Sunflower oil methanolysis over modified CaO catalysts

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Abstract

Oil methanolysis over modified CaO catalysts was studied to assess the catalytic performance and to define an appropriate kinetic model. CaO was modified by commercial glycerol and a deep eutectic solvent (DES), choline chloride : glycerol (ChCl : Gly), to obtain catalytically active complexes of CaO and glycerol. The main goal was to investigate the effect of the obtained complexes on the reaction rate and fatty acid methyl ester (FAME) content and to describe the variation of the triacylglycerol (TAG) conversion degree during the reaction time. Fourier transform infrared spectroscopy (FTIR) was applied to confirm the formation of CaO complexes with glycerol or the glycerol-based DES. Different catalyst loadings (0.5, 1, and 5 % of oil weight) and methanol-to-oil molar ratios (6 : 1 and 12 : 1) were applied for investigation of the sunflower oil methanolysis at 60 °C. Two kinetic models were employed yielding the kinetic parameters, which depended on the catalyst loading and the methanol-to-oil molar ratio. Both models showed valid applicability for describing the kinetics of the reactions catalyzed by both complexes (the mean relative percent deviation was lower than 10 %).

Keywords: biodiesel; calcium oxide; choline chloride-glycerol; deep eutectic solvents; kinetics.

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1. INTRODUCTION

Biodiesel, a mixture of fatty acid methyl (FAMEs) or ethyl (FAEEs) esters is considered a feasible alternative fuel to mineral diesel in engines with internal combustion because of many advantages in its application. It can be used as pure or blended in various ratios with petroleum-derived diesel. Its combustion produces significantly fewer particulates than that of diesel fuel and a lower sulfur emission, while it can be considered a carbon-neutral fuel if produced in a sustainable manner. Usually, the biodiesel production processes involve homogeneously or heterogeneously catalyzed transesterification of triacylglycerols (TAGs) sources, such as edible, non-edible, used, and waste vegetable oils or animal fats, and esterification of free fatty acids (FFA) with aliphatic alcohols. Since the reactants are not miscible at room temperature and atmospheric pressure, addition of a co-solvent, such as organic solvents [1], biodiesel itself [2], and ionic liquids (IL) [3] in the reaction mixture increases the solubility of alcohol in the oil phase. The co-solvent use provides a pseudo-homogeneous system [4], especially at lower temperatures when the mass transfer limits the chemical reaction [5].

Solid base catalysts are preferred over homogeneous catalysts in the transesterification reaction for biodiesel production. Despite having several advantages, such as easy separation and recovery, low waste and by-products, avoidance of corrosion, and facilitation of continuous process operation, solid base catalysts can require a complicated preparation procedure involving expensive precursors and exhibit variable quality and short lifetime [6]. For that reason, many studies were aimed at developing stable and active solid catalysts for biodiesel production processes, such as catalysts in nano-form [7]. Among various heterogeneous catalysts, calcium oxide (CaO), as a common base earth metal oxide, is one of the most promising for biodiesel production [8]. Kouzu *et al.* [9,10] pointed out that CaO shows activity only at the beginning of the reaction until the FAME content is below 30 %. As the methanolysis reaction proceeds, the

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synthesized by-product glycerol can react with calcium ions from CaO producing a new highly active catalyst, calcium diglyceroxide (glyceroxide), $Ca(C_3H_7O_3)_2$. The CaO-glycerol complex formation provides a hydrophilic-hydrophobic active layer on the surface of CaO allowing easy access of hydrophobic TAG molecules to the active sites, thus increasing the methanolysis reaction rate [11].

The use of ionic liquids and deep eutectic solvents can also significantly improve the biodiesel production processes [12,13]. Presence of a DES, such as ChCl : glycerol, as a co-solvent in homogeneously catalyzed methanolysis of rapeseed oil [14] and waste cooking oil [12], or ethanolysis of palm oil [15,16], increased the biodiesel yield, reduced the side saponification reaction, and improved product separation and purification.

The use of ChCl-based DESs in heterogeneously catalyzed transesterification of vegetable oils has been rarely investigated. A DES prepared from ChCl and glycerol was applied in CaO-catalyzed methanolysis of rapeseed oil as a solvent and an activator of commercial CaO [6]. The presence of DES can eliminate inactive layers consisting of $CaCO_3$ and $Ca(OH)_2$ on the catalyst surface and can facilitate the separation of catalyst from the reaction mixture and enable achievement of a higher biodiesel yield. Troter *et al.* [17] have studied the impact of the ChCl-based DESs, with different amides or polyols as co-solvents, on the yield of ethyl esters obtained from expired sunflower oil using calcined and non-calcined CaO as a catalyst.

