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Optimization of CaO-catalyzed sunflower oil methanolysis with crude biodiesel as a cosolvent

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Abbreviations: ANOVA - Analysis of variance; RCCD - rotatable central composite design; FAME – fatty acid methyl ester; RSM - Response surface methodology.

22 **Abstract**

23 Crude biodiesel was proven as a cosolvent in the methanolysis of sunflower oil by calcined

24 CaO. This reaction was modeled and optimized statistically in terms of reaction temperature

25 (33.2-66.8 °C), methanol:oil molar ratio (3.5:1-8.5:1) and catalyst concentration (0.219-1.065

26 mol/L). The cosolvent loading was 10 wt% (based on oil weight). The optimum reaction

27 conditions were found to be: the methanol-to-oil molar ratio of 7.1:1, the catalyst

28 concentration of 0.74 mol/L and the reaction temperature 52 °C, ensuring the best esters

29 content of 99.8%, for the reaction time of 1.5 h, which is close to the reported experimental

30 value of 98.9% Also, the used catalyst was recycled with no additional treatment in the further

31 four consecutive cycles under the following reaction conditions: methanol-to-oil molar ratio

32 6:1, the concentration of catalyst 0.642 mol/L (only in the first run), the reaction temperature

33 50 °C, cosolvent-crude biodiesel loading 10 wt% to oil weight. The second recycling reaction

34 provided the highest FAME content of 97.7% after 5 h.

35

36 **Keywords**: Biodiesel; CaO; Cosolvent; Methanolysis; Recycling; Calcium leaching.

37

1. Introduction

As an alternative fuel, biodiesel possesses advantages from technical, economic and environmental points of view. It is commercially produced mainly by transesterification of vegetable oils and animal fats in the presence of various homogeneous base catalysts at moderate conditions for a relatively short reaction time. This process suffers from several disadvantages, such as impossibility of catalyst reuse, high energy demand for biodiesel separation and purification and large wastewater generation in the purification stage. These obstacles can be overcome by using heterogeneous (solid) catalysts, which can be easily separated from the reaction mixture and reused with or without any treatment. Among the heterogeneous catalysts, the CaO-based catalysts have become very popular for biodiesel production because they are cheap, highly alkaline and effective under mild reaction conditions, ensure high biodiesel yield, can be prepared from natural or waste materials [1] and are used in batch stirred and continuous packed-bed reactors [2]. Besides the sensitivity to free fatty acids, CO_2 and moisture, calcium leaching during the reaction is also a negative characteristic of CaO-based catalysts because it spoils the purity of both products and reduces, to some degree, their reusability and activity. Another disadvantage of CaO-based catalysts is mass transfer limitations that slow down the reaction rate especially in the initial reaction stage. This obstacle can be solved by addition of a cosolvent, which is soluble in both liquid reactants (oil and alcohol), to the reaction mixture in order to increase the liquid-liquid interfacial area. Usually, cosolvents are organic solvents [3] or ionic liquids and deep eutectic solvents [4]. In addition to the reduced reaction time and temperature, the cosolvent method can improve some properties of the produced biodiesel [5, 6]. Because of the possible toxicity and hazard risk, it is extremely important to completely remove cosolvent residues from the produced glycerol and biodiesel [7]. Crude biodiesel can also be used as a cosolvent as fatty acid methyl esters (FAMEs) increases miscibility of the immiscible reactants in biodiesel

63   production [8]. As a cosolvent, crude biodiesel increases esters yield [9-11] or reaction rate

64   [12] while it does not pollute the reaction products. There is no agreement among the

65   researchers on the optimum amount of crude biodiesel. According to López Granados and

66   coworkers [12], the optimum amount of crude biodiesel is 3 wt% of the oil weight, whereas

67   Kumar et al. [13] reported that 7.5 wt. % of FAME provided the maximum FAMEs yield.

68   In the present work, crude biodiesel was used as a cosolvent in the methanolysis of sunflower

69   oil catalyzed by CaO under the moderate reaction conditions and atmospheric pressure. The

70   advantages of adding crude biodiesel are: (a) the reduction of the mass transfer limitation

71   present in the initial reaction stage caused by the immiscibility of the reactants that slows

72   down the reaction rate, (b) no need for removal of this cosolvent from the final reaction

73   mixture as it is also a product of the reaction, and (c) a faster phase separation at the end of

74   the reaction. The influence of reaction temperature, methanol-to-oil molar ratio and catalyst

75   concentration was studied using the response surface methodology (RSM) combined with a

76   rotatable central composite design (CCD). The main goal was to evaluate the impact of the

77   selected process factors on FAME content, to correlate FAME content with the process

78   factors and to define the optimal process conditions ensuring the best FAME content.

79   Additionally, in order to estimate the potential of CaO for biodiesel production at a

80   commercial scale, calcium leaching and catalyst reusability were also investigated. According

81   to the best knowledge of the authors, there is no study on the statistical optimization of

82   vegetable oil transesterification reactions in the presence of a solid catalyst and crude

83   biodiesel as a cosolvent.

2. Material and methods

2.1. Materials

Edible sunflower oil (Dijamant, Zrenjanin, Serbia) was purchased in a local shopping store. The main physicochemical properties of the oil were: density 918.40 kg/m³, viscosity 77.10 mPa·s (both properties at 20 °C), acid value 0.29 mg KOH/g, saponification value 190 mg KOH/g and iodine value 139 g I_2/100 g. CaO (99.00%, Sigma Aldrich, St. Louis, USA) was calcined at 550 °C for 2 h immediately before use [14]. The activated CaO was cooled and stored in a well-closed, glass bottles in a desiccator with $CaCl_2$. Certified methanol of 99.5% purity was purchased from Zorka Pharma (Šabac, Serbia). Methanol, 2-propanol and *n*-hexane, all of HPLC grade, were purchased from Lab-Scan (Dublin, Ireland). Hydrochloric acid (36 wt%) was purchased from Centrohem (Stara Pazova, Serbia). Ethyl acetate (99.5%, Merck Millipore, Darmstadt, Germany), *n*-hexane (99%, LGC Promochem, Wesel, Germany) and glacial acetic acid (Zorka, Šabac, Serbia) were also used. The standards containing methyl 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 provided from Sigma Aldrich (St. Louis, USA).

