.92	79.51	-6.1
20	0	0	0	20.00	70.00	12.00	73.29	79.51	-8.5

X_1, X_2 and X_3 are the amount of cosolvent, % of the oil weight; reaction temperature, °C and ethanol-to-oil molar ratio, respectively; FAEE$_{exp}$ and FAEE$_{calc}$ are the experimentally obtained and calculated FAEE contents after 20 min of reaction; Y is the FAEE content

2. 5. Catalyst reusability test

To test the effect of TEOA on the CaO reusability, two series of experiments were conducted under the optimal reaction conditions. In the first series, after the upper layer was decanted, the used CaO catalyst, ethanol and TEOA were stirred for 30 min, then the corresponding amount of oil, heated separately, was added and the stirring was continued for 20 min. This was repeated in the next two batches. In the second series, TEOA was added only in the first run.

3. RESULTS AND DISCUSSION

3. 1. Influence of TEOA on the CaO-catalyzed sunflower oil ethanolysis

A major drawback of CaO-based catalysts is mass transfer limitations related to the three-phase system that reduces the reaction rate, particularly in the initial reaction stage [22]. The calcined CaO-catalyzed sunflower oil ethanolysis usually takes a long reaction time. For instance, Avramović *et al.* [23] reported the FAEE content of 89.7±1.7 % after 4 h, which increased slightly with the progress of the reaction. In addition, the phase separation of the final reaction mixture was also time-consuming, taking longer than a day for completing. However, the presence of TEOA in the present work resulted in a continual FAEE content increase since the start of the reaction. In this case, even after only 20 min, the FAEE content was 79.3±6.5 %, which was much higher than that achieved in the absence of TEOA (2.3±1.6 %). TEOA alone did not show catalytic activity as the FAEE content after 6 h in the absence of CaO was practically neglectable (0.5 %). The positive action of TEOA was related to the visually noticed reduction of the viscosity of the reaction mixture due to the improved mutual miscibility of the reactants in the initial stage of the reaction, thus reducing the mass transfer resistance and increasing both the reaction rate and FAEE yield [24]. Also, hydrophilic TEOA mixed well with ethanol and was able to penetrate faster into the pores of CaO, which resulted in easier diffusion passage of the oil and ethanol to the active sites of the catalyst, resulting in a higher reaction rate [9]. In addition, TEOA could form a deep eutectic solvent with glycerol (a by-product), shifting the equilibrium to the right and increasing the FAEE content [8]. Since TEOA possesses strong water affinity, it can limit the availability of water molecules for triacylglycerols hydrolysis and soap formation. Moreover, the formed esters acted as a cosolvent, further improving the miscibility of the reactants [25].

3. 2. Statistical modeling and optimization of the ethanolysis reaction

3. 2. 1. Adequacy of the RCCD-based model

The adequacy of the RCCD-based models was first checked by the sequential sum of squares, lack of fit and model summary statistic tests to select the highest order non-aliased polynomial model where the additional terms were significant, the model with insignificant lack-of-fit and the model maximizing the R_{adj}^2 and the R_{pred}^2, respectively. These tests suggested disregarding the aliased cubic model (Tables D1-D3, Supplementary material). The second-order polynomial model was suggested as it had the highest R^2-values among the other models. However, for this model, the R_{pred}^2-value of 0.643 was not as close to the R_{adj}^2-value of 0.902 as one might normally expect, i.e. the difference between these two coefficients was larger than the recommended value of 0.2. Hence, as compromised, the second-order (quadratic) polynomial model was disregarded. In order to check if there was any problem with the developed model and/or data, outliers and model modification were considered. Since the RCCD dataset did not contain any outliers, the quadratic model was modified by including a three-factor interaction term ($X_1X_2X_3$), resulting in the more complex reduced third-order (quadratic) model, which was further analyzed by the ANOVA (Table 2).