It was confirmed in literature that a CaO-glycerol-methanol complex was formed during transesterification, which was the active phase of the catalyst [10]. Furthermore, the catalytic activity of the used catalyst, showed to be higher than that of the fresh catalyst. So far, CaO-glycerol complexes were synthesized by using different methods, such as mixing of CaO with the mixture of methanol and glycerol at temperatures in the range 60-70 °C, followed by separation and washing with methanol or tetrahydrofuran [10,11,18-20], mixing of CaO with the mixture of methanol and glycerol under sonication [21] and mechanochemical treatment of CaO dispersed in glycerol [22]. Activation of CaO in the presence of ChCl : Gly as a co-solvent in sunflower oil methanolysis, was investigated by analyzing the spent catalyst [6], but modification of CaO with ChCl : Gly induced directly by mixing, has not been investigated yet. Therefore, this study aimed to investigate the effect of the complexes obtained by modification of CaO by mixing with glycerol and ChCl : Gly on the reaction rate and FAME content and to describe the variation of the TAG conversion degree during the reaction time.

2. EXPERIMENTAL

2. 1. Materials

Refined sunflower oil (Dijamant, Zrenjanin, Serbia) and methanol (purity of 99.5 %, Zorka Pharma, Šabac, Serbia) were used as the reactants. CaO (purity of ≥98, Sigma Aldrich, USA) was used for the catalyst preparation. Mixture of ChCl : Gly (molar ratio of 1 : 2) was prepared by using ChCl (purity of ≥98, Sigma Aldrich, USA) and glycerol (purity of 99.5 %, Ph. Eur, MeiLab Belgrade, Serbia). Methanol, 2-propanol, and *n*-hexane, HPLC grade (purity of 99.7 %, J.T. Baker, USA), were used for High Performance Liquid Chromatography (HPLC) analyses.

3.1. Catalyst preparation

CaO-glycerol complexes were prepared using two procedures. The first procedure [20], consisted of mixing CaO (3 g) with glycerol (10 g) and methanol (44 g) at 60 °C for 2 h. The obtained catalyst, here denoted as the C-G complex, was recovered by filtration and dried at 105 °C for 2 h. In the second procedure, CaO was modified with the ChCl : Gly, as a DES, prepared from ChCl and glycerol (molar ratio of 1: 2), which was then mixed (in the amount of 10 g) with CaO (3 g) at 60 °C for 1 h and dried at 105 °C for 2 h. This catalyst was denoted as the C-ChG complex. Both catalysts were stored in the well-closed glass bottles in a desiccator containing calcium chloride and potassium hydroxide pellets.

3.3. FTIR analysis

Fourier-transform infrared (FTIR) spectra of the obtained catalysts were recorded with a Michaelson Bomen MB-series spectrophotometer (BOMEM MB-100, Hartmann & Braun, Canada), using the KBr pellet (1 mg / 100 mg) technique.

3.4. Methanolysis reaction

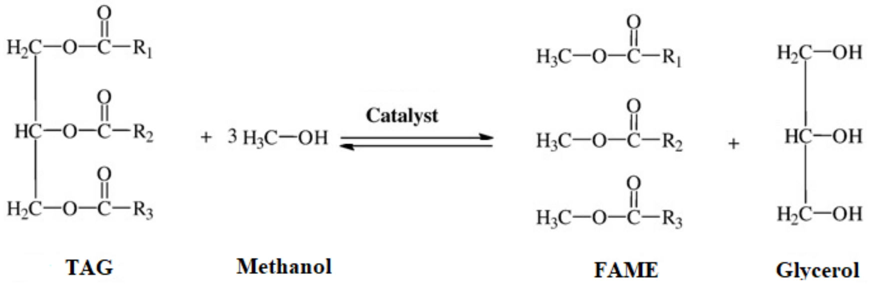
The sunflower oil methanolysis was carried out in a 250 cm^3 two-neck round bottom glass flask, equipped with a condenser and a magnetic stirrer, placed in a chamber. The reaction was performed at 60 °C and under atmospheric pressure. The temperature was maintained constant (60 ± 0.1 °C) by water circulating from a thermostated water bath. Desired amounts of the catalyst (0.5, 1, or 5 % of oil weight) and methanol, corresponding to the initial methanol-to-oil molar ratio of 6 : 1 or 12 : 1, were added to the flask and agitated (400 rpm) at 60 °C for 30 min. Afterward, sunflower oil (30 g) that was preheated (at 60 °C) separately, was added to the methanol-catalyst suspension so that the total reaction mixture volume was 41.13 or 49.50 cm^3 (depending on the methanol-to-oil molar ratio), and the agitation intensity was raised to 900 rpm for 160 min.

Leaching experiments were performed in parallel in order to investigate leaching of the catalyst from the complex by mixing the C-G and C-ChG complexes (0.3 g) with methanol (16.76 cm^3) for 30 min at 60 °C. Then, the methanol-catalyst suspension was filtered under a vacuum to separate the catalyst from the methanol phase. The separated methanol phase was used for the reaction keeping the constant methanol-to-oil molar ratio of 12 : 1.

In all experiments in order to monitor the change of the reaction mixture composition, the samples (0.4 cm^3) were taken during the reaction at timed intervals (the total volume withdrawn was less than 10 %), quenched by immersing in ice water, and prepared for HPLC analysis [23]. HPLC analysis was performed by HPLC chromatography (Agilent 1100 Series, Agilent Technologies, Germany) [24]. All experiments were performed in duplicate.