Crude biodiesel, used as a cosolvent, was prepared by the CaO-catalyzed sunflower oil methanolysis carried out at the methanol-to-oil molar ratio of 6:1 (91.92 g of oil and 20.29 g of methanol), CaO concentration of 0.642 mol/L (4.97 g), reaction temperature of 50 °C and reaction time of 5 h; it contained 99.9% FAME. The reaction was repeated six times. The phases of the final reaction mixture were separated in a separation funnel. During the separation stage, three layers were observed: the upper layer (mostly FAMEs), the middle layer (a mixture of glycerol and excess methanol), and the lower layer (the precipitated CaO).

5

2.2. 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 reaction flask was placed in a water chamber kept at a desired temperature by circulating water from a thermostated bath. A CCD with five central points was used to optimize the reaction conditions; the complete experimental matrix with coded and uncoded levels of the process factors (methanol-to-oil molar ratio X_1, catalyst concentration X_2 and reaction temperature X_3) and FAME content is presented in **Table 1**. All experiments were carried out in a randomized order. The cosolvent (crude biodiesel) amount was 10 wt% of the oil weight in all experiments. Lower amounts of crude biodiesel than 10% were less efficient as it was shown in a preliminary study (Fig. S1, Supplementary material). This study indicated also that a larger crude biodiesel amount than 10% would not further improve the FAME synthesis as the curves corresponding to 7.5% and 10% were close or even overlapped (in the final stage of the reaction). In addition, the fastest separation of the phases at the end of the reaction occurred with 10 wt% of crude biodiesel. The desired amounts of methanol, crude biodiesel and CaO were added to the flask and stirred at 900 rpm for 30 min at the desired temperature. After the stirrer was turned off, the corresponding amount of sunflower oil, heated separately at the same temperature, was added to the reaction flask, the stirrer was switched on, and the reaction was timed. During the reaction, the samples were taken from the reaction mixture, immediately quenched by adding a required amount of aqueous hydrochloric acid solution (5 mol/L) to neutralize the catalyst and centrifuged (Sigma 2-6E, Germany; 3500 rpm) for 15 min. Three layers were noticed after centrifugation: the top layer containing FAME, triacylglycerols (TAG), diacylglycerols (DAG) and monoacylglycerols (MAG), the middle layer consisted of glycerol and methanol and the bottom layer of precipitated CaO. After centrifugation, the supernatant (ester/oil fraction) was withdrawn, dissolved in the 2-

132 propanol/*n*-hexane (5:4 v/v) mixture in an appropriate ratio (1:10 or 1:200 for qualitative TLC

133 or quantitative HPLC analysis, respectively), and filtered through a 0.45 μm Millipore filter.

134 The resulting filtrate was used for thin layer (TLC) and liquid chromatography (HPLC)

135 analyses. The ester and alcohol phases of the final reaction mixture were separated in a

136 separation funnel. The samples of the separated phases were analyzed for calcium to evaluate

137 the catalyst leaching. At the end of the reaction, the CaO catalyst was separated from the

138 reaction mixture by centrifugation, filtered, washed with methanol, dried for 2 h at 110 °C and

139 analyzed by the X-ray powder diffraction (XRD) method.

140

141   **Table 1** Experimental matrix for CCD.[a]

Run	Coded levels			Actual (uncoded) levels			Response
	Factor X_1	Factor X_2	Factor X_3	Factor X_1	Factor X_2	Factor X_3	FAME (Y), %
1	-1	-1	-1	4.5	0.39	40	85.7
2	1	-1	-1	7.5	0.39	40	96.7
3	-1	1	-1	4.5	0.894	40	86.6
4	1	1	-1	7.5	0.894	40	98.1
5	-1	-1	1	4.5	0.39	60	94.6
6	1	-1	1	7.5	0.39	60	98.7
7	-1	1	1	4.5	0.894	60	97.0
8	1	1	1	7.5	0.894	60	99.2
9	-1.68	0	0	3.5	0.642	50	85.8
10	1.68	0	0	8.5	0.642	50	99.2
11	0	-1.68	0	6	0.2186	50	97.0
12	0	1.68	0	6	1.065	50	97.6
13	0	0	-1.68	6	0.642	33.2	89.2
14	0	0	1.68	6	0.642	66.8	99.3
15	0	0	0	6	0.642	50	98.0
16	0	0	0	6	0.642	50	99.1
17	0	0	0	6	0.642	50	99.1
18	0	0	0	6	0.642	50	97.3
19	0	0	0	6	0.642	50	96.0
20	0	0	0	6	0.642	50	96.6

142   [a] Methanol-to-oil molar ratio (mol/mol) - X_1, catalyst concentration (mol/L) - X_2 and reaction
143   temperature (°C) - X_3.

144

145 *2.3. Catalyst reusability test*

146 After the completion of the reaction, the catalyst was separated from the ester phase by

147 centrifugation (3500 rpm, 15 min), vacuum-filtered, left to dry and reused without any

148 additional treatment (no regeneration or recalcination) in the consecutive batch reactions.

149 Catalyst reusability was tested under the following reaction conditions: the methanol-to-oil

150 molar ratio 6:1, the catalyst concentration in the first batch 0.642 mol/L, the reaction

151 temperature 50 °C, the cosolvent-crude biodiesel loading 10 wt% to oil weight, and the

152 reaction time 5 h.

153 *2.4. Analytical methods*

154 The chemical composition of ester/oil fraction samples was first determined qualitatively by

155 TLC and then quantitatively by HPLC as described elsewhere [14]. The calibration curves

156 were prepared by using the standard mixture of FAMEs and standard triacylglycerols and

157 used for quantifying FAMEs and acylglycerols present in the ester/oil fraction of the reaction

158 mixture.

159 The XRD measurements were performed by a Philips PW 1050 X-ray powder diffractometer

160 using Ni-filtered Cu K$\alpha_{1,2}$ (λ = 1.54178 Å) radiation and the Bragg–Brentano focusing

161 geometry. Measurements were done at room temperature over the 2θ range of 7–70° with a

162 scanning step width of 0.05° and a counting time of 3 s per step.

163 The physicochemical properties of the biodiesel obtained under the optimum reaction

164 conditions (methanol-to-oil molar ratio 7.1:1, the catalyst concentration 0.74 mol/L and the

165 reaction temperature 52 °C) were determined according to the appropriate standard methods,

166 namely density (EN ISO 3675:1988), kinematic viscosity (EN ISO 3104:2003), iodine value

167 (EN 14111:2003), acid value (EN 14104:2003), water content (EN ISO 12937:2000), FAME

Calcium in upper (crude biodiesel) and middle layer was determined by atomic absorption

spectrometry, flame technique. For this analysis, the samples were prepared by microwave

digestion (MBS-9, CEM Innovators, Great Britain) with a mixture of concentrated HCl and

HNO_3 (metal-free). After filtering, all samples were diluted with metal-free ultrapure water.

