

# Adsorptive pretreatment of waste cooking oil using quicklime for fatty acid methyl esters synthesis

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## Abstract

Synthesis of biodiesel from various plant oils is realized by the transesterification of triglycerides with methanol or by a reaction usually defined as methanolysis. The usage of low-quality oils, such as waste cooking oil (WCO), is followed by undesirable side reactions as a result of the increased content of free fatty acids (FFA), and water. The presence of FFA in WCO usually requires a pretreatment stage before subjecting it to methanolysis. In the present work, heterogeneously catalyzed methanolysis of WCO with and without pretreatment was investigated. Removal of FFA from WCO was conducted by using only quicklime or with the addition of a small amount of methanol (FFA to methanol = 1:3 molar ratio). The obtained results showed that pretreatment of WCO with quicklime at 30 °C after 1 h reduces the FFA content by 72 %, while the adsorption capacity was determined to be 910 mg g<sup>-1</sup>. The adsorptive pretreatment, as a simple operation, using low-cost quicklime under mild conditions, had a positive effect on the transesterification rate with CaO-ZnO as a catalyst, enabling the achievement of over 96 % of biodiesel yield in only 15 min, compared to 1 h without the pretreatment. Furthermore, pretreated WCO allows an increase in repeated catalyst use and overall savings in the necessary amount of catalyst. The present study showed that quicklime is an economic, environmental-friendly, and sustainable material for FFA removal from WCO.

**Keywords:** biodiesel; adsorption; CaO-ZnO; methanolysis.

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## 1. INTRODUCTION

Biodiesel, a mixture of fatty acid methyl esters (FAME), has gained significant attention over the past couple of decades due to its environmental benefits, such as nontoxicity and biodegradability, and the fact that it is made from renewable resources. The current commercial use of refined vegetable oils for biodiesel production receives harsh criticism, primarily due to the use of oils, which are human nutrition sources. Besides, the high cost of biodiesel is the major limiting factor against large-scale biodiesel production and its commercialization, while the raw material cost typically contributes about 70–80 % of the total cost of biodiesel production [1,2].

Therefore, researchers have focused on other alternative sources of triglycerides (TG), such as non-edible oils or waste cooking oils (WCO), as feedstock for biodiesel production. Although the use of non-edible crops resolves the fuel vs. food debate, it is being discouraged because economic yields of non-edible crops can be only achieved by using arable land and appropriate agricultural practices. The mentioned shortcomings highlight waste resources as the most promising feedstock for biodiesel production. Besides, using WCO as a feedstock also resolves the issue of waste oil disposal, which is otherwise often inappropriate and could cause severe environmental challenges. However, the synthesis of biodiesel from these low-quality oils is challenging due to undesirable side reactions because of the presence of free fatty acids (FFA), water, and solid particles. Solid particles and other impurities could be removed by filtration, centrifugation, or washed away with hot water [2]. To remove water from the oil, it can be heated to above 100 °C [3] or dried with silica gel, magnesium sulphate, or calcium chloride [2,4]. The presence of high FFA contents in

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the oil can cause undesirable soap formation when homogeneous base catalysts are used for transesterification, which reduces the FAME yield, causes catalyst loss, and complicates phase separation. Acid catalysts are insensitive to FFA, but the process is much slower compared to the alkali-catalyzed transesterification.

To solve this problem, a two-step transesterification method was proposed. In the first step, pretreatment of WCO is performed to reduce the FFA content, while in the second, WCO is subjected to the transesterification process. Different methods for WCO pretreatment were proposed, including esterification, neutralization, adsorption, and distillation. Esterification of FFA with methanol produces FAME and usually is performed in the presence of an acid catalyst such as  $H_2SO_4$  [5] or a solid acid catalyst [6,7]. The lack of this process is the catalyst removal in both stages – esterification and later transesterification. FFA can be removed by neutralization using alkali (KOH or NaOH) as soaps, which can be separated by decantation [8]. Distillation as a method for FFA removal requires more severe conditions, such as higher temperature and pressure, and consumes a large amount of energy [8].

Among all techniques, the adsorption process appears to be the best choice, as a simple, efficient, environmentally friendly, and low-energy method for the removal of FFA from waste vegetable oil [2]. Furthermore, the adsorption process reduces WCO losses and soap formation, enabling also, simple separation of solid phase and treated WCO by filtration [9]. Different materials have been used as adsorbents for the FFA removal, such as clays (montmorillonite, kaolinite and bentonite) [10-13], ion-exchange resins [14-16], zeolite [17],  $Ca(OH)_2$  nanoplates supported on activated carbon [18],  $K_2O$ /dolomite [19], charcoal from *Pongamia Pinnata* shells [20],  $Fe_3O_4$  [21], Mg- and Na-silicate from rice hull ash and rice husk [22-26],  $nanoTiO_2$ /chitosan nanocomposite fibers [27] or nickel ferrite [28].

Many of these studies relate to the FFA removal from virgin oils or isoctane to which pure acids have been added as model compounds [11-17]. WCO is a more complex mixture, since it is formed during the usage of virgin vegetable oils for high-temperature cooking, which leads also to the formation of other unwanted compounds that can affect the FFA removal by their interaction with the adsorbent. Some of the applied adsorbents were obtained by complicated and/or expensive procedures [18,27,28], while others showed relatively low capacity, from 18 to  $650\text{ mg g}^{-1}$  [10-12,14-17,20,23]. Pereira *et al.* reported high values of adsorption capacity ( $2750\text{--}7000\text{ mg g}^{-1}$ ) for  $Ca(OH)_2$  nanoplates supported on activated carbon as adsorbents [18]. However, synthesis of this adsorbent was energy and time-consuming, including pyrolysis of palm endocarp at  $700\text{ }^\circ\text{C}$  and subsequent activation in a  $CO_2$  atmosphere at  $825\text{ }^\circ\text{C}$  to obtain activated carbon, followed by impregnation with  $Ca(OH)_2$  nanoparticles prepared from calcium chloride dihydrate and ethylene glycol [18]. On the other hand, quicklime used in the present study is a cheap, natural and easily available material. It can be used as an adsorbent, as received, without any preparation, including thermal activation, and thus it is economic, environmental-friendly, and sustainable material for FFA removal.