3. KINETIC MODELING

The overall reaction of methanol and TAGs can be represented by the overall stoichiometric equations 1a and 1b:



(1a)

$$A + 3B \rightleftarrows 3R + S \tag{1b}$$

where A, B, R, and S denote TAGs, methanol, FAMEs, and glycerol, respectively. For modeling the kinetics of sunflower oil methanolysis over CaO modified with glycerol and ChCl : Gly, two kinetic models were tested.

a) The semi-empirical model developed for the quicklime-catalyzed methanolysis [23] is expressed as:

$$\frac{\mathrm{d}x_\mathrm{A}}{\mathrm{d}t} = k_\mathrm{app} \cdot \frac{\left(1 - x_\mathrm{A}\right)\cdot\left(c_\mathrm{R0} + 3 \cdot c_\mathrm{A0} \cdot x_\mathrm{A}\right)}{K + c_\mathrm{A0} \cdot \left(1 - x_\mathrm{A}\right)} \tag{2}$$

where x_A is the conversion degree of TAGs, t is time, k_app is the apparent reaction rate constant, c_R0 is the hypothetic initial FAME concentration corresponding to the initial available active catalyst surface, c_A0 is the initial TAG concentration, and K is the model parameter defining the TAG affinity for the catalyst active sites.

b) The model developed for CaO·ZnO catalyzed methanolysis [25] is expressed as:

$$\frac{\mathrm{d}x_\mathrm{A}}{\mathrm{d}t} = \frac{k'\cdot(k_\mathrm{mt,A})_0 \cdot \left[1 + \alpha x_\mathrm{A}{}^{\beta}\right]}{k' + (k_\mathrm{mt,A})_0 \cdot \left[1 + \alpha x_\mathrm{A}{}^{\beta}\right]} \cdot \left(1 - x_\mathrm{A}\right) \tag{3}$$

where x_A and t designate the same variables as in the model (a), k' is the effective pseudo-first-order reaction rate constant, $(k_\mathrm{mt,A})_0$ is the overall TAG volumetric mass transfer coefficient at the beginning of the process, and α and β are fitting parameters.

General assumptions were as follows:

1. The reaction was performed in the batch stirred reactor. High intensity of mixing provided a perfectly mixed reaction mixture with uniform composition and catalyst distribution.

2. The methanolysis reaction occurs between methoxide ions and carbonyl groups of approaching hydrophobic TAG molecules [18].
3. TAG mass transfer limitations are negligible in the initial period of the methanolysis reaction and are not included in the kinetics modeling of methanolysis, catalyzed by CaO modified with commercial glycerol and ChCl-Gly.
4. The internal diffusion rate within catalyst particles did not affect the methanolysis reaction rate due to the small specific surface area of the Ca-diglyceroxide complex [18].
5. Neutralization of free fatty acids can be ignored since the refined sunflower oil was used. Hence, the catalyst concentration was constant during the methanolysis.

4. RESULTS AND DISCUSSION

4. 1. FTIR analysis

Surfaces of neat CaO and its complexes with glycerol and ChCl : Gly were characterized by FTIR spectra (Figure 1) while the numerical data are given in Table 1. The spectrum of neat CaO contains a weak band at 3424 cm^{-1} due to ν(OH) stretching vibration. The band originates from the OH group located in $Ca(OH)_2$. Namely, the surface of CaO is covered with $Ca(OH)_2$ and $CaCO_3$, due to hydration and carbonization of CaO. The spectrum of the C-ChG complex contains a wide and strong band at 3388 cm^{-1}, due to ν(OH) stretching vibration. Appearance of this band suggests the formation of an intramolecular hydrogen bond since the ChCl molecule contains both donor and acceptor of hydrogen. The bending OH vibration can be observed at 1650 cm^{-1} while stretching (ν_{as}(CH)) and (ν_s(CH)) vibrations are at 2933 and 2843 cm^{-1}, respectively. A similar finding was observed in the FTIR spectrum of CaO after the transesterification process in the presence of the same DES (ChCl-Gly) as a co-solvent showing the characteristic peaks for Ca-diglyceroxide [6]. These characteristic vibrations for the spectrum of Ca-diglyceroxide complex are not present in the spectrum of the neat CaO. The same analysis can be applied to the modified CaO with commercial glycerol. Formation of the C-G complex can be confirmed by a strong and wide band at 3404 cm^{-1}, which can be assigned to stretching ν(OH) vibration of hydrogen-bonded hydroxyl group, and proper bending vibration at ~1648 cm^{-1}, as well as the symmetrical and asymmetrical stretching vibrations of a methylene group (Table 1). The spectra of C-G and C-ChG complexes, after washing with methanol (Figure 1c,e) did not show appreciable changes in the band positions and intensities. This indicated the complex stability.