2.5. Statistical modeling and optimization of the methanolysis reaction

FAME content (Y) was correlated with methanol-to-oil molar ratio (X_1), catalyst concentration

(X_2) and reaction temperature (X_3) by the second order polynomial (quadratic) equation:

$$Y = b_0 + b_1 X_1 + b_2 X_2 + b_3 X_3 + b_{12} X_1 X_2 + b_{13} X_1 X_3 + b_{23} X_2 X_3 + b_{11} X_1^2 + b_{22} X_2^2 + b_{33} X_3^2 \qquad (1)$$

The regression coefficients (b_0, b_i, b_{ii} and b_{ij}, $i = 1, 2, 3, j > i$) were calculated using multiple

non-linear regression. The statistical significance of the independent variables on the FAME

content and the model fit quality were evaluated at a confidence level of 95% ($p < 0.05$) using

the analysis of variance (ANOVA). Optimal reaction conditions for achieving the maximum

FAME content were determined by solving the model equation. R–Project software (open

source, http://cran.us.r-project.org) was used for developing the models, testing their

adequacy, performing the ANOVA and optimizing the process factors.

3. Results and discussion

3.1. Sunflower oil methanolysis with CaO as a catalyst and crude biodiesel as a cosolvent

The variations of FAME content during the sunflower oil methanolysis over CaO both with

and without the presence of crude biodiesel as a cosolvent at 50 °C are shown in **Fig. 1**. For

comparison, the variation of FAME content at the most frequently used reaction temperature

for carrying out the transesterification reactions of vegetable oils over CaO (60 °C) is also

191   shown. The curves representing the transesterification reactions in the absence of crude

192   biodiesel as a cosolvent at 50 and 60 °C were sigmoid, indicating an initial induction period,

193   which was attributed to the mass transfer limitations related to the three-phase system [12].

194   However, in the presence of crude biodiesel, the FAME content increased continually from

195   the start of the reaction. This was ascribed to the increased miscibility of the reactants [15],

196   responsible for facilitating their passage to the active sites of CaO and increasing the reaction

197   rate, which was already observed [12, 16]. Furthermore, **Fig. 1** shows only a slight

198   improvement of the reaction by increasing the temperature from 50 °C to 60 °C. Also, it

199   indicates a good reproducibility of the FAME content measurement (standard deviation:

200   ±1.5%; number of data: 72). The XRD patterns of the calcined CaO used in combination with

201   different amounts of crude biodiesel as a cosolvent indicated that the dominant phase in all

202   the cases was Ca-diglyceroxide (**Fig. S2**, Supplementary material), known as a highly active

203   catalyst for the methanolysis reaction [17].
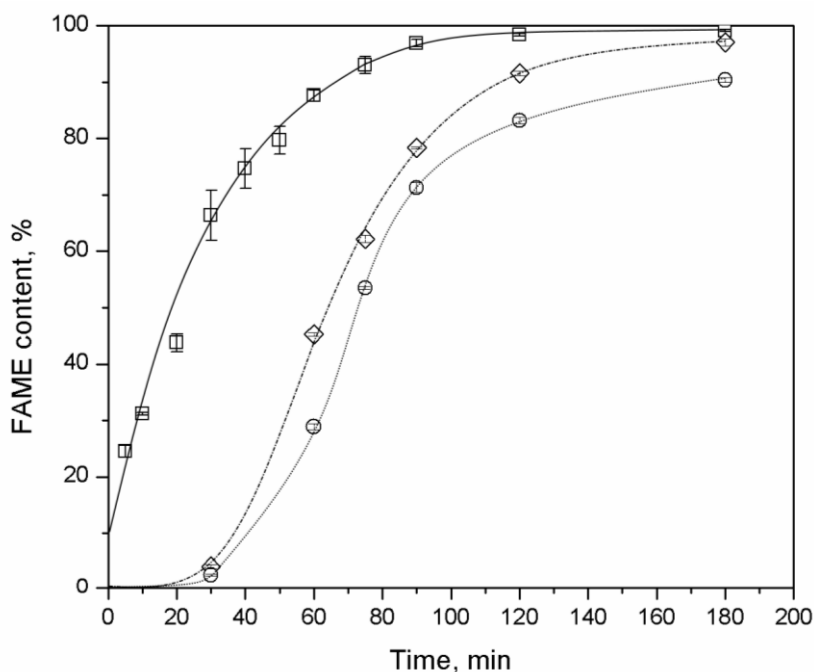
204

205   **Fig. 1.** Variation of FAME content during the sunflower oil methanolysis with CaO as a
206   catalyst and crude biodiesel as a cosolvent (methanol-to-oil molar ratio: 6:1, concentration of
207   CaO: 0.642 mol/L, reaction temperature: 50 °C and crude biodiesel: 10 wt% of the oil weight)
208   – □; without cosolvent at 50 °C – ○; without cosolvent at 60 °C – ◇.

209 *3.2. Modeling and optimization of the methanolysis reaction*

210 First, the adequacy of the regression model was checked by sequential sum of squares, lack of

211 fit and model summary statistic tests in order to select the non-aliased polynomial model

212 having highest order where the additional terms were significant, the model with insignificant

213 lack-of-fit and the model maximizing the adjusted and predicted coefficients of determination,

214 R^2_{adj} and R^2_{pred}, respectively. These tests suggested disregarding the cubic models as being

215 aliased and accepting the quadratic model, Eq. (1), as the best. The suggested model had an

216 insignificant lack–of–fit, which was advisable ($p = 0.921 > 0.050$), the highest F-value and

217 the lowest p-value (20.26 and 0.0001, respectively), the highest R^2-value (0.975) and the

218 R^2_{pred}– and R^2_{adj}–values (0.930 and 0.953, respectively) that were close to each other as

219 desirable (**Table 2**). Therefore, the quadratic model was selected for further modeling and

220 optimization of the sunflower oil methanolysis with CaO and crude biodiesel as a cosolvent.