Table 2. ANOVA results for the fitted quadratic polynomial model

Source ofvariation	Sum of squares	Degree of freedom	Mean square	*F*-value	*p*-value
Model	8285.47	10	828.55	48.29	< 0.0001
X_1	3267.37	1	3267.37	190.41	< 0.0001
X_2	2246.64	1	2246.64	130.93	< 0.0001
X_3	59.01	1	59.01	3.44	0.097
X_1X_2	199.50	1	199.50	11.63	0.008
X_1X_3	150.08	1	150.08	8.75	0.016
X_2X_3	348.08	1	348.08	20.29	0.002
X_1^2	1402.46	1	1402.46	81.73	< 0.0001
X_2^2	10.66	1	10.66	0.62	0.451
X_3^2	204.62	1	204.62	11.92	0.007
$X_1X_2X_3$	282.86	1	282.86	16.48	0.003
Residual	154.43	9	17.$_{7}$16		
Lack of Fit	31.38	4	7.85	0.32	0.855
Pure Error	123.05	5	24.61		
Corrected total	8439.90	19			

R^2 = 0.982; R_{adj}^2 = 0.961; R_{pred}^2 = 0.928; C.V. (coefficient of variation) = 5.54 %; and MRPD (mean relative percentage deviation) = 2.8 %

Distribution of data was normal, so the ANOVA results are valid (Fig. D1a). Besides that, values of the Cook's distance were lower than 0.4 (away from the limit value of 1.0), indicating that outliers were absent from the dataset (Fig. D1b).

3. 2. 2. Statistical modeling

The experimental data were fitted by the reduced cubic equation using the multiple nonlinear regression, and the resulting equation in terms of coded values of the process factors is as follows:

$$Y = 79.51 + 15.47X_1 + 12.83X_2 + 2.08X_3 - 4.99X_1X_2 - 4.33X_1X_3 - 6.60X_2X_3 + 5.95X_1X_2X_3 - 9.86X_1^2 - 0.86X_2^2 + 3.77X_3^2 \quad (2)$$

According to its F_{model}- and p- values (48.29 and <0.0001, respectively), the model was significant, meaning that it fitted well the experimental data. The R^2-value (0.982) implied excellent goodness of fit of the model while the R_{pred}^2 value (0.928) was in a reasonable agreement with the R_{adj}^2 value (0.961). The accuracy of the model was confirmed by the coefficient of variation (*C.V.*), which amounted 5.54 % indicating low variability with respect to the mean value. The insignificant model lack of fit ($p = 0.855$) and the low mean relative percentage deviation (*MRPD)* of ±2.8 % (based on 20 data) confirmed the prediction ability and accuracy of the derived model equation (Fig. D1c). Furthermore, the ANOVA results showed that only the ethanol-to-oil molar ratio (X_3) and the quadratic term of the reaction temperature (X_2^2) did not have a statistically significant influence on the FAEE content, while all other terms were statistically influential on the FAEE content at the 95 % confidence level ($p < 0.05$).

As can be concluded from Eq. (2), all individual process factors as well as the quadratic term of the ethanol-to-oil molar ratio X_3^2 and the three-way interaction $X_1X_2X_3$ positively influenced the FAEE content since their regression coefficients were positive. In accordance with the ANOVA results, the largest positive effect on the FAEE content had the cosolvent amount followed by the reaction temperature since their regression coefficients had the highest values, while the ethanol-to-oil molar ratio had the least positive effect on the FAEE content. The increase in the TEOA amount resulted in a higher FAEE content because of improved solubility of sunflower oil and ethanol in TEOA, which homogenized the reaction mixture, reduced the mass transfer limitation and increased the reaction rate. The increase in the reaction temperature increased the reaction rate constant and reduced the reaction mixture viscosity, promoting the more efficient mass transfer of triacylglycerols, which both favored the FAEE formation. All two-way interactions and the quadratic terms of the cosolvent amount and reaction temperature negatively influenced the FAEE formation in the investigated ranges of the process factors. Among them, the major negative effect on the FAEE formation had the quadratic term of the cosolvent amount and the interaction between the reaction temperature and the ethanol-to-oil molar ratio (X_2-X_3).

3. 2. 3. Response surface analysis

Figure 1 shows the response surface for the FAEE content as functions of the ethanol-to-oil molar ratio and reaction temperature (Fig. 1a), ethanol-to-oil molar ratio and the amount of cosolvent (Fig. 1b), and the reaction temperature and amount of cosolvent (Fig. 1c); the third process factor was fixed at a constant value.