Table 1. Numerical data of the FTIR spectra for the neat CaO and C-G and C-ChG complexes

Band assignation	Wavenumber, cm^{-1}		
	Neat CaO	C-G complex	C-ChG complex
ν(OH)	3424	3404	3388
ν_{as}(CH)		2926	2933
ν_s(CH)		2860	2843
δ(OH)	1470	1648	1650
δ(CH)		1416	1419
ν(C-O)	1114	1108	1123

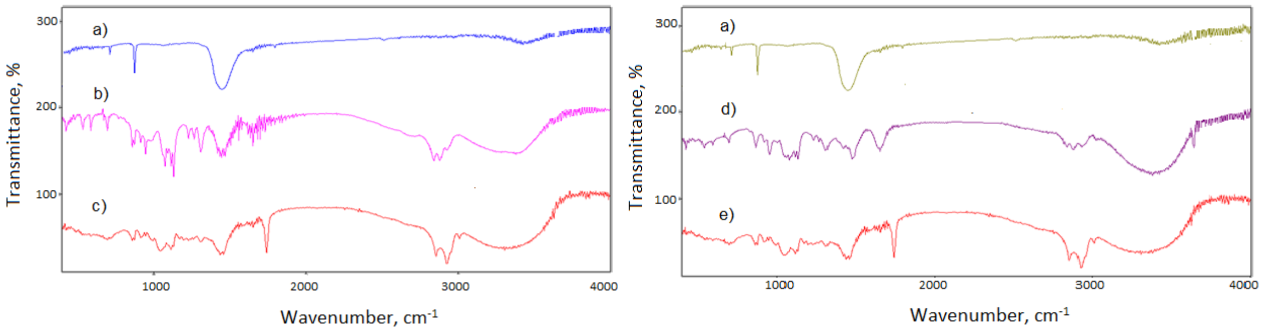


Figure 1. FTIR spectra of the neat CaO (a), the C-G complex before (b) and after (c) washing with methanol and the C-ChG complex before (d) and after (e) washing with methanol

4. 2. Sunflower oil methanolysis over the modified CaO catalysts

Variation of the FAME content during the sunflower oil methanolysis catalyzed by the C-G and C-ChG complexes at different initial methanol-to-oil molar ratios and catalyst loadings is shown in Figure 2. In both catalyst cases, independently of the initial methanol-to-oil molar ratio, the overall reaction rate and the content of FAMEs were lower at the lowest catalyst loading (0.5 %). It was probably the result of a lower available catalytic surface for the reaction. With increasing the catalyst loading to 1 %, the mass transfer resistance in the initial period of the reaction did not occur. More available catalytic active sites were provided by increasing the catalyst loading so that it affected the overall reaction rate, reaching the highest FAME content at a shorter reaction time. However, a further increase in the catalyst loading (5 %) decreased the reaction rate and the FAME content. This higher catalyst loading provided larger catalytically active surface but lower mixing efficiency of the reaction mixture at the beginning due to higher viscosity of the reaction mixture. A similar effect of the catalyst loading on the FAME content has been already observed [21,22].

The effect of the initial methanol-to-oil molar ratio on the reaction rate and FAME content depended on the catalyst loading and was more emphasized with the C-G complex (Figure 2a,b) than with the C-ChG complex (Figure 2c,d). A lower FAME content was observed at the C-G complex loading of 1 % when a higher methanol-to-oil molar ratio was employed. This could be the result of the higher methanol amount, which increased the total volume of the reaction mixture and diluted the catalyst concentration relative to methanol. A significant effect of the methanol amount on the reaction rate and FAME content was not observed at the lowest catalyst loading (0.5 %) due to the lower catalyst concentration. Moreover, the excess of methanol provides a better solubility of the produced glycerol that will more likely cover the active layer of the catalyst. This could be the reason for the insignificant effect of the methanol-to-oil molar ratio on the reaction rate and FAME content in the case of the C-ChG complex. Lukić *et al.* [22] have reported that the increase of the methanol-to-oil molar ratio affected only the final period of the reaction. On the other hand, when the methanol-oil molar ratio decreased from 14 : 1 to 7 : 1, Ferrero *et al.* [21] noticed a decrease of the FAME yield by 5 and 2 % in the initial and final periods of the reaction, respectively.