221 By applying multiple regression analysis, FAME content was correlated with the process

222 factors (in terms of coded and uncoded values) by the following quadratic equations that were

223 valid only within the applied experimental region:

224   -   Coded values

225
$$Y = 97.68 + 3.76X_1 + 0.45X_2 + 2.88X_3 - 0.17X_1X_2 - 2.03X_1X_3 + 0.08X_2X_3 - 1.82X_1^2 - 0.12X_2^2 - 1.2X_3^2$$
(2)

226   -   Uncoded (actual) values

227
$$Y = -34.07 + 19.24X_1 + 5.52X_2 + 2.28X_3 - 0.46X_1X_2 - 0.14X_1X_3 + 0.03X_2X_3 - 0.81X_1^2 - 1.89X_2^2 - 0.01X_3^2$$
(2)

228 The ANOVA results, summarized in **Table 2**, showed that the model was statistically

229 significant at the 95% confidence level with a high F-value (43.46) and a small p-value (<

230 0.0001). The lack of fit was not significant relative to the pure error since its p-value (0.921)

12

231 was higher than 0.05, meaning that the model was adequate for predicting FAME content

232 within the applied ranges of the process factors. The value of the coefficient of determination

233 (R^2) of 0.975 implied a good fit, because even 97.5% of the variation in FAME content could

234 be explained by the regression model. The accuracy of the model was also confirmed by the

235 coefficient of variation ($C.V.$) of 1.07%. Only methanol-to-oil molar ratio (X_1) and reaction

236 temperature (X_3) as well as their interaction (X_1X_3) and squares (X_1^2 and X_3^2) have a

237 statistically significant effect on FAME content. By increasing both the reaction

238 temperature and the amount of methanol, the synthesis of FAME was favored and occurred at

239 higher rate. Also, with increasing the reaction temperature, the viscosity of the reaction

240 mixture was reduced, which promoted the mass transfer of TAGs towards the active sites at

241 the surface of the CaO catalyst particles and enhanced the overall process rate.

242 **Table 2** The results of ANOVA.[a]

Source of variation	Sum of squares	Degree of freedom	Mean square	F-value	p-value
Model	405.48	9	45.05	43.46	< 0.0001
X_1	192.97	1	192.97	186.14	< 0.0001
X_2	2.82	1	2.82	2.72	0.130
X_3	113.59	1	113.59	109.57	< 0.0001
X_1X_2	0.24	1	0.24	0.24	0.637
X_1X_3	32.80	1	32.80	31.64	< 0.001
X_2X_3	0.05	1	0.05	0.04	0.839
X_1^2	47.58	1	47.58	45.90	< 0.0001
X_2^2	0.21	1	0.21	0.20	0.664
X_3^2	20.69	1	20.69	19.96	0.001
Lack of fit	10.37	10	1.04		
Pure error	2.10	5	0.42	0.25	0.921
Corrected total	8.27	5	1.65		

243 [a] $R^2 = 0.975$, $R_{adj}^2 = 0.953$, $R_{pred}^2 = 0.930$ and $C.V. = 1.07\%$.

13

244 The predicted FAME content is in agreement with the actual FAME as confirmed by a very

245 small mean relative percent deviation ($MRPD$) of ±0.2%. Also, there was no problem in the

246 normality of experimental data distribution, verifying the validity of the ANOVA results. In

247 addition, the Cook's distance values were much lower than the limit (0.8), indicating that there

248 was no outlier in the used dataset. Since there has been no report on the statistical

249 optimization of the CaO-catalyzed methanolysis of vegetable oils in the presence of crude

250 biodiesel as a cosolvent, the obtained results of the statistical assessment could not be

251 compared with another study.

252 *3.3. Influence of process factors and optimization of FAME content*

253 **Fig. 2** shows the response surface plots for FAME content as a function of methanol-to-oil

254 molar ratio and catalyst concentration (**Fig. 2a**), methanol-to-oil molar ratio and reaction

255 temperature (**Fig. 2b**) and catalyst concentration and reaction temperature (**Fig. 2c**); in all

256 cases, the third variable was fixed at a constant value. As it can be concluded from **Figs. 2a**

257 and **c**, the catalyst concentration in the applied range had practically no influence on FAME

258 content, which agreed with the ANOVA results. The slight increase of FAME content with

259 increasing the catalyst concentration was observed at the highest reaction temperature and

260 methanol-to-oil molar ratio, which was attributed to the lower viscosity of the reaction

261 mixture that reduced the mass transfer limitation in the three-phase system. With increasing

262 the reaction temperature, FAME content increased (**Figs. 2b** and **c**) because of the positive

263 effect of the reaction temperature on the TAG mass transfer and FAME formation. The

264 influence of the reaction temperature on FAME content became less significant with

265 increasing the methanol amount; after reaching the plateau, FAME content slightly decreased,

266 thus confirming the negative effect of the X_1-X_3 two-way interaction. FAME content increased

267 with increasing the methanol-to-oil molar ratio under the all applied conditions. Excess of

268 methanol favored the direct reaction that increased FAME content. The impact of methanol

14

269   amount was independent of the catalyst concentration, which verified the statistically

270   insignificant influence of the X_1-X_2 interaction. On the other side, the impact of methanol

271   amount depended on the reaction temperature. At higher reaction temperatures, an increase of

272   the methanol-to-oil molar ratio above 7:1 slightly decreased FAME content, which could be

273   attributed to the favored reverse glycerolysis reaction [9].