With increasing the reaction temperature, the FAEE content increased as it can be seen in Figures 1a and 1c because of the positive effect of the reaction temperature on the FAEE formation and due to the reduction of the reaction mixture viscosity allowing better triacylglycerols mass transfer. The influence of the reaction temperature was less significant at the higher ethanol-to-oil molar ratio (Fig. 1a) and the amount of cosolvent (Fig. 1c) confirming the negative effect of X_1-X_2 and X_2-X_3 two-way interactions. This impact might be attributed to the favored FAEE glycerolysis or saponification reactions, which reduced the FAEE content at higher reaction temperatures and higher ethanol amounts.

The influence of the ethanol-to-oil molar ratio depended on the reaction temperature and the cosolvent amount. This impact was more significant at lower reaction temperatures and cosolvent amounts and positively influenced the FAEE content (Fig. 1a and b). At higher reaction temperatures (Fig. 1a) and cosolvent amounts (Fig. 1b), the effect of the ethanol-to-oil molar ratio became less significant, due to the negative effect of X_1-X_3 and X_2-X_3 interactions, as it can be seen in Eq. (2). At the cosolvent amount of 30 % of the oil weight and the reaction temperature of 70 °C, the increase in the ethanol amount even caused a decrease in the FAEE content, which was attributed to the promoted reverse reaction. According to Lam and Lee [26], in the presence of alcohol in excess, along with the favored conversion of triglycerides into monoglycerides, monoglycerides also increase the glycerol solubility in fatty acid alkyl esters, causing glycerolysis [27]. In this reaction, the produced esters react with glycerol, thus reducing the ester yield. The FAEE content generally increased with the increase in the TEOA amount, as can be seen in Figures 1b and 1c. However, at higher reaction temperatures and ethanol amounts, the FAEE content increased with the increase in the cosolvent amount and reached a plateau so that further increase did not affect the FAEE content.