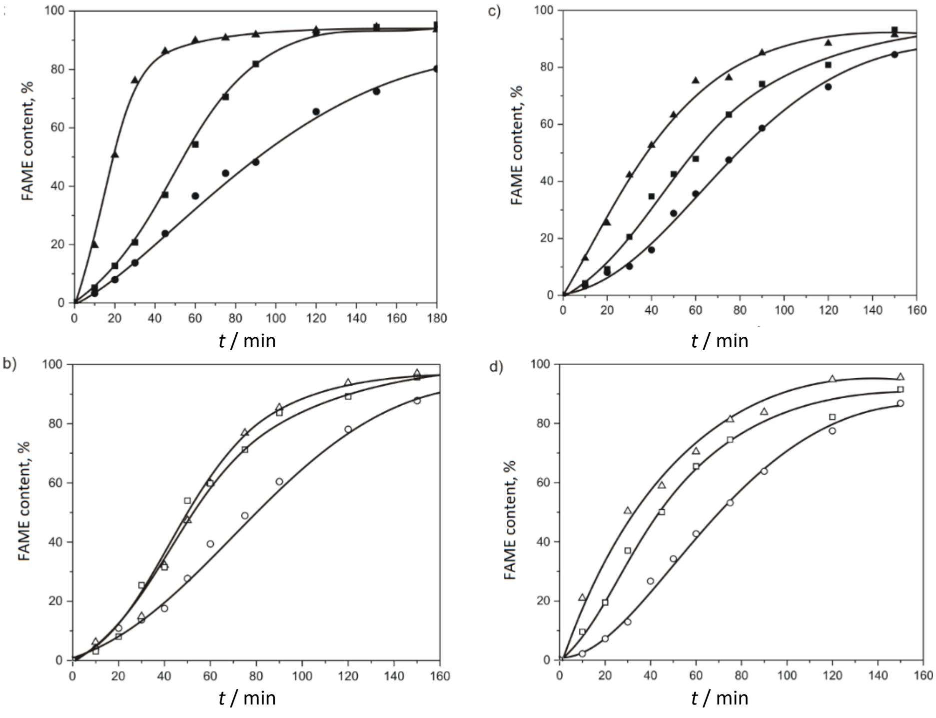


Figure 2. FAME content over time during the reaction catalyzed by the C-G (a,b) and C-ChG (c,d) complexes (catalyst loading: circles –0.5 %, triangles – 1 %, squares – 5 %; methanol-to-oil molar ratio: 6 : 1 – solid symbols and 12 : 1 – open symbols) (data are average of n = 240, average SD=1.12 CL=95 %)

Comparison of the sunflower oil methanolysis catalyzed by the C-G and C-ChG complexes and by quicklime [23], at the same operating conditions (methanol-to-oil molar ratio and catalyst loading), is shown in Figure 3. With the C-ChG complex, the fastest reaction in the initial reaction period and a lower FAME content in the final reaction period were achieved due to the reduced TAG mass transfer resistance and to a reverse reaction promoted by increasing the glycerol concentration, respectively. The TAG concentration decreased near the active sites of the catalyst and the reaction between the produced FAME and glycerol was more likely to happen [22]. When quicklime was used as a catalyst, the formation of the CaO-glycerol complex during the reaction happened gradually, and the concentration of glycerol as a by-product still was not at the level to promote the reverse reaction as in the reactions catalyzed by the C-G and C-ChG complexes. The transformation of CaO into Ca-glyceroxide during the methanolysis requires a higher amount of glycerol [9,26]. Thereby, Ca-glyceroxide was formed at the end of the reaction (after 2 h), while at the beginning of the reaction (after 1 h) it could hardly be distinguished because of the low amount of glycerol [26]. It was concluded that Ca-glyceroxide can be generated on the surface of CaO particles by pre-treating them with glycerol; however, an excess of glycerol would cover the surface of Ca-glyceroxide and decreases its activity. This was supported by the observed decreased FAME content as more glycerol was added into the reaction mixture [10,26]. Also, with Ca-diglyceroxide, the TAG conversion degree increases proportionally to the catalyst loading, reaching 100 % at the catalyst loading of 1.46 % [19]. Therefore, optimization of the reaction conditions is suggested to maximize the FAME content.

Figure 4 shows the FAME formation during the sunflower oil methanolysis, catalyzed by the leachates obtained by mixing the C-G and C-ChG complexes with methanol for 30 min (60 °C) and separating the liquid phase by filtration. In both cases, the FAME content did not exceed the value of 2 % indicating a low catalyst leaching and the heterogeneous nature of the C-G and C-ChG complexes.

Many researchers have investigated the stability of Ca-diglyceroxide. Ca-diglyceroxide synthesized directly from hydrated lime and glycerol was not stable in biodiesel, methanol, water, and castor oil at 60 °C and its lixiviation was affected by the oil acidity [19]. The complex obtained by immersing CaO into glycerol blended with methanol was poorly soluble [10]. In the present study, the C-G and C-ChG complexes were synthesized in the presence of a large amount of methanol and directly from CaO and ChCl : Gly, respectively. Therefore, the nature of catalysis (homo- or heterogeneous) depends on the method of the synthesis of CaO/glycerol complexes and the type and acidity of oily feedstock. In the case of refined sunflower oil used in the present study, the influence of the oil acidity on the lixiviation of the C-G and C-ChG complexes can be ignored.

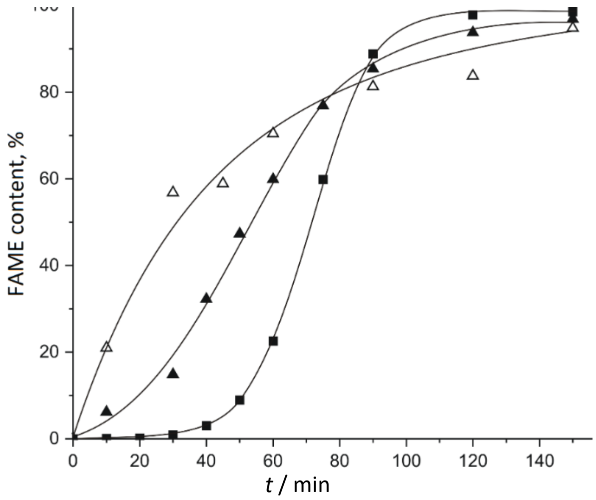


Figure 3. Comparison of FAME formation during the sunflower oil methanolysis catalyzed by the C-G (▲) and C-ChG complexes (△), and quicklime [23] (■) (methanol-to-oil molar ratio of 12 : 1, catalyst loading of 1 %) (data are average of n = 52, average SD = 1.24, CL = 95 %)