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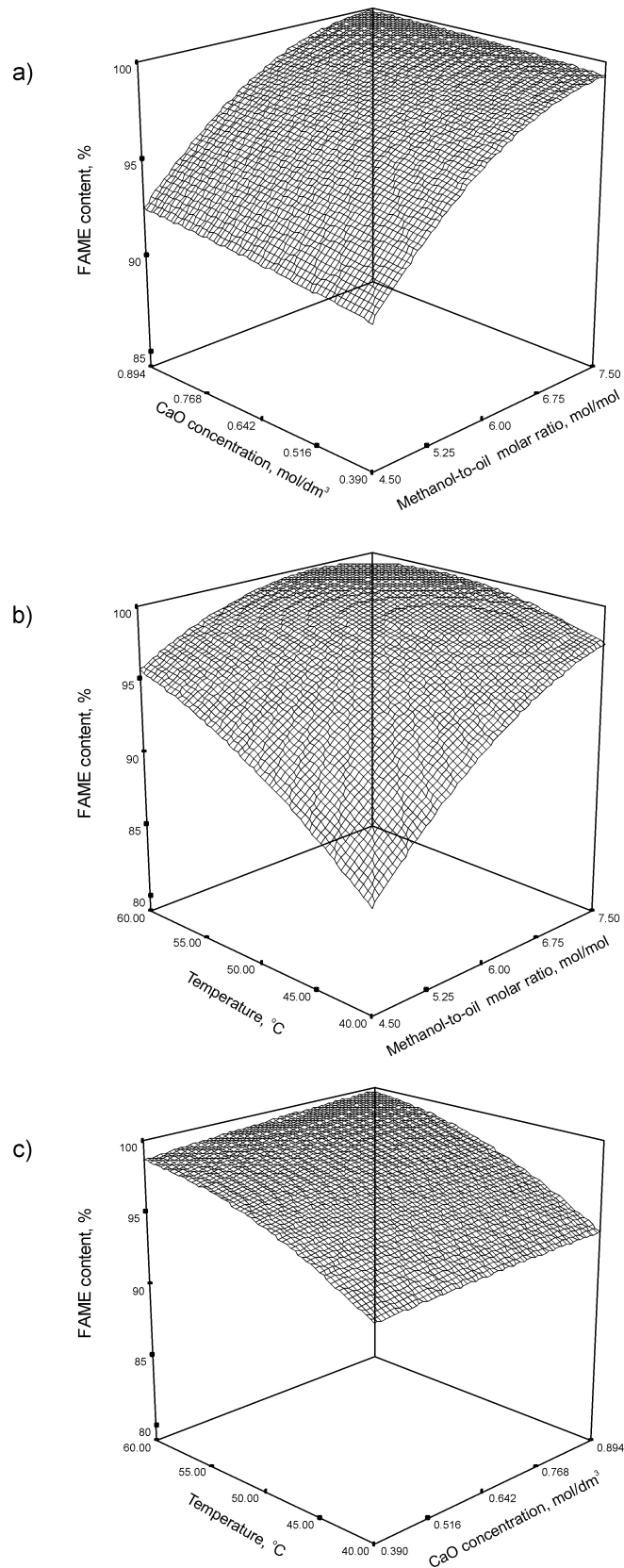
Fig. 2. Response surface for FAME content as a function of (**a**) methanol-to-oil molar ratio
and catalyst concentration at the reaction temperature of 50 °C, (**b**) methanol-to-oil molar
ratio and reaction temperature at the catalyst concentration of 0.642 mol/L and (**c**) catalyst
concentration and reaction temperature at the methanol-to-oil molar ratio of 6:1.

279   The optimum reaction conditions ensuring the maximum FAME content were found to be the

280   following: the molar ratio methanol-to-oil 7.1:1, the catalyst concentration 0.74 mol/L and the

281   reaction temperature 52 °C. This maximum FAME content of 99.8% was close to the

282   experimental FAME content of 98.9% obtained under the optimum reaction conditions. For

283   this reaction, the FAME yield was calculated on the basis of the mass balance of sunflower oil

284   (90.28 g), crude biodiesel (added as a cosolvent, 9.23 g), and the CaO catalyst (5.95 g) at the

285   start of the reaction, as well as the FAME amount (89.37 g) and the dried CaO paste (19.40

286   g); hence, the produced FAME amount was 80.14 g, corresponding to the yield of be 88.8 g

287   per 100 g of sunflower oil. Obviously, a part of the produced FAMEs was caught by the

288   catalyst as indicated by the increased amount of the CaO paste compared to the CaO added

289   initially as a catalyst. Marinković et al. [18] proved the presence of FAME molecules on the

290   surface of the used $CaO/\gamma\text{-}Al_2O_3$ catalyst by the ATR FTIR analysis.

291   *3.4. The reusability of the recycled CaO*

292   The change of FAME content during the sunflower oil methanolysis catalyzed by the fresh

293   and recycled CaO catalysts in the presence of crude biodiesel as a cosolvent at the methanol-

294   to-oil molar ratio 6:1, the cosolvent-crude biodiesel 10 wt% (of the oil weight) and the

295   reaction temperature 50 °C is shown in **Fig. 3**, whereas the CaO concentration used as a

296   catalyst, the loss of catalyst weight (reducing the initial catalyst concentration from 0.642

297   mol/L to 0.471 mol/L) and the maximum FAME content in the six consecutive batches are

298   given in **Table 3**. The reaction was accelerated, the induction period was shortened and the

299   maximum FAME content increased from the first to the third batch, when the reaction was the

300   fastest and with no induction. Similarly, a commercial CaO activated by a small amount of

301   crude biodiesel was reused for three consecutive cycles, showing a significant drop of

302   catalytical activity in the fourth cycle [12]. When crude biodiesel was not added as a

303   cosolvent, the used CaO was most active in the second run [19] or its activity decreased in

304 four consecutive runs [20]. The activity of the river snail shells-derived CaO catalyst used

305 without cosolvent was also reduced in four consecutive reuses [21].
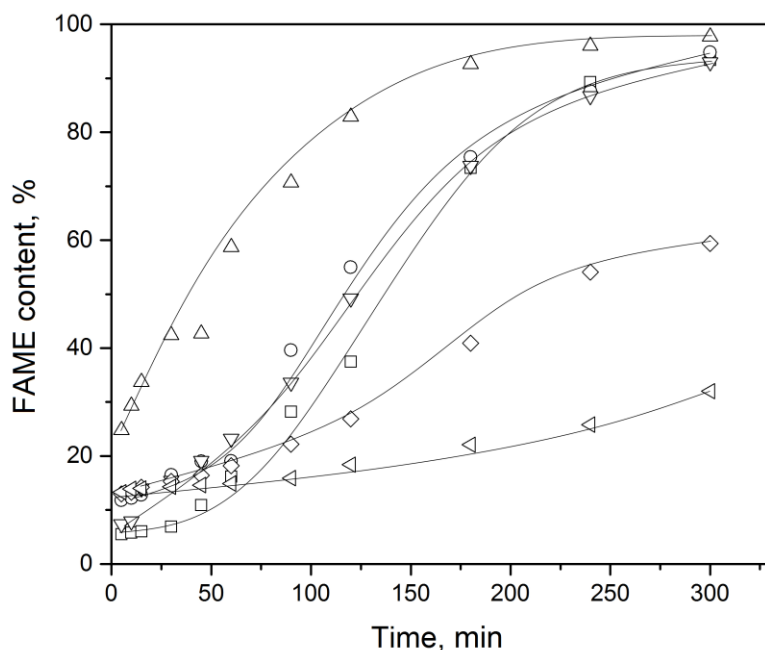

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307 **Fig. 3.** The change of FAME content with time in the sunflower oil methanolysis with crude
308 biodiesel as a cosolvent and a fresh CaO catalyst (□) or the recycled CaO catalyst in the
309 second batch (○), the third batch (△), the fourth batch (▽), the fifth batch (◇), and the sixth
310 batch (◁). Reaction conditions: methanol-to-oil molar ratio 6:1, 10 wt% crude biodiesel (to
311 oil weight), reaction temperature 50 °C.