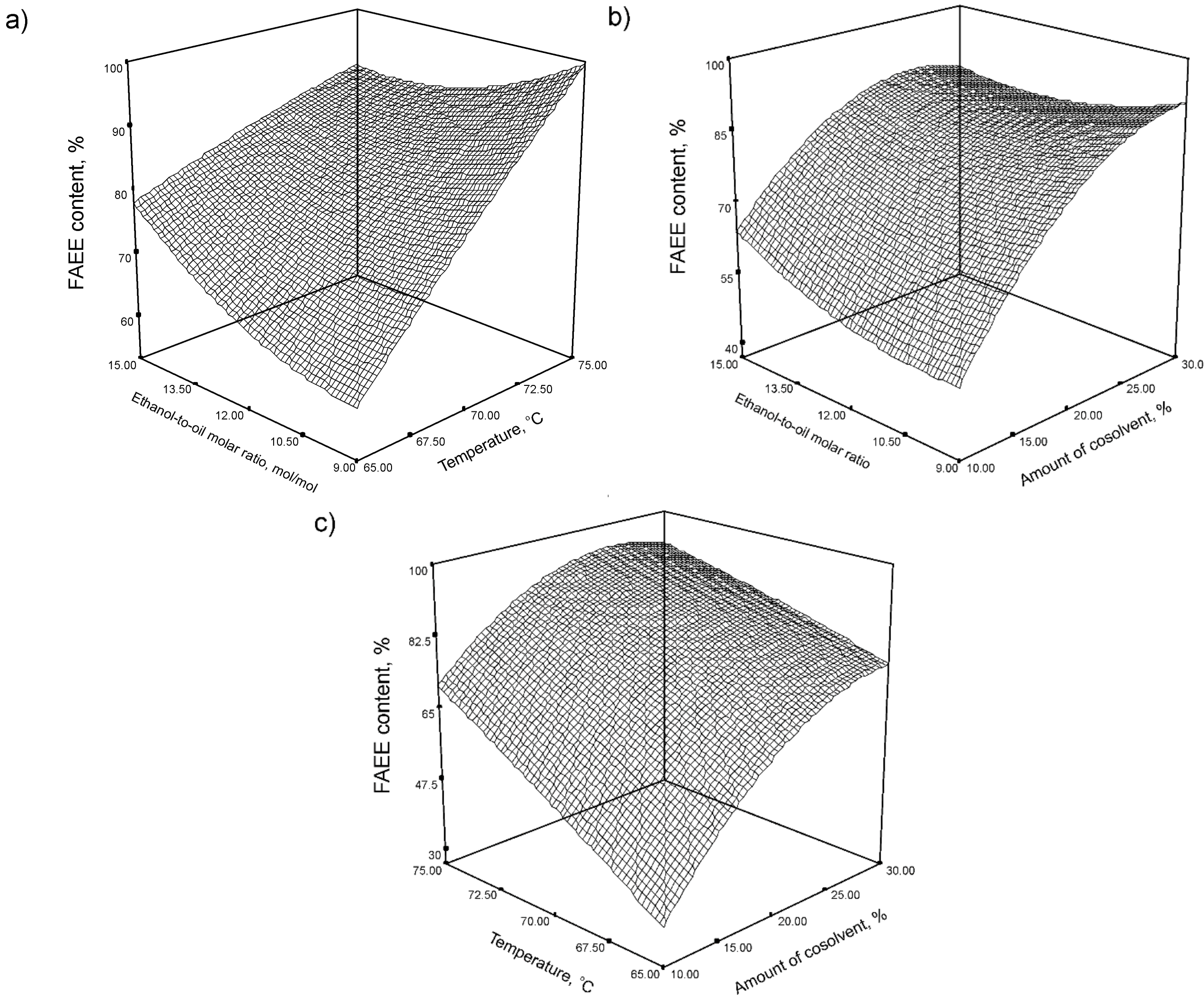

Figure 1. Response surface for the FAEE content as a function of: a) ethanol-to-oil molar ratio and reaction temperature at the amount of cosolvent of 20 % of the oil weight; b) ethanol-to-oil molar ratio and amount of cosolvent (% of the oil weight) at 70 °C; c) reaction temperature and amount of cosolvent (% of the oil weight) at the ethanol-to-oil molar ratio of 12:1; (CaO concentration: 1.374 mol·dm^{-3})

3. 2. 4. RSM optimization

The optimum reaction conditions for achieving the maximum FAEE content were found by solving the developed regression equation, Eq. (2), in the ranges between the lower and upper limits of each process variable. With the CaO concentration of 1.374 mol·dm^{-3}, the optimal reaction conditions were: the amount of cosolvent of 30 % (based on the oil weight), the reaction temperature of 75 °C and the ethanol-to-oil molar ratio of 9:1, which provided the actual FAEE content of 97.9 ± 1.3 % in 20 min of the reaction, close to the predicted FAEE content of 98.8 %.

3.3. Changes of the CaO catalyst during the ethanolysis reaction

XRD patterns of the fresh calcined CaO and used CaO pastes are shown in Figure 2.

The XRD analysis of the fresh calcined CaO sample revealed an almost single well-crystallized CaO phase. Its characteristic peaks at 32.22, 37.36, 53.86, 64.16, and 67.38° 2θ agreed with the literature values (JCPDS Card 43-1001). Also, the weak peaks at 17.98, 34.1 and 47.18° 2θ and the small peak at 2θ = 29.4° indicated the presence of small amounts of $Ca(OH)_2$ (JCPDS Card 84-1263) and $CaCO_3$ (JCPDS Card 81-2027), respectively.