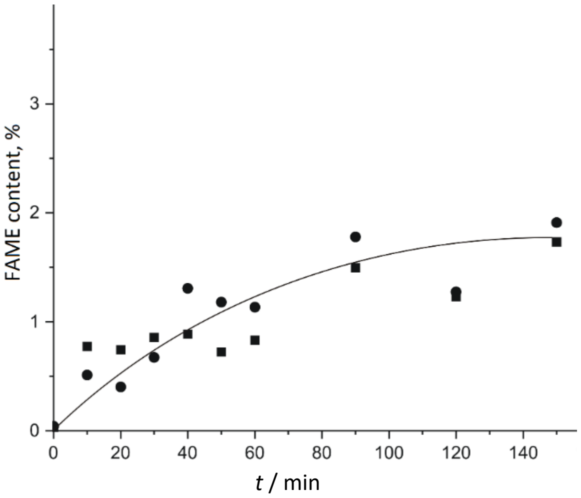


Figure 4. The FAME content achieved in the reaction catalyzed by leachate of the C-G (●) and C-ChG (■) complexes (methanol-to-oil molar ratio 12 : 1) (data are average of n = 36, SD = 0.19, CL = 95 %)

4. 3. Kinetics of the sunflower oil methanolysis over the modified CaO catalysts

The kinetic models, originally developed for the reactions catalyzed by quicklime [23] and Ca-diglyceroxide [22], were applied for the kinetic analysis of the sunflower methanolysis over the modified CaO catalysts. Both models have been shown applicable for describing the kinetics of the reactions catalyzed by CaO, quicklime, $Ca(OH)_2$, and $CaO{\cdot}ZnO$ if the catalyst loading is higher than 0.5 % [27,28]. The values of the kinetic parameters are presented in Tables 2 and 3 along with the mean relative percent deviation (MRPD) between the calculated and experimental values of TAG conversion degree. The comparison of experimental data of TAG conversion degree with the predicted values, calculated by both kinetic models, is shown in Figure 5.

Generally, the apparent reaction rate constant k_{app}, depended on the reaction conditions. Independently of the catalyst type, the k_{app}-values decreased above the catalyst loading of 1 % (Table 2). Although the higher catalyst loading in the reaction mixture provided more active sites, which facilitated the reaction rate, a higher catalyst loading could hinder efficient mixing. Therefore, an increase in the methanol-to-oil molar ratio did not significantly affect the k_{app}-values at catalyst loadings above 1 %. The parameter K for the C-G and C-ChG complexes was not affected by the reaction conditions as being constant. The values of parameter c_{R0} did not show a consistent trend concerning the catalyst loading and the methanol-to-oil molar ratio.

The values of the effective pseudo-first-order reaction rate constant (k') of the second model [22,25] for both catalysts (Table 3) increased with increasing the catalyst loading up to 1 % and then decreased with the further catalyst loading increase. Beyond 1 % of the catalyst loading, the k'-value of the C-G complex decreased with the increase of the methanol-to-oil molar ratio but not in the case of the C-ChG complex. The values of the overall TAG volumetric mass transfer coefficient at the beginning of the reaction $(k_{mt,A})_0$ followed a similar pattern as the reaction rate constant k' with respect to the catalyst loading (Table 3). The methanol-to-oil molar ratio affected the $(k_{mt,A})_0$ -values positively in the case of the C-ChG complex but an opposite effect was observed for the C-G reaction system. The α-values for both catalysts increased with increasing the catalyst loading up to 1 %, followed by a decrease at a higher catalyst load (5 %). A positive effect of the methanol-to oil molar ratio on the α-values was observed only for the reaction catalyzed by the C-G complex. Higher values of the fitting parameter β were obtained for the catalyst loading over 1 % and did not change with the methanol-to-oil molar ratio. The shape of the TAG conversion curves depended on the catalyst loading and methanol-to-oil molar ratio and shifted from exponential to slight sigmoidal. The $(k_{mt,A})_0$-values depended on the transition from the heterogeneous to the pseudo-homogeneous regime. If the reaction system was pseudo-homogeneous, the $(k_{mt,A})_0$-values increased, becoming closer to the k'-values or even higher. The $(k_{mt,A})_0$-values were lower when the curve departed from the exponential pattern, which can be ascribed to the presence of the lower catalyst amount in the reaction mixture that did not provide sufficient quantity of catalytic active sites or the higher catalyst amount that hindered mixing efficiency of the reaction mixture at the beginning of the reaction.