In this study, two different routes of FAME synthesis from WCO were proposed, investigated, and compared. The first route was simple one-step WCO methanolysis at  $60\text{ }^\circ\text{C}$  using  $CaO\cdot ZnO$  as a solid catalyst [29,30]. The effect of catalyst amount, stirring speed, and methanol to oil molar ratio on the rate of methanolysis was analyzed. The second route was based on a two-step scheme where the first step involved the pretreatment of WCO in order to remove FFA by adsorption onto quicklime or by esterification in the presence of a small amount of methanol catalyzed by quicklime. The first step was analyzed with the goal to define the optimal adsorption temperature, adsorbent particle size, and calcination procedure, as well as the necessary amount of quicklime to be used. The efficiency of quicklime in the FFA removal from the WCO was also determined. It should be noted, that application of quicklime as an adsorbent for FFA removal from WCO was not yet described in literature. In this study, the best WCO pretreatment conditions were determined, and then, the pretreated WCO was used in the second step of FAME synthesis using  $CaO\cdot ZnO$  as a heterogeneous catalyst. The possibility to reuse the catalyst in methanolysis of WCO with and without pretreatment was also investigated. To the best of our knowledge, a two-step process of FAME synthesis using adsorption with quicklime as an adsorbent in the first step and followed by heterogeneously catalyzed methanolysis in the second has not been published in the literature so far.

## 2. EXPERIMENTAL

### 2. 1. Materials

Quicklime, obtained from the local market in the southern part of Serbia, was a donation by colleagues from Leskovac [31]. CaO·ZnO catalyst was obtained by mechanochemical treatment of CaO (obtained by calcination of quicklime) and ZnO (Kemika, Zagreb, Croatia) in the molar ratio of 1:2 with stoichiometrically required addition of water in the planetary ball mill Fritsch Pulverisette 5 (Fritsch, Germany), as previously described [29,30]. The mechanochemically prepared precursor was calcined at 700 °C for 3 h in air atmosphere in the furnace Instrumentaria LP-07 (Zagreb, Croatia). The WCO was collected from restaurants in Belgrade, Serbia and methanol (99.5 % purity) was purchased from Fluka, Switzerland. The physical and chemical properties of WCO [29] are listed in Table 1.

Table 1. Physical and chemical properties of WCO [29]

Property	Content, wt. %
Water	0.07
FFA	1.27
Monoglycerides	2.00
Diglycerides	0.10
Myristic, C 14:0	0.98
Palmitic, C 16:0	26.84
Stearic, C 18:0	4.58
Oleic, C 18:1	16.54
Linoleic, C 18:2	43.22
Acid value, mg KOH g <sup>-1</sup>	2.54
Density, kg m <sup>-3</sup>	922.2
Viscosity, mPa s	90.33

### 2. 2. Methanolysis reaction

Methanolysis of the WCO was performed at 60 °C in a 250 cm<sup>3</sup> three-necked thermostated glass flask with a condenser and magnetic stirrer and the effects of mixing intensity (300 and 1000 rpm), the mass percentage of catalyst (2 and 1 wt.%) or the molar ratio of reactants (6:1 and 10:1) on the rate of methanolysis were analyzed. The samples were taken out from the reactor at different reaction times at intervals of 15 min for 6 h. The beginning of methanolysis ( $t = 0$ ) was defined as the time point when the reaction temperature was reached. The samples were analyzed after filtration by gas chromatography (Varian 3400, Varian, Ireland) with a FID detector, on-column injector and a MET-Biodiesel capillary GC column (14 m × 0.53 mm, film thickness 0.16 μm) [29,30,32]. The schematic diagram of the one and two-step transesterification routes is presented in Figure 1.

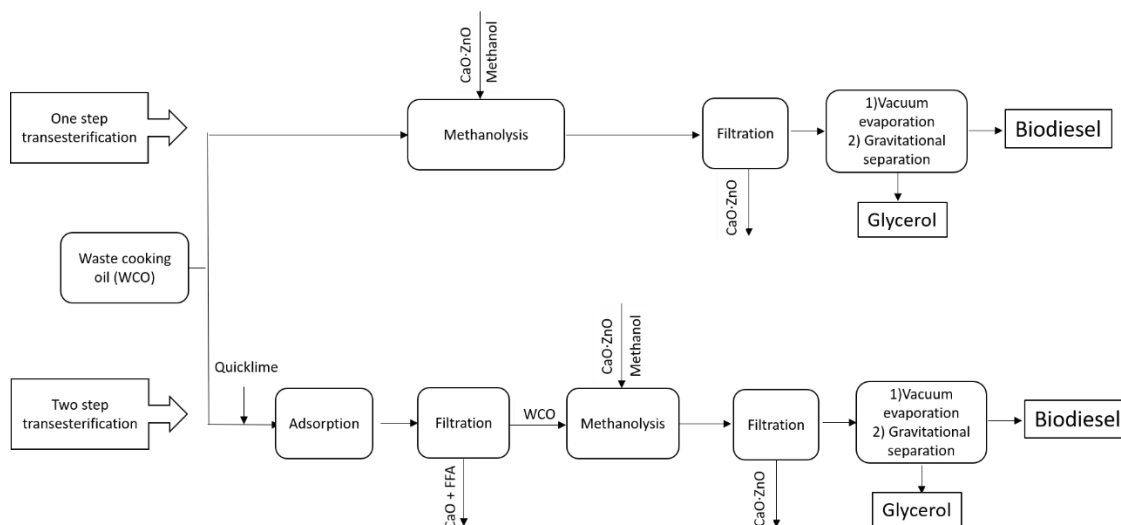


Figure 1. Process diagram of one and two-step transesterification processes applied in the study



### 2. 3. Pretreatment of WCO

The pretreatment of WCO was performed in a thermostated three-necked glass flask with a magnetic stirrer. When quicklime as an adsorbent was used to remove FFA, the WCO and a defined amount of quicklime were placed in the flask and mixed for 1 h at the preset temperature. The influence of quicklime calcination, amount, particle size, and pretreatment temperature on the efficiency of FFA removal was tested. In order to remove FFA by esterification, quicklime and a small amount of methanol (FFA to methanol = 1 : 3 molar ratio) and WCO were placed in the flask and mixed for 1 h at the desired temperature. Analysis of adsorption kinetics was performed under the condition determined as optimal (uncalcined quicklime, 30 °C,  $d < 0.2$  mm, 1 wt.%). The samples were taken out from the flask at different times, and after filtration, analyzed by volumetric titration to determine FFA content.