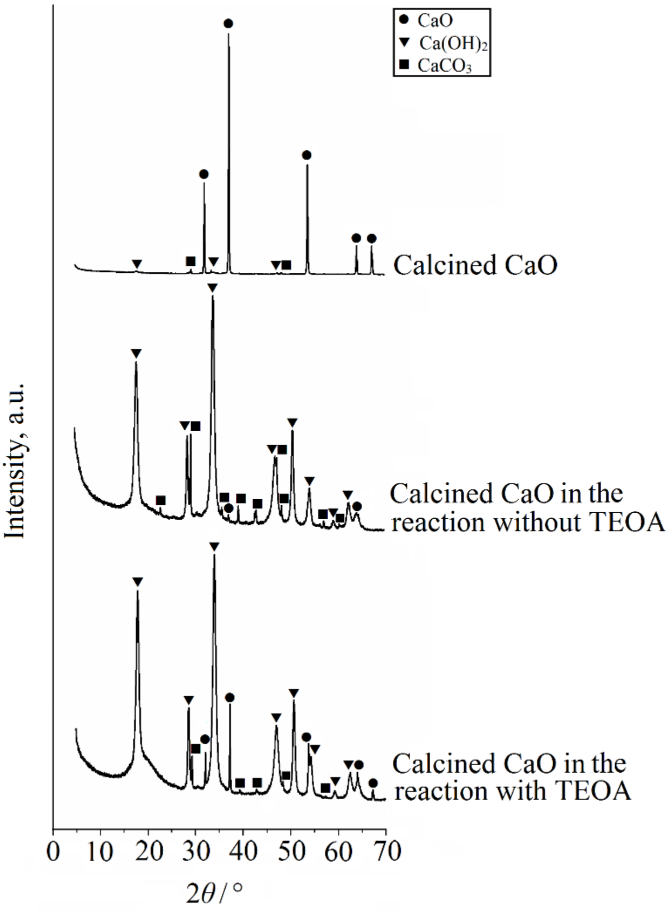

Figure 2. XRD patters of the fresh calcined CaO sample and the used CaO pastes, without or with TEOA after ethanolysis for 20 min

This implied successful activation of CaO by calcination. Substantial changes of CaO occurred during the ethanolysis up to 20 min, regardless of the presence of TEOA. In the samples of CaO taken from the reactions carried out in the presence or the absence of TEOA, the dominant phase was $Ca(OH)_2$ (peaks at about 17.94 (17.98), 28.7 (28.72), 34.08 (34.12), 47.16 (47.18), 50.8 (50.84), 54.54, 59.4 and 62.62 (62.64)°). A small peak, which could be resolved at about 29.4° 2θ, indicated presence of the $CaCO_3$ phase. Also, the peaks at 32.22, 37.38, 53.88, 64.16 and 67.42° indicate the presence of the CaO phase. These results agreed with those reported by Kouzu *et al.* [28], who identified only CaO and $Ca(OH)_2$ in XRD patterns of the catalyst after 15 min of the CaO-catalyzed soybean oil methanolysis. Also, Sánchez-Cantú *et al.* [29] identified only $Ca(OH)_2$ and $CaCO_3$ in the CaO sample taken from the final reaction mixture of the castor oil methanolysis. Since the ethanolysis in the present study lasted only 20 min, the amount of the produced glycerol was too low to react with CaO and to produce sufficient amounts of catalytically active Ca-diglyceroxide. Moreover, TEOA combined with the produced glycerol could provide a deep eutectic solvent that could have a positive influence on the reaction [8].

3. 4. Ethanolysis of different oily feedstocks catalyzed by CaO in the presence of TEOA

The CaO-catalyzed ethanolysis of several other oily feedstocks in the presence of TEOA was also conducted at the following reaction conditions: the reaction temperature 75 °C, the same ethanol amount as in the reaction where sunflower oil was used, the amount of cosolvent 30 % based on the oily feedstock amount and CaO concentration of 1.374 $mol\cdot dm^{-3}$.

As can be seen in Figure 3, the FAEE contents after 20 min with sunflower, expired sunflower and hempseed oils (97.9±1.3 %, 96.8±0.7 % and 98.9±0.5 %, respectively) were higher than that achieved with the waste lard (86.6±1.0 %), which was ascribed to different compositions of the tested feedstocks. Therefore, the CaO/TEOA system can be successfully used in the ethanolysis of various oily feedstock.