312 **Table 3** FAME content in the esters phase of the final reaction mixture and the loss of CaO
313 during the use in repeated batches.[a]

Batch	Amount of CaO		Concentration of	FAME[b]
	Mass per a batch (g)	Compared to the initial amount (%)	CaO, mol/L	(%)
1	4.97	100.0	0.642	93.4
2	4.18	84.1	0.540	94.8
3	4.07	81.9	0.526	97.7
4	3.87	77.9	0.500	93.0
5	3.71	74.7	0.480	59.4
6	3.65	73.4	0.471	32.0

314 [a] Reaction conditions: methanol-to-oil molar ratio 6:1, reaction temperature 50 °C and cosolvent-
315 crude biodiesel loading 10 wt% to oil weight. [b] FAME content after 5 h.

18

The higher activity of the recycled CaO in the first two repeated batches was probably

because of the presence of leftover Ca-diglyceroxide formed in the previous batch, which

provided a soluble "calcium-X" precursor [22] and displayed a superior catalytic activity

compared to CaO [23], even compensating for about the 16-18% loss in the mass of the

catalyst (**Table 3**). **Fig. 4** shows the XRD patterns of the fresh and recycled CaO catalysts,

which proves the presence of Ca-diglyceroxide by its characteristic peaks 8.2, 10.2, 21.2,

24.4, 26.6, 34.4 and 36.2° θ [17]. However, in the next three batches, the reaction slowed

down, the induction appeared again and the maximum FAME content decreased because the

catalyst concentration added to the next batches became smaller and smaller because of an

incomplete CaO separation from the reaction mixture and, to a lesser degree, CaO leaching. If

a sufficient concentration of CaO catalyst is applied, the CaO leaching does not interfere with

the reuse for a number of runs [20, 24]. However, at lower CaO concentrations, the catalyst

solubilization and the associated loss of mass is more significant [12]. Also, catalyst

deactivation during the reaction and separation might contribute to these negative trends in the

last three batches. The reaction products might cover the surface of CaO catalyst, thus

reducing the number of active sites and the catalyst activity [21]. Glycerol-induced poisoning

is particularly causing the loss of catalytic activity of Ca-diglyceroxide and "calcium-X"

precursor [22].
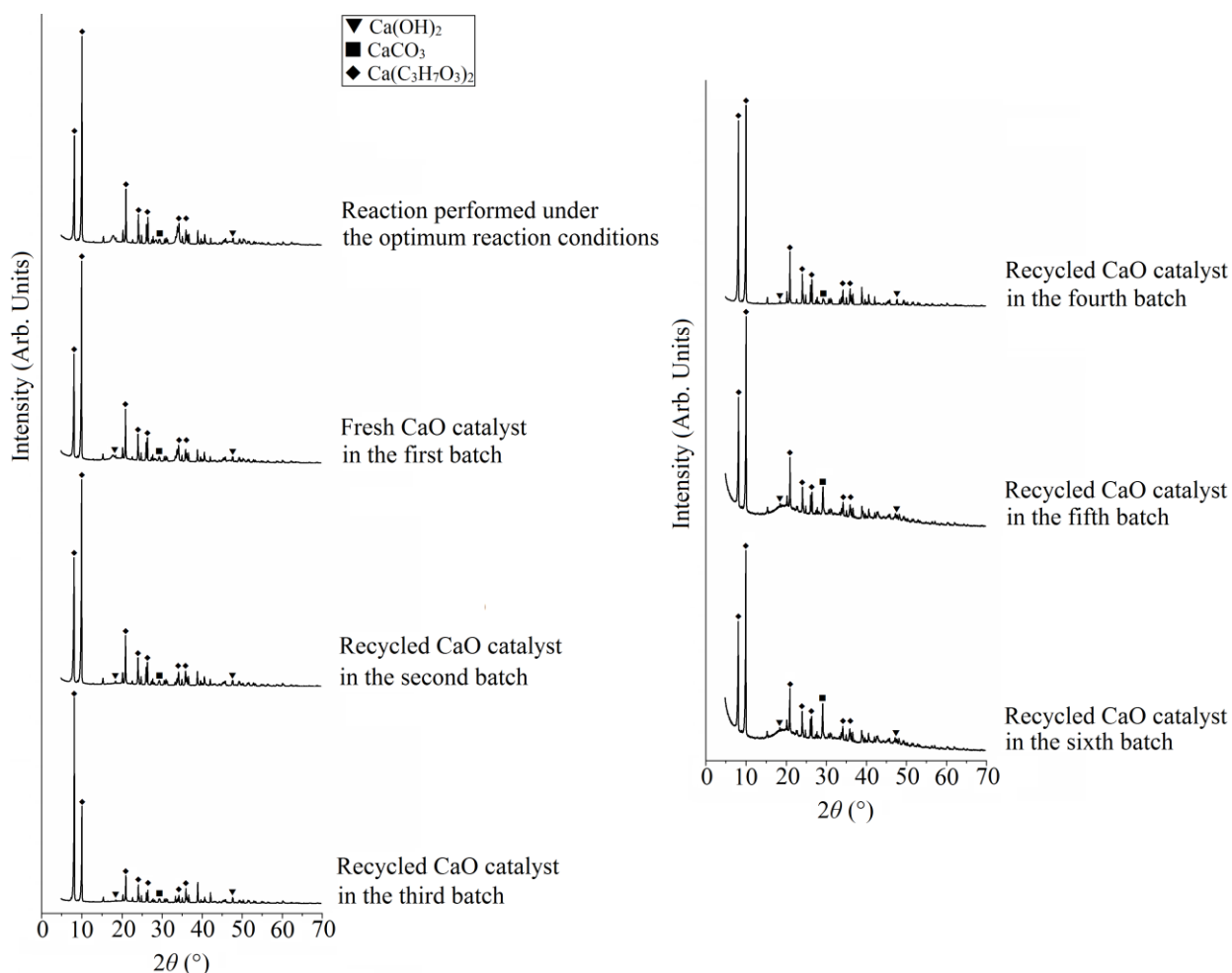
Fig. 4. The XRD patterns of the fresh and recycled CaO catalysts. The XRD pattern of CaO catalyst used under the optimum reaction conditions was provided for comparison.

3.5 Calcium leaching

Fig. 4, where the change of the calcium content in the FAME and alcohol phases is shown, demonstrates that the main part of the leached calcium is in the former part. The calcium content in the FAME and alcohol phases increased in the beginning of the reaction, reached a maximum of about 360 and 1940 ppm, respectively after about 45-60 min and then decreased; after 180 min, it started to increase again in the alcohol phase. Since the calcium content in the used sunflower oil was low (19 ppm), its increase in both phases was attributed to the CaO leaching. A higher CaO solubility in glycerol-methanol mixtures than in biodiesel-glycerol-methanol mixtures resulted in a higher calcium content in the alcohol phase than in the FAME phase [24, 25]. Higher amounts of leached species in the presence of glycerol were because of

20

347 the reaction between CaO and glycerol that provided Ca-diglyceroxide, which is more soluble

348 than CaO [24].