### 2. 4. Acid number determination

Volumetric titration was applied to determine the acid value of oil [16]. The sample of WCO was dissolved in a mixture of toluene ( $\geq 99.7$  % purity, VWR Chemicals, Austria) and isopropanol ( $\geq 99.8$  % purity, Sigma-Aldrich, Germany). and phenolphthalein was added as an indicator. The prepared solution of WCO sample was titrated with potassium hydroxide solution and acid value was expressed as mg KOH  $g^{-1}$  of sample, required to titrate the sample to a specified endpoint. The acid value was calculated by using the following equation:

$$AN = (A - B)C \frac{56.1}{W} \quad (1)$$

where:  $AN$  is the acid number,  $A$  is the volume of KOH used to reach the endpoint ( $cm^3$ );  $B$  is the volume of KOH used for titration of the mixture without WCO or the so-called blank test ( $cm^3$ );  $C$  is the concentration of KOH ( $mol\ dm^3$ ), and  $W$  is the mass of WCO sample (g). All the experiments and titrations were repeated three times and mean values were used. The experimental errors were less than  $\pm 2$  %.

The FFA removal efficiency ( $X_{FFA}$ ) was defined as the fraction of the FFA removed and determined from the acid value ratio:

$$X_{FFA} = \left[ \frac{AN_0 - AN_t}{AN_0} \right] 100 \quad (2)$$

where  $AN_0$  is the acid value of the WCO at the beginning and  $AN_t$  is the acid value of the oil at the end of treatment (after 1 h).

### 2. 5. Adsorption kinetics

Among a number of kinetic models that have been proposed for the adsorption process, pseudo-first and second-order models are the most widely used because they are simple to describe the adsorption kinetics and the adsorbent-adsorbate interactions [14,29-31]. In the present study, these two models were used to describe the FFA adsorption on quicklime as the adsorbent. The correlated kinetic parameters were also obtained by the least square fitting method of the adsorption model with experimental adsorption data.

#### 2. 5. 1. Pseudo-first order model

The pseudo-first order model [14,33,34] is proposed based on the assumption that the adsorption rate is proportional to the number of vacant adsorption sites. The adsorption rate can be expressed as:

$$\frac{dq}{dt} = k_1 (q_e - q_t) \quad (3)$$

where,  $q_e$  and  $q_t$  are the adsorption capacities at equilibrium and a given time, respectively,  $k_1$  is the pseudo-first order kinetic constant.

The linear form of the Lagergren pseudo- first order equation can be written as [14]:

$$\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \quad (4)$$

The  $q_e$  and  $k_1$  were determined from the intercept and slope of the best linear fit of the plot  $\log(q_e - q_t)$  vs. time. The pseudo-first order model represents the reversible interaction between the adsorbent and adsorbate, which is suitable to predict the adsorption behavior of physical adsorbents [34].

### 2. 5. 2. Pseudo-second order model

The pseudo-second order model is based on the assumption that the adsorption rate is proportional to the square of the number of vacant adsorption sites [34]. This model can be written as follows:

$$\frac{dq}{dt} = k_2 (q_e - q_t)^2 \quad (5)$$

where  $k_2$  is the pseudo-second order rate constant. The linear form of second order equation is:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (6)$$

The parameters  $q_e$  and  $k_2$  were determined from the intercept and slope of the least square linear fit of the plot  $t/q_e$  vs. time. The pseudo-second order model assumes that the interaction between the adsorbent and adsorbate is caused by the strong binding of adsorbate to the adsorbent surface, which is suitable to predict adsorption behavior which involves chemical interactions [35].

The significance of both kinetic models was statistically evaluated using the mean relative percent deviation (MRPD) between the experimentally determined and predicted values of  $q_e$ :

$$\text{MRPD} = \frac{100}{n} \sum_{i=1}^n \left| \frac{q_{e,\text{mod}} - q_{e,\text{exp}}}{q_{e,\text{exp}}} \right| \quad (7)$$

where  $q_{e,\text{mod}}$  and  $q_{e,\text{exp}}$  are predicted and experimental values, of  $q_e$ , respectively, and  $n$  is the number of experimental points.

### 2. 5. 3. Adsorption capacity

Experimental adsorption capacity of quicklime,  $q$ , was calculated by using equation [20]:

$$q = \frac{(C_0 - C_t)V}{m_{\text{ads}}} \quad (8)$$

where  $m_{\text{ads}}$  is the mass of the adsorbent,  $V$  is the volume of the solution, and  $C_0$  and  $C_t$  are the initial and the adsorbate concentration in the solution at time  $t$ , respectively.

## 2. 6. FTIR analysis

Fourier-transform infrared (FTIR) spectra were recorded by using a BOMEM (Hartmann & Braun, Australia) spectrometer. Measurements were conducted in the wave number range of 4000–400  $\text{cm}^{-1}$ , with 4  $\text{cm}^{-1}$  resolution.

## 2. 7. XRD analysis

The phase composition was determined by the X-ray diffraction analysis (Cu  $K\alpha$  radiation,  $\lambda = 0.15418$  nm, in the range of  $2\theta = 10\text{--}80^\circ$ , step-length:  $2\theta = 0.01^\circ$  scan time: 5 s) by using D/MAX–RB powder X-ray diffractometer (Rigaku Corporation, Japan).