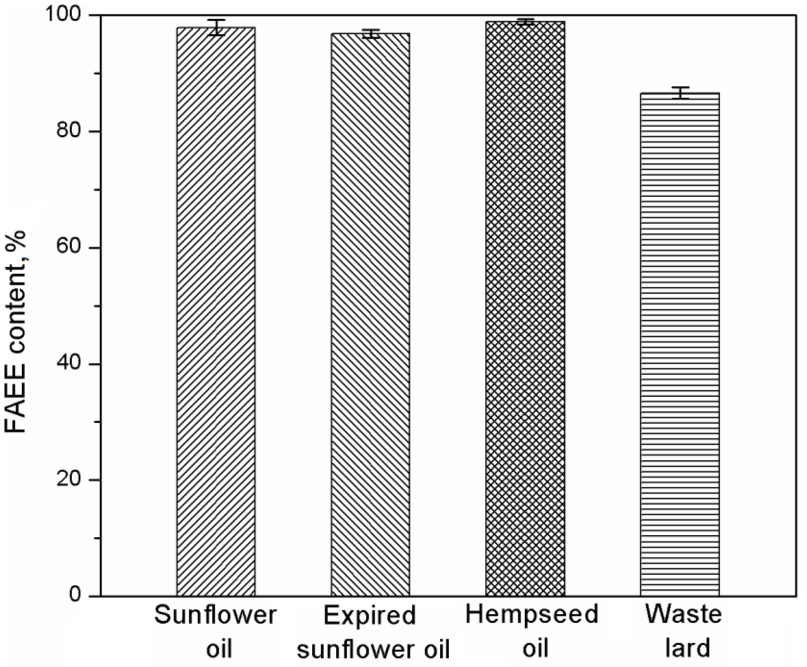

Figure 3. FAEE contents achieved after 20 min of the ethanolysis of different feedstock catalyzed by the fresh CaO catalyst in the presence of TEOA as a cosolvent. Reaction conditions: the reaction temperature 75 °C, the same ethanol amount as in the reaction where sunflower oil was used, the amount of cosolvent 30 % based on the oily feedstock amount and CaO concentration of 1.374 mol·dm^{-3}.

3. 5. Reusability of CaO

Besides the catalytic activity, the reusability of CaO-based catalysts is also an important property for their potential industrial applications. FAEE contents after 20 min obtained in four consecutive batches of the sunflower oil ethanolysis catalyzed by the fresh and recycled CaO in the presence and the absence of TEOA under the optimal reaction conditions (30 % TEOA of the oil weight, the reaction temperature 75 °C, and the ethanol-to-oil molar ratio 9:1) are shown in Fig. 4.

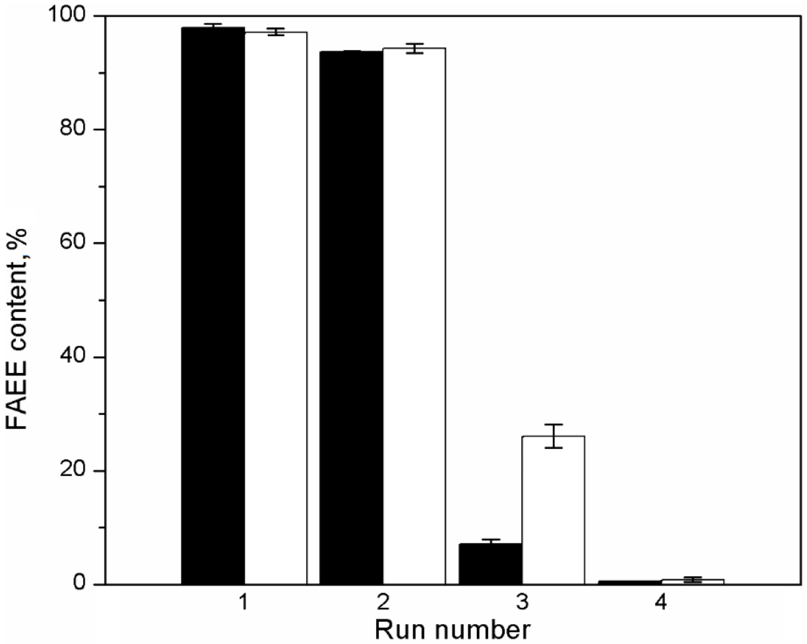

Figure 4. FAEE contents after 20 min in four consecutive batches of the sunflower oil ethanolysis catalyzed by the fresh and recycled CaO catalysts in the presence of TEOA at the optimal reaction conditions (30 % TEOA based on the oil weight, 75 °C, and the ethanol-to-oil molar ratio 9:1). The CaO concentration of 1.374 mol·dm^{-3} was only in the first reaction. Black bars - the first series in which TEOA was added in all runs. White bars - the second series in which TEOA was added only in the first run

In the second run (when CaO was recycled for the first time), the FAEE content values were close to each other regardless of TEOA addition, namely 93.7±0.1 % and 94.3±0.8 %, respectively. However, in the third run, significantly lower FAEE contents were observed in both series (7.2±0.78 % and 26.1±2.1 %). Finally, in the fourth run, the FAEE content was lower than 1 % in both series. The reduction of the FAEE content was attributed to the loss of CaO because of its incomplete separation from the reaction mixture and a possible catalyst deactivation by the surface coverage by reaction products [30].