349 The observed variations in calcium content in the two phases was ascribed to the change in

350 polarity of the reaction mixture leading to a greater or lesser solubility of the calcium

351 compounds formed during the reaction. In the initial stage of the reaction (up to about 45-60

352 min), when the liquid part of the reaction mixture consisted mainly of the oil, methanol,

353 FAMEs (cosolvent plus product), and smaller amounts of the other reaction products

354 (glycerol, diglycerides and monoglycerides), the calcium leaching into the reaction medium

355 increased with time. As the transesterification reaction progressed (up to 180 min), CaO

356 reacted with the produced glycerol, forming Ca-diglyceroxide. Since the reaction mixture now

357 contained a smaller amount of the unreacted oil and a higher amount of diglycerides,

358 monoglycerides and FAMEs, calcium leaching into the reaction medium started to decrease.

359 After 180 min, the reaction mixture contained a large amount of glycerol, favoring the

360 dissolution of Ca-diglyceroxide. This resulted in increasing the calcium content in the alcohol

361 phase. The calcium content in the FAME phase started to decline rapidly after 60 min, and

362 after 120 min, it was only 1.65 ppm far below the biodiesel quality standard limit (5 ppm). In

363 the second batch (not shown in **Fig. 5**), where the recycled CaO was used as a catalyst, the

364 leaching intensity in the FAME phase was significantly reduced. For instance, the calcium

365 content in the FAME phase was 6 ppm after 5 min and 4 ppm after 5 h, while it was much

366 higher in the alcohol phase (about 980 and 550 ppm after 5 min. and 5 h, respectively).

367
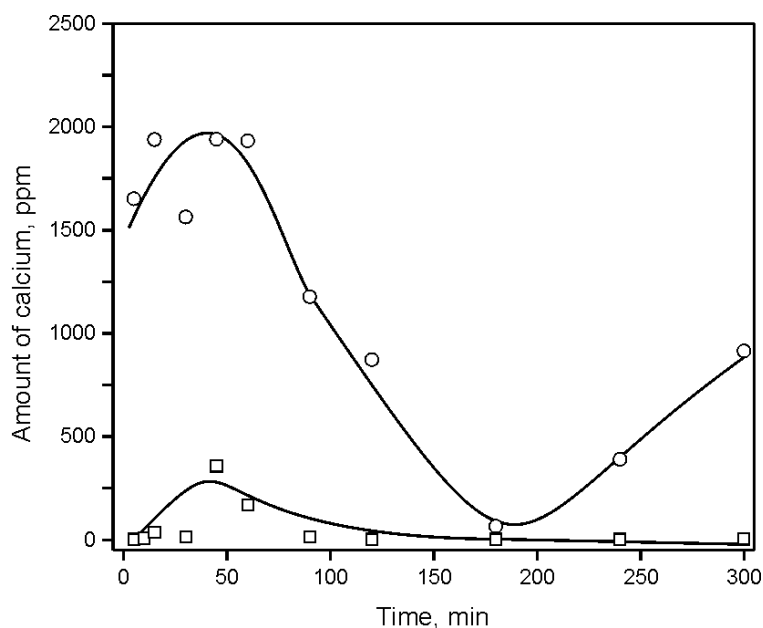
Fig. 5. The change of the calcium contents with time the FAME (□) and alcohol (○) phases
for the reaction carried out at the methanol-to-oil molar ratio 6:1, the concentration of CaO
0.642 mol/L, the 10 wt% crude biodiesel (to oil weight) and the reaction temperature 50 °C.

3.6 Separation of phases

The separation of phases in the separation funnel occurred much faster when crude biodiesel

was used as a cosolvent (90 min) than in the reaction system containing CaO without crude

biodiesel (24 h). This was ascribed to a higher amount of total FAMEs (produced FAME +

FAME as cosolvent) at the end of the reaction, which reduced the viscosity of the reaction

mixture and increased the density difference between the immiscible phases [26, 27]. In

addition, a reduced soap formation in the presence of the FAME cosolvent because of the

reduced viscosity of the reaction mixture [27] helps with faster phase separation.

3.7 Physicochemical properties of biodiesel

The physicochemical properties of the biodiesel obtained under the optimum reaction

conditions (methanol-to-oil molar ratio 7.1:1, the catalyst concentration 0.74 mol/L and the

reaction temperature 52 °C) are summarized in **Table 4**. The biodiesel standard EN 14214

specifications are also provided for comparison. The major biodiesel properties including

ester and water contents, acid value, density, and kinematic viscosity were within the limits

22

specified by the EN 14214. The Ca+Mg and DAG contents were higher than the specified

limits, thus requiring the inclusion of an adequate purification stage in the overall biodiesel

production process. The iodine value was also above the standard limit, but this biodiesel

would be oxidatively stable [28].

Table 4 Physicochemical properties of biodiesel obtained under the optimum reaction
conditions (methanol-to-oil molar ratio 7.1:1, catalyst concentration 0.74 mol/L, reaction
temperature 52 °C, and crude biodiesel amount 10 wt% of the oil weight).

Property	Value	EN 14214
Density (15 °C) (kg/m^3)	877	860–900
Viscosity (40 °C) (mm^2/s)	3.8	3.5–5.0
Acid value (mg KOH/g)	0.30	0.50 max
Iodine value (g I$_2$/100 g)	125	120 max
Water (mg/kg)	455	500 max
Ca + Mg (ppm)	36.8	5 max
FAME (%)	99.0	96.5 min
MAG (%)	0.1	0.8 max
DAG (%)	0.9	0.2 max
TAG (%)	0.0	0.2 max

4. Conclusion

The presence of crude biodiesel (10 wt% based on oil weight) as a cosolvent in CaO-

catalyzed sunflower oil methanolysis drastically reduced the initial induction period,

providing faster increase of the FAME content from the start of the reaction. The optimum

reaction conditions for achieving the highest FAME content were: the molar ratio methanol-

to-oil 7.1:1, the catalyst concentration 0.74 mol/L and the reaction temperature 52 °C, which

399 provided a FAME content of 99.8%, which was close to the experimental value of 98.9%. The

400 addition of crude biodiesel as a cosolvent caused a positive influence on the catalyst

401 reusability. The reaction accelerated in the first three uses of the CaO catalyst and the highest

402 FAME content of 97.7% after 5 h was achieved in the third batch.

403 **Acknowledgements**

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483 32.