## 2. 8. ICP analysis

The content of calcium leached in the oil during the pretreatment with CaO, and in biodiesel during the methanolysis with the CaO-ZnO catalyst was determined by inductively coupled plasma optical emission spectrometry, ICP-OES (iCAP 6500 Duo ICP, Thermo Fisher Scientific, Cambridge, United Kingdom). For this analysis, the samples were prepared by microwave digestion in an Advanced Microwave Digestion System (Ethos 1, Milestone, Italy) using a HPR-1000/10S high-pressure segmented rotor. The external calibration solutions were made from the certified plasma standard solution:



Multi-Element Plasma Standard Solution 4, Specpure®, 1000  $\mu\text{g cm}^{-3}$  (Alfa Aesar GmbH & Co KG, Germany). Quantification of calcium was done at the emission wavelength: Ca II 315.887 nm. Calcium concentration in the samples was expressed as  $\text{mg kg}^{-3}$  (ppm).

### 3. RESULTS AND DISCUSSION

#### 3.1 One-step transesterification of WCO using the CaO-ZnO catalyst: influence of different reaction conditions

Since the mechanochemically synthesized CaO-ZnO catalyst has shown good activity in the methanolysis of sunflower and used vegetable oils [29], the influence of different reaction conditions on the rate of methanolysis was further studied.

The agitation speed has a significant influence on the rate of the process since its increase causes a reduction in the dispersed phase (methanol) drop size and an increase in the specific interfacial area between the two immiscible phases (WCO and methanol). This effect enables faster TG mass transfer and the period of usually slow period of transesterification is significantly shorter [29,32]. When agitation speed in methanolysis of WCO was 300 rpm, the initial period lasted 45 min, while for 1000 rpm it was practically eliminated, indicating that the mass transfer resistance at the beginning of methanolysis of WCO is less pronounced (Fig 2a). It can be concluded that more intensive mixing, *i.e.* higher agitation speeds, increased the methanolysis rate as a result of reduced mass transfer resistance and better suspension of the catalyst in the reaction mixture.

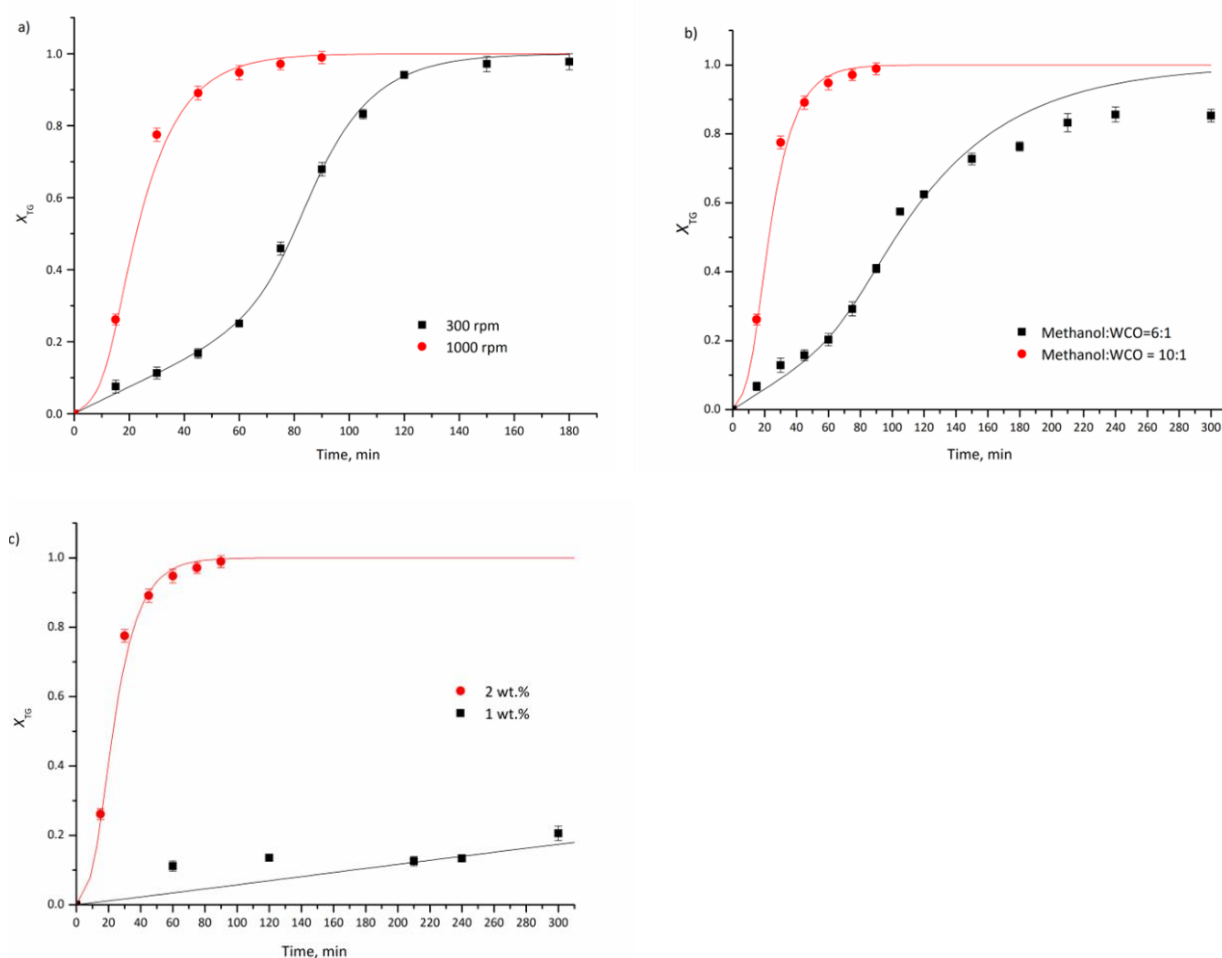


Figure 2. Triglyceride conversion versus time for WCO methanolysis at 60 °C as a function of a) agitation speed (methanol to oil molar ratio = 10:1, 2 wt.% of catalyst); b) methanol to oil molar ratio (agitation speed 1000 rpm, 2 wt.% catalyst); c) catalyst amount (methanol to oil molar ratio =10:1; agitation speed 1000 rpm)

Fig. 2b) shows the influence of the molar ratio of methanol to oil on the methanolysis rate. At the lower ratio, the fraction of dispersed phase (methanol) in the reaction mixture is decreased, and also the specific interfacial area between methanol and oil, which is directly proportional to the fraction of dispersed phase. Because of that, the molar ratio of methanol to oil mostly affects the TG mass transfer, but the initial period is not so pronounced as in the case of methanolysis of sunflower oil at a lower agitation speed [32]. The rate of the chemical reaction on the catalyst surface was lower at a lower molar ratio, and also the maximum obtained yield of FAME which did not exceed 85 %. The lower molar ratio affects the slow and final period of transesterification, which is characterized by approaching the equilibrium composition between FAME and glycerol. A smaller concentration of TG and an increased concentration of glycerol close to the surface of a solid catalyst, with the very low methanol concentration, improve the rate of the reversible reaction between FAME and glycerol, which could be the main reason for the achieved lower FAME yield.