3. 6. Calcium leaching

A well-known drawback of CaO as a catalyst is its leaching during the reaction, leading to contamination of reaction products and hampering the commercialization. Calcium contents in the crude FAEE phases in three successive reaction runs of the first series (when TEOA was added in all runs) were 2006, 646 and 110 ppm, respectively. In the second series (when TEOA was added only in the first run), calcium contents in the second and the third runs were also low, namely 634 and 78 ppm, respectively. High calcium contents in the crude FAEE phase were noticed when expired sunflower oil, hempseed oil and waste lard were transesterified with ethanol under the optimum reaction conditions (2118, 2295 and 2121 ppm, respectively). Since the observed calcium content was high, the crude FAEE should be purified by using an adequate method [31].

4. CONCLUSION

TEOA was used as an efficient „green" cosolvent in the CaO-catalyzed ethanolysis of sunflower oil conducted in a batch stirred reactor. Statistical modeling and optimization showed that the amount of cosolvent and the reaction temperature influenced significantly the FAEE content. The optimal reaction conditions for achieving the highest FAEE content (predicted 98.8 %; actual 97.9±1.3 %) in 20 min at the catalyst concentration of 1.374 mol·dm^{-3} were: the 30 % TEOA (based on the oil weight), the reaction temperature 75 °C, and the ethanol-to-oil molar ratio 9:1. Since the CaO-catalyzed ethanolysis of sunflower oil was fast and significantly improved at a moderate temperature, TEOA could be recommended as a cosolvent for this reaction. Moreover, high FAEE contents were also obtained with the use of expired sunflower oil, hempseed oil and waste lard. However, CaO combined with TEOA can be reused only twice, indicating the need for improvement of the catalyst separation from the reaction mixture and/or development of a procedure for regeneration of the spent catalyst. In addition, since calcium leaches into the reaction mixture, an additional purification stage should be included in the overall process.

5. NOMENCLATURE

ANOVA - Analysis of variance; C.V. - Coefficient of variation; FAEE - Fatty acid ethyl ester;
HPLC - High performance liquid chromatography; MRPD - Mean relative percentage deviation;
RCCD - Rotatable central composite design; RSM - Response surface methodology; TEOA - Triethanolamine;
TAG - Triacylglycerol; TLC - Thin layer chromatography.

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SUPPLEMENTARY MATERIAL

Supplementary material can be downloaded from the web site of the journal *Hemijska industrija*.

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SAŽETAK

Optimizacija proizvodnje biodizela etanolizom suncokretovog ulja: primena trietanolamina kao efikasnog kosolventa i kalcijum-oksida kao katalizatora

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(Naučni rad)

Trietanolamin je korišćen kao efikasni „zeleni" kosolvent za proizvodnju biodizela putem etanolize suncokretovog ulja u prisustvu CaO kao katalizatora. Reakcija je izvedena u šaržnom reaktoru sa mešalicom i optimizovana u odnosu na temperaturu (61.6-78.4 °C), molski odnos etanol:ulje (7:1-17:1) i količinu kosolventa (3-36 % u odnosu na masu ulja) primenom centralnog kompozitnog rotatabilnog eksperimentalnog plana (RCCD) u kombinaciji sa metodologijom površine odziva (RSM). Optimalni uslovi reakcije su: molski odnos etanol:ulje 9:1, temperatura 75 °C i količina kosolventa 30 % (u odnosu na masu ulja), na kojima je predviđena vrednost sadržaja etil-estara masnih kiselina (EEMK) posle samo 20 min reakcije iznosila 98.8 % dok je eksperimentalno dobijena vrednost bila 97.9±1.3 %. Veliki sadržaji EEMK su dobijeni i prilikom primene suncokretovog ulja kome je istekao rok upotrebe, ulja konoplje i otpadne svinjske masti. Rendgenska difrakciona analiza (engl. X-ray diffraction, XRD) je korišćena sa ciljem razumevanja strukturnih promena CaO katalizatora. CaO katalizator se mogao koristiti bez bilo kakvog dodatnog tretmana u dva uzastopna ciklusa. Usled luženja kalcijuma u proizvod, dodatni postupak prečišćavanja se mora uključiti u celokupni proizvodni proces.

Ključne reči: etil-estri masnih kiselina; heterogena kataliza; transesterifikacija; XRD