Table 2. Determined model parameters for the model proposed by Miladinović et al. [23], Eq.(2)

Catalyst loading, %	k_{app} / min^{-1}	K / mol dm^{-3}	c_{R0} / mol dm^{-3}	R^2	MRD, %*
		C-G complex			
		Methanol to oil molar ratio 6 : 1			
0.5	0.010	3.019	2.407	0.939	9.19
1.0	0.094	3.019	0.909	0.920	5.77
5.0	0.052	3.019	0.331	0.970	2.53
		Methanol to oil molar ratio 12 : 1			
0.5	0.040	3.019	0.361	0.928	7.54
1.0	0.052	3.019	0.305	0.976	7.74
5.0	0.051	3.019	0.539	0.946	5.52
		C-ChG complex			
		Methanol to oil molar ratio 6 : 1			
0.5	0.028	3.019	0.658	0.922	8.39
1.0	0.032	3.019	1.625	0.940	3.45
5.0	0.028	3.019	1.076	0.972	8.37
		Methanol to oil molar ratio 12 : 1			
0.5	0.026	3.019	0.963	0.965	9.32
1.0	0.034	3.019	2.009	0.995	7.00
5.0	0.032	3.019	1.206	0.999	5.58

*Mean relative deviation

Table 3. Determined model parameters for the model proposed by Lukić et al. [22,25], Eq. (3)

Catalyst loading, %	k' / min^{-1}	$(k_{mt,A})_0$ / min^{-1}	α	β	R^2	MRD*, %
C-G complex						
Methanol-to-oil molar ratio 6 : 1						
0.5	0.011	0.009	11.79	1	0.948	10.74
1.0	0.080	0.029	27.09	2	0.944	7.34
5.0	0.055	0.009	15.12	2	0.961	6.45
Methanol-to-oil molar ratio 12 : 1						
0.5	0.035	0.002	28.29	1	0.955	9.55
1.0	0.048	0.005	66.49	2	0.979	6.37
5.0	0.033	0.008	41.39	2	0.953	6.49
C-ChG complex						
Methanol-to-oil molar ratio 6 : 1						
0.5	0.025	0.003	16.17	1	0.943	8.64
1.0	0.031	0.026	28.68	2	0.977	2.71
5.0	0.027	0.011	23.18	2	0.990	7.73
Methanol-to-oil molar ratio 12 : 1						
0.5	0.045	0.007	5.17	1	0.989	9.18
1.0	0.031	1.153	22.73	2	0.999	7.51
5.0	0.030	0.017	8.85	2	0.994	4.75