TG conversion vs. time is shown in Fig. 2c) for different initial amounts of catalyst. When the reaction mixture contained 1 wt.% of catalyst, even after 5 h of reaction, TG conversion reached only 23 %. WCO contains a certain amount of FFA (Table 1) and other compounds formed during the use of fresh vegetable oil at high temperature for food preparation (thermal processing of food). Thus, the reason for very slow transesterification could be mainly FFA adsorption on the catalyst active sites, blocking them, and causing the part of the catalyst not to be available for TG transesterification.

### 3. 2. Pretreatment of WCO

#### 3. 2. 1. Adsorption using quicklime

Results of WCO methanolysis with a smaller amount of catalyst indicated the negative effect of FFA on the methanolysis process, suggesting that some pretreatment should be applied. The idea of using quicklime for the pretreatment was to reduce the amount of FFA present in WCO by simple adsorption. Detailed characterization of used material has been reported previously and only a short overview of these results is reported in the present paper. The XRD analysis indicated the peaks originated from the well-crystallized CaO phase, which is the main phase of raw quicklime, with only barely noticeable peaks of Ca(OH)<sub>2</sub> [31]. Raw quicklime has a low specific surface area of 4.6 m<sup>2</sup> g<sup>-1</sup>, with the total pore volume of 85 mm<sup>3</sup> g<sup>-1</sup>, and the basic strength in the range of 9.3–10.0 [31]. According to the results of the analysis of textural properties, quicklime used without calcination has a very low porosity and can be even classified as a nonporous material [31].

The efficiency of FFA removal was investigated with respect to the influence of quicklime calcination, amount, particle size, and pretreatment temperature (Table 2). The use of quicklime without calcination resulted in a slightly better decrease in the FFA content. It was higher at higher temperatures, however, at 60 °C formation of soaps was visually observed, not present at lower temperatures.

Table 2. Removal efficiency of FFA at different conditions (*t* = 1h in all experiments)

<i>T</i> / °C	Calcination temperature, °C	Particle size, mm	Quicklime content, wt.%	<i>X</i> <sub>FFA</sub> / %
60	550	<0.2	1	88
60	/	<0.2	1	94
40	/	<0.2	1	58
30	/	<0.2	1	72
30	/		1	41
30	/	0.2<d<0.6	2	55
30	/		1	8
30	/	0.6<d<0.8	4	33

The reason for this finding could be desorption of the formed compound between CaO and FFA, which is an endothermic process and, thus, at lower temperatures adsorption of FFA at the surface of the particles is more pronounced. An increase in temperature causes desorption of the molecules from the surface [2], in this case soaps formed in the reaction of CaO with FFA, which became visible in the mixture. When smaller particle sizes were used (diameter < 0.2 mm), a higher FFA removal was achieved, caused by a higher surface area available for the adsorption. The amount



of  $\text{Ca}^{2+}$  present in the oil after the pretreatment at optimal conditions (uncalcined quicklime, 30 °C,  $d < 0.2$  mm, 1 wt.%) was determined to be  $12.64 \text{ mg kg}^{-1}$ , showing that very small amount of calcium from CaO was dissolved in the treated WCO.

### 3. 2. 2. Adsorption kinetics

The removal of FFA on quicklime adsorbent as a function of contact time, under condition determined as optimal (uncalcined quicklime, 30 °C,  $d < 0.2$  mm, 1 wt.%) was studied with the aim to determine the required time to reach the equilibrium conditions and results are presented in Fig. 3a.

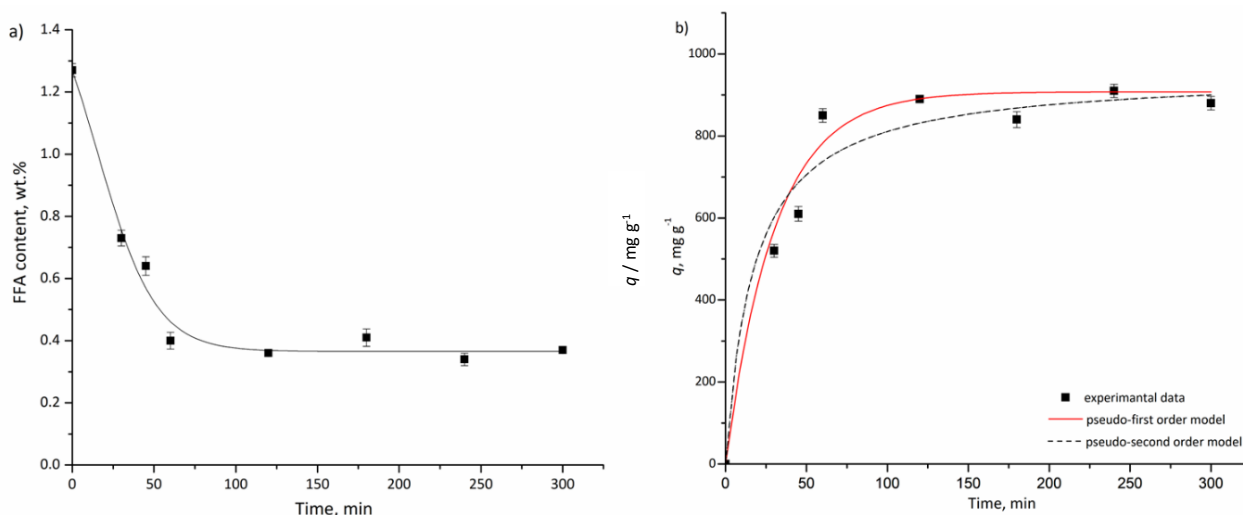


Figure 3. FFA adsorption at quicklime over time at optimal adsorption conditions (30 °C,  $d < 0.2$  mm, 1 wt.%): a) FFA content reduction; b) adsorption capacity of quicklime determined experimentally and calculated by using kinetic models with kinetic parameters determined by least-squares fits