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485 **Supplementary material**

486 **Optimization of CaO-catalyzed sunflower oil methanolysis with crude biodiesel as a**
487 **cosolvent**

488

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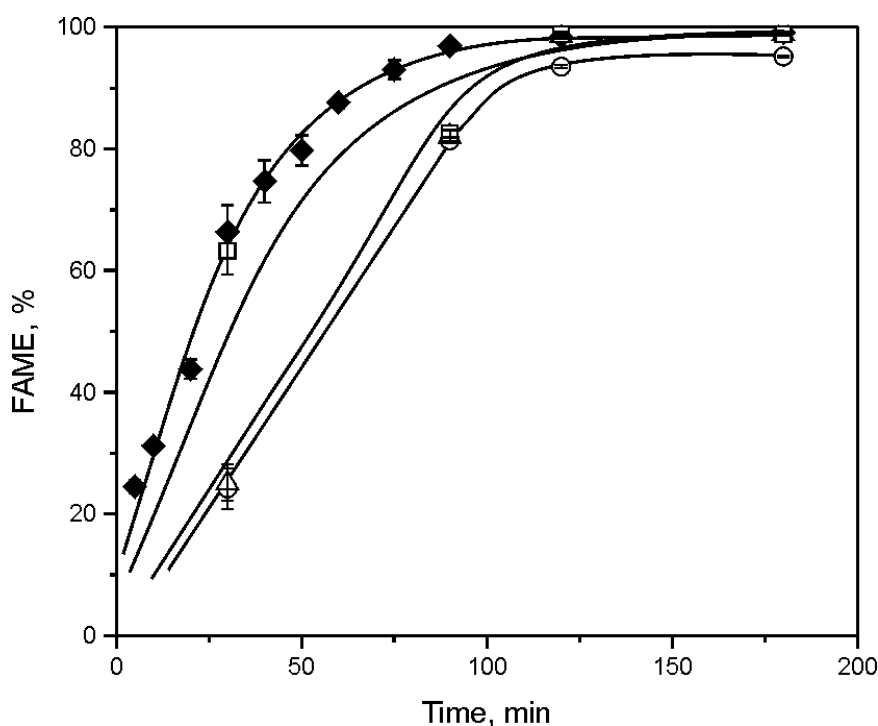
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498 **Fig. S1.** Variation of FAME content during the sunflower oil methanolysis with CaO as a
499 catalyst and crude biodiesel as a cosolvent (methanol-to-oil molar ratio: 6:1, concentration of
500 CaO: 0.642 mol/L, reaction temperature: 50 °C, and crude biodiesel amount, wt% of the oil
501 weight: 2.5– ○; 5– Δ; 7.5 – □; and 10 – ♦).

502

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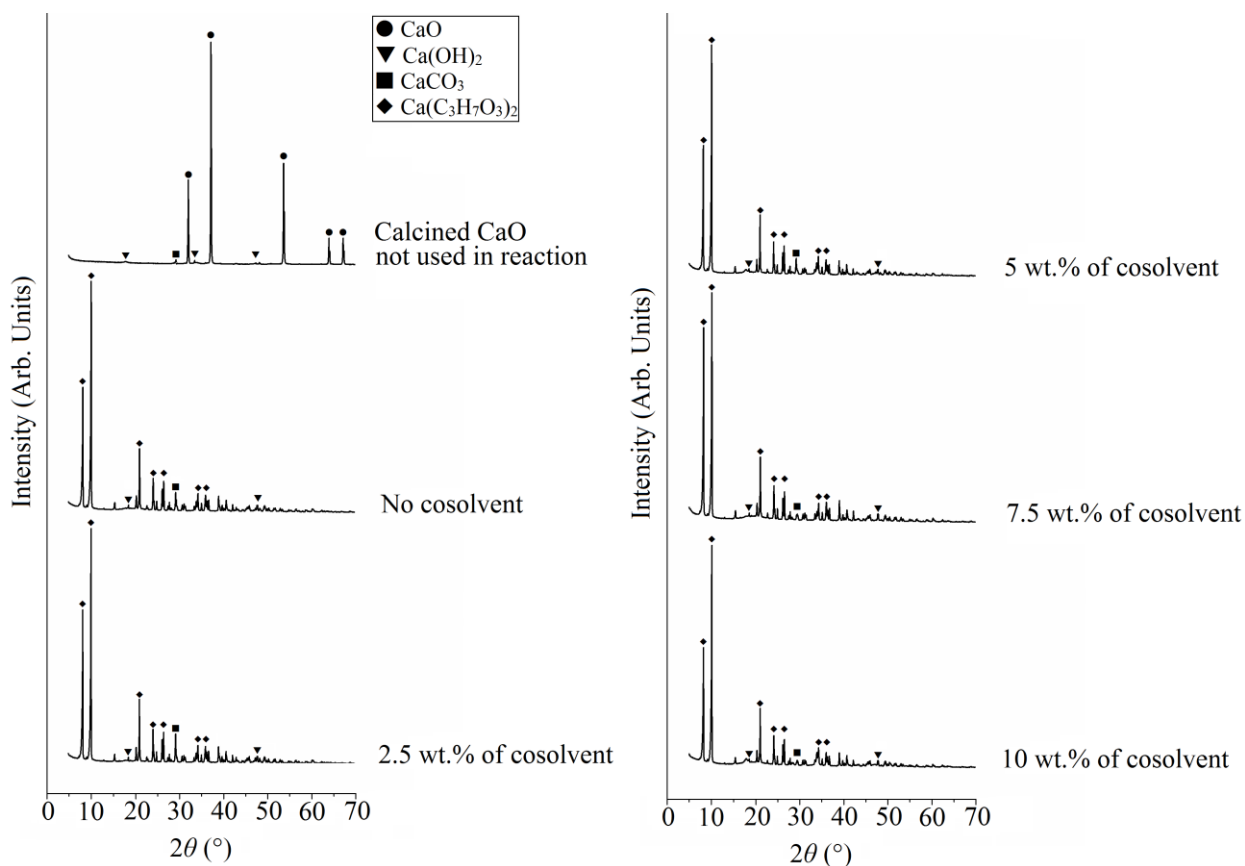
Fig. S2. XRD patterns of the calcined CaO used in as a catalyst in combination with different amounts of crude biodiesel as a cosolvent. XRD pattern of the calcined CaO not used in the reaction was also provided for comparison.