*Mean relative deviation

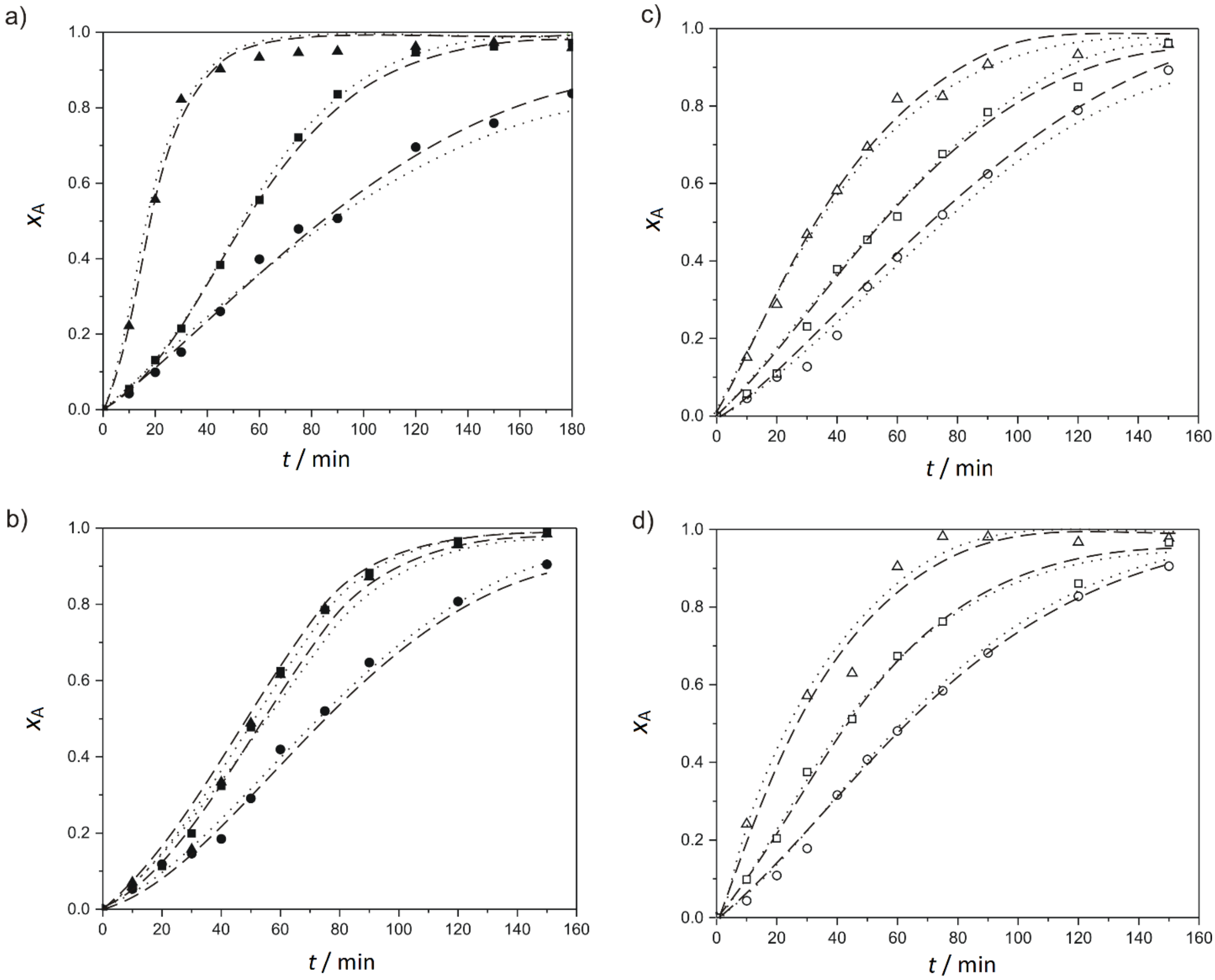


Figure 5. Comparison of the experimental and predicted values of the TAG conversion degree calculated by the kinetic models based on Miladinović et al. [23], Eq. (2) (——) and Lukić et al. [22,25], Eq. (3) (···) in the presence of the C-G (solid symbols; a,b) and C-ChG (open symbols; c,d) complexes (methanol-to-oil molar ratio: (a,c) 6 : 1, (b,d) 12 : 1; catalyst loading: 0.5 % - circles, 1 % - triangles, 5 % - squares) (experimental data are average of n = 240)

5. CONCLUSION

Catalytically active complexes of CaO and glycerol were obtained by modifying CaO with commercial glycerol and the ChCl : glycerol DES. The FTIR analysis confirmed formation of the CaO-glycerol complexes, both for the CaO modification with glycerol and ChCl : glycerol. When the CaO-glycerol complexes were employed as catalysts, the TAG mass transfer resistance was reduced in the initial period of the reaction and depended on the catalyst loading and the methanol-to-oil molar ratio. The optimal catalyst loading was 1 % based on the oil weight. The pseudo-homogeneous regime was more pronounced in the case of the C-ChG complex. The reactions catalyzed by the C-G and C-ChG complexes were faster in the initial period compared to the reaction catalyzed by quicklime. However, a shorter initial reaction period was achieved with the C-ChG complex than with the C-G complex. These reactions take place in the pseudo-homogeneous regime, but the maximum FAME content was lower as compared to the reaction catalyzed by quicklime at the same reaction conditions, likely due to the reversible reaction. Furthermore, the C-G and C-ChG complexes provided heterogeneous catalysis, confirmed by a negligible content of FAME synthesized in the presence of leachate. Two different kinetic models, originally developed for the quicklime and $CaO \cdot ZnO$ catalyzed reactions, successfully described the kinetics of the sunflower oil methanolysis catalyzed by the C-G and C-ChG complexes. The obtained results will have a significant contribution to the research of reducing the mass transfer limitation by modification of CaO surface, which improves the reaction kinetics.

NOMENCLATURE

c_{A0}- Initial TAG concentration, mol dm^{-3}
c_{B0}- Initial methanol concentration, mol dm^{-3}
c_{cat}- Catalyst concentration, mol dm^{-3}
c_{R0} - Hypothetic initial FAME concentration corresponding to the initial available active catalyst surface, mol dm^{-3}
CL - Confidence level
k_{app} - Apparent reaction rate constant, Eq. (2), min^{-1}
k' - Effective pseudo first-order reaction rate constant, Eq. (3), min^{-1}
K - Model parameter defining the TAG affinity for the catalyst active sites, mol dm^{-3}
$(k_{mt,A})_0$ - Overall TAG volumetric mass transfer coefficient at the beginning of the process, min^{-1}
SD - Standard deviation
t - Time, min
x_A- Conversion degree of TAG
α - Fitting parameter Eq. (3)
β –Fitting parameter Eq. (3).

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Metanoliza suncokretovog ulja katalizovana modifikovanim CaO

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Izvod

Metanoliza ulja u prisustvu katalizatora na bazi modifikovanog CaO proučavana je u cilju određivanja katalitičke aktivnosti novih katalizatora i definisanja odgovarajućeg kinetičkog modela. CaO je modifikovan komercijalnim glicerolom i eutektičkim rastvaračem (ES), holinhlorid : glicerolom (ChCl : Gly), da bi se dobili katalitički aktivni kompleksi CaO i glicerola. Cilj istraživanja bio je da se potvrdi katalitički uticaj dobijenih kompleksa na brzinu reakcije i sadržaj metilestara masnih kiselina (MEMK), a zatim opiše promena stepena konverzije triacilglicerola (TAG) sa vremenom. Na osnovu analize infracrvenom spektroskopijom sa Furijeovom (Fourier) transformacijom (engl. *Fourier Transform Infrared Spectroscopy*, FTIR) potvrđeno je formiranje kompleksa CaO sa glicerolom i ES na bazi glicerola. Metanoliza ulja izvedena je na 60 °C pri različitim količinama katalizatora (0,5; 1 i 5 %) i molskim odnosima methanol : ulje (6 : 1, 12 : 1). Rezultati analize pokazali su da kinetički parametri dva primenjena modela zavise od količine katalizatora i molskog odnosa methanol : ulje. Oba modela se mogu uspešno primeniti za opisivanje kinetike reakcija katalizovanih kompleksima CaO sa glicerolom (srednje relativno procentualno odstupanje je manje od 10 % u oba slučaja).

Ključne reči: biodizel; kalcijum oksid; holinhlorid-glicerol; eutektički rastvarači; kinetika