It can be seen that the concentration of FFA present in the oil (1.27 wt.% at the beginning) decreased over time and reached a constant value (0.44 wt.%), indicating the attainment of equilibrium at which further adsorption was not possible. The time necessary to reach equilibrium was about 60 min under the operating conditions used in this work. Similarly, it has been reported that 60 min was required to reach the equilibrium for adsorption of oleic acid added to sunflower oil (3 wt.%) on zeolite 13X at 30 °C, but with 10 wt.% of the adsorbent [17], while much longer contact time, 240–300 min was necessary for oleic acid adsorption from vegetable oils onto different anion exchange resins [15,16] as well as for FFA adsorption from crude palm oil on magnesium silicate derived from rice husk [23]. Additionally, Ilgen reported that adsorption of oleic acid from sunflower oil on Amberlyst A26 (OH) resin reached equilibrium after 360 min regardless of the temperature and adsorbent amount [14].

Analysis of the adsorption kinetics was performed by using the pseudo-first (Eq. 4) and pseudo-second order (Eq. 6) kinetic models. The pseudo-first model parameters  $q_e$  and  $k_1$  were determined from the intercept and slope of plot  $\log(q_e - q_t)$  versus time (Fig. D-1a, Supplementary material), while pseudo-second model parameters  $q_e$  and  $k_2$  were determined from the intercept and slope of  $t/q_e$  versus time (Fig. D-1b, Supplementary material) and the obtained values are presented in Table 5. Comparison of the experimental data and calculated using kinetic models is presented in Fig. 3b. According to the obtained values of correlation coefficient  $R^2$ , the pseudo-second order model better describes the adsorption of FFA from WCO onto quicklime as adsorbent. In addition, in order to provide more relevant information on the models' adequacy, MRPD between the values of  $q_e$  determined experimentally and predicted by models was calculated. The MRPD of  $\pm 6.2$  and  $8.0$  % for the pseudo-first and the pseudo-second model, respectively, suggested that slightly better agreement was accomplished with pseudo-first order model. Due to the contradictory results of  $R^2$  and MRPD, as well as the fact that 5 out of 7 measured data are already at equilibrium, no definite conclusion about the best kinetic model can be drawn. In the literature, both models were successfully used to describe adsorption kinetics. It was reported that adsorption of oleic acid from sunflower oil on Amberlist 26 (OH) resin [14], iron



oxide magnetic nanoparticles [21] and zeolite 13X at higher temperatures of 50 and 75 °C [17] followed the pseudo-second order kinetic model, while for adsorption onto the zeolite 13X at 30 °C and ion-exchange resin [15] followed the pseudo-first order kinetic model. It was also observed that both models describe the data well with correlation coefficients greater than 0.99 in adsorption process using two mixed bed ion-exchange [16].

Table 3. Kinetic model parameters

$q_e$ (exp) / mg g <sup>-1</sup>	Pseudo-first order			Pseudo-second order		
	$k_1$ / min <sup>-1</sup>	$q_e$ (calc) / mg g <sup>-1</sup>	$R^2$	$k_2$ / g mg <sup>-1</sup> min <sup>-1</sup>	$q_e$ (calc.) / mg g <sup>-1</sup>	$R^2$
910	0.033	907.8	0.898	$6.01 \cdot 10^{-5}$	952.4	0.992

The experimentally determined equilibrium adsorption capacity of quicklime was 910 mg g<sup>-1</sup>. This value is higher than most of the removal capacities reported in literature for different adsorbent materials, which were in the range from 18 to 647 mg g<sup>-1</sup> [10–12,14–17,20,23]. Only Pereira *et al.* obtained much higher values of adsorption capacity (2750–7000 mg g<sup>-1</sup>) for Ca(OH)<sub>2</sub> nanoplates supported on activated carbon as adsorbents [18]. However, it is necessary to highlight the advantage of quicklime used in this study - it is a cheap, available, natural material and can be used without any heat treatment.

### 3.2.3 FTIR analysis

FTIR spectra of quicklime before and after different times of the adsorption process are shown in Fig. 4.

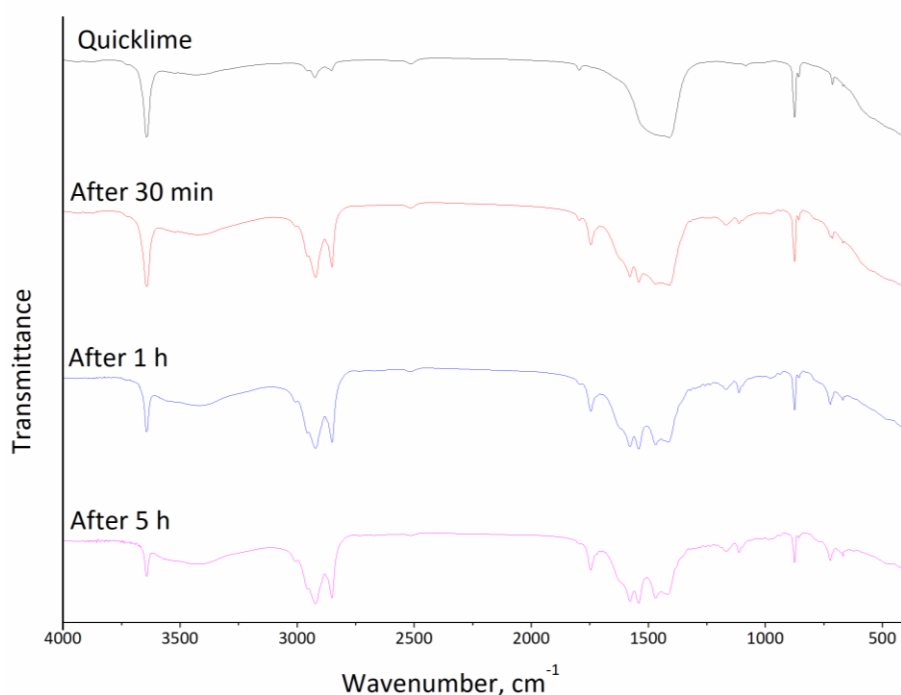


Figure 4. FTIR spectra of quicklime before and at different times of the adsorption process

The spectrum of quicklime indicates only the presence of calcium carbonate (the broad band centered at 1465 cm<sup>-1</sup> and bands at 874 and 712 cm<sup>-1</sup>) as well as OH groups of Ca(OH)<sub>2</sub> (the sharp band at 3643 cm<sup>-1</sup>). Also, the regions at 3000–3500 cm<sup>-1</sup> correspond to the possible contribution of water physisorbed on the surface of CaO, which is the result of very rapid carbonation and hydration of CaO in air [30]. After FFA adsorption, bands at 2932, 2882, and 2846 cm<sup>-1</sup> appeared, associated with symmetrical and asymmetrical C–H stretching vibrations of –CH<sub>2</sub> and CH<sub>3</sub> groups of FFA. The carboxylate bands typically exist in pairs corresponding to the asymmetric and symmetric carboxylate vibrations at 1575–1530 and 1460–1400 cm<sup>-1</sup>, respectively [36]. A doublet band of carboxylate groups associated with calcium ions at around 1540 and 1575 cm<sup>-1</sup> appears at higher concentrations of adsorbed FFA [18,37]. According to Lu and Miller, it

is assigned to physically adsorbed FFA [37], while Cano *et al.* reported that the presence of vibration bands of coordinated carboxylate groups ( $1524$  and  $1408\text{ cm}^{-1}$ ) indicates covalent binding of FFA [21]. The peak at  $1453\text{ cm}^{-1}$  corresponds to CH bending, and the peak at  $1436\text{ cm}^{-1}$  to symmetric COO<sup>-</sup> stretching [37], while absorption in the  $1746\text{ cm}^{-1}$  region is characteristic of ester stretching of carbonyl group C=O and indicates possible oil contamination on quicklime [18]. The presence of carboxylate ion is clearly visible at all spectra of quicklime after the adsorption of FFA confirming the interaction of the carboxyl group in FFA with the active site of the adsorbent.

#### 3.2.4. Esterification using quicklime

In the present work, the idea of adding a small amount of methanol (FFA to methanol molar ratio = 1:3) was explored with the intention to remove FFA in the reaction with methanol and not only by adsorption, where quicklime would act as a catalyst for esterification. At  $30\text{ }^{\circ}\text{C}$  almost the same efficiency in the FFA removal was achieved as without methanol (68 % compared to 72 %, Table 2), while at  $60\text{ }^{\circ}\text{C}$  it was much lower (57 % compared to 94 % removal, Table 2). It might be concluded that the use of methanol during pretreatment of WCO did not have a significant effect on the FFA removal and that methanol decreased the CaO capacity for FFA adsorption. The same conclusion was derived when methanol was added to an oleic acid/soybean oil system with the mixture of two mixed bed ion-exchange resins (Dowex Monosphere MR-450 UPW and Amberlite MB-150) [16].

According to the above results, the following conditions for pretreatment of WCO were proposed: 1 wt.% of quicklime based on the amount of oil; temperature of  $30\text{ }^{\circ}\text{C}$ , the particle size  $d < 0.2\text{ mm}$  and 1 h time in the batch process with mixing intensity of 1000 rpm.

### 3.3. Methanolysis of pretreated WCO

After the pretreatment, quicklime was removed by filtration, and the oil with the decreased FFA content to 0.44 % was subjected to methanolysis with using CaO-ZnO as a catalyst at  $60\text{ }^{\circ}\text{C}$ . The results are compared to those obtained in the direct methanolysis of WCO under the same conditions (Fig. 5). As can be seen, the WCO pretreatment had a positive effect on the methanolysis process rate. The achieved FAME yield was over 96 % after 15 min, while the same FAME yield was detected only after 1 h of transesterification without the pretreatment.

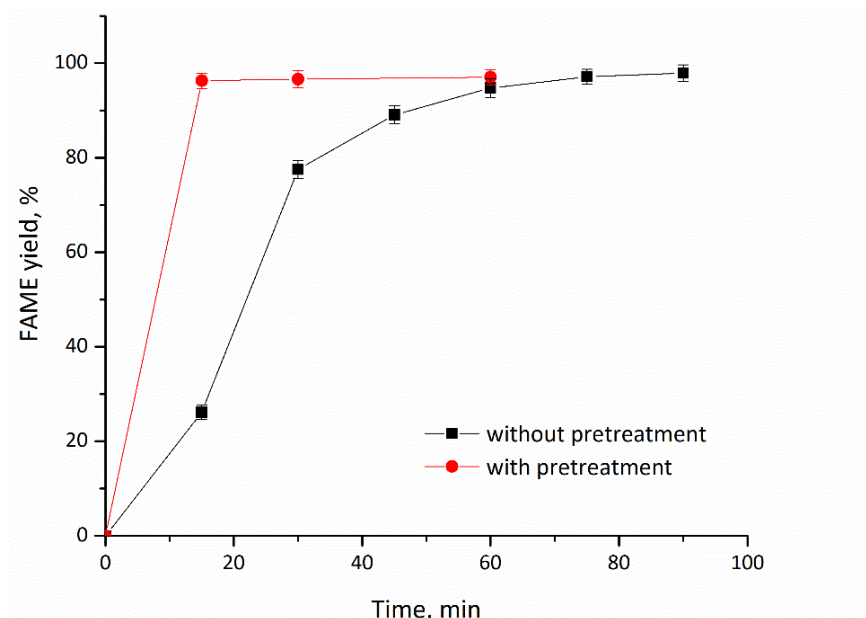


Figure 5. FAME yield in WCO methanolysis with the use of CaO-ZnO catalyst (reaction conditions:  $60\text{ }^{\circ}\text{C}$ , 1000 rpm, methanol to oil molar ratio of 10:1, 2 wt.% of catalyst)

Two-step processes were frequently reported in literature, however, studies in which the FFA content is decreased by adsorption in the first stage of the two-step process are few. Ilgen reported that after the oleic acid content was

decreased to 0.2 % via adsorption by using Amberlyst 26 (OH), transesterification with KOH enabled the biodiesel yield of 94 % [14]. Similarly, after the pretreatment of soybean oil mixed with oleic acid using  $\text{Ca}(\text{OH})_2$ /activated carbon, transesterification with the use of NaOH as a homogeneous catalyst, resulted in FAME yields of 96-98 % [18]. Results from the present study are in line with the majority found in the literature reported for CaO or CaO-based catalysts [38]. Most of pure CaO catalysts or modified by doping with different compounds, supporting onto carriers, or mixing with other metal oxides are efficient in transesterification of virgin oils or feedstock with low free fatty acid contents, however, weaker catalytic activity in the presence of moisture and high FFA feedstock was observed [38]. Moreover, methanolysis of WCO using CaO derived from waste oyster shells gave a maximum biodiesel yield of 87.3 % after 3 h of reaction time under the optimized conditions (9:1 methanol to oil molar ratio, 6 wt.% of catalyst) [39]. Similarly, biodiesel yield of 93.4 % was obtained in a pilot-scale microreactor using WCO with the acid value of only 0.04 mg KOH  $\text{g}^{-1}$  oil and limescale as a catalyst [40]. The maximum FAME yield was 93.7 % in methanolysis of WCO with the FFA content of 1.1 wt.% catalyzed with zeolite supported CaO derived from chicken eggshell [41], while with Zn doped CaO nanocatalyst the yield of 96.7 % was attained under the reaction conditions of 20:1 methanol to oil molar ratio, 5 wt.% catalyst loading after 4 h with WCO containing 0.84 wt.% of FFA [42]. Magnetic  $\text{CaO}/\text{ZnFe}_2\text{O}_4$  hollow microspheres showed high catalytic performance with 98 % biodiesel yield obtained under optimized conditions, including the molar ratio of methanol to oil of 12:1 and catalyst concentration of 6 wt.% at 65 °C for 3 h, but the acid value of WCO was only 0.73 mg KOH  $\text{g}^{-1}$  oil [43]. An algal biochar/CaO/ $\text{K}_2\text{CO}_3$  catalyst enabled the yield of 98.8 % in transesterification of WCO, however, a two-step process was applied, and transesterification was performed after reducing the FFA content to < 1 % by esterification with HCl [44]. The two-step process proposed in the present study allowed obtaining a high FAME yield from WCO with the FFA content > 1 % in a shorter time compared to most of the results reported in literature, as well as compared to the one-step process with mixed oxides CaO-ZnO used as a catalyst.

Possibility to reuse the catalyst in methanolysis was also examined. After each run, the liquid product was separated from the solid catalyst that remained at the bottom of the flask. A new batch of oil and methanol were added to the flask and the subsequent cycle was carried out under the same reaction conditions. The solid catalyst was reused without any purification in several repeated FAME synthesis. In the case of WCO use without pretreatment, in the second repeated test, a substantial decrease in the catalyst activity and FAME yield of only 11.8 % were observed, Figure 6. Still, the reusability test with pretreated oil showed that the FAME yield in the second run, although higher than without pretreatment, was still unsatisfactory amounting to only 46.6 % (Figure 6).

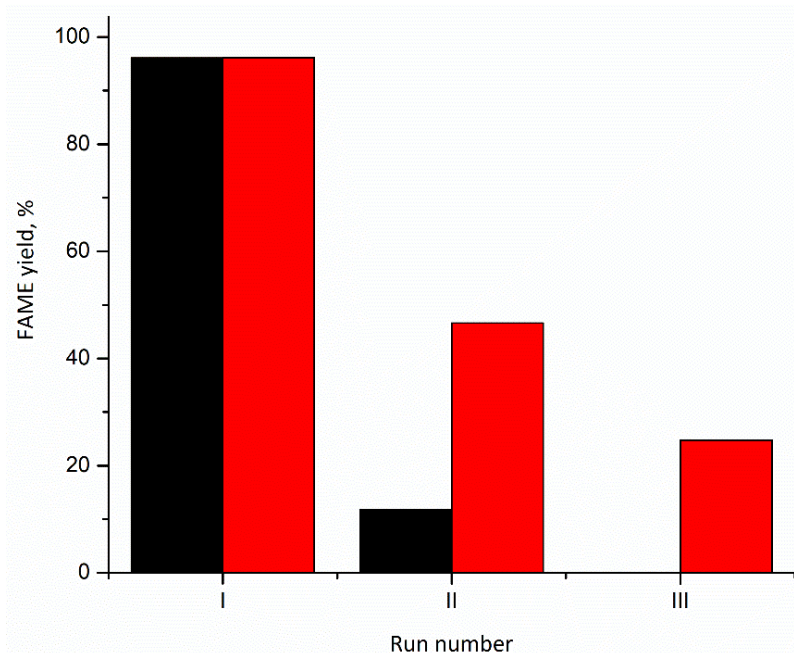


Figure 6. Reuse of the catalyst: FAME yields in 3 consecutive runs; ■—WCO without the pretreatment; ■—WCO after pretreatment with quicklime

Leaching of active species from the solid catalyst could be one of the reasons for the drop in activity. Solubility of the CaO-ZnO catalyst in methanol was negligible [29,30], however, López Granados *et al.* showed that the solubility of pure CaO is one order of magnitude higher in a biodiesel-glycerol-methanol mixture than in methanol [45]. Thus, the concentration of  $\text{Ca}^{2+}$  ions present in the FAME phase after methanolysis of the pretreated WCO and catalyst removal was analyzed, amounting to  $229 \text{ mg kg}^{-1}$ . This value is lower than some other reported for CaO-based catalysts. Namely, leaching from CaO from eggshell supported on a fly ash-based zeolitic material into sunflower oil yielded the concentration of  $1170.4 \text{ mg kg}^{-1}$  [46], while from the CaO-based catalyst derived from palm kernel shell biochar it was  $722 \text{ mg kg}^{-1}$  [47]. Besides, solubility of the neat CaO in the modeled biodiesel-methanol-glycerol mixture was reported to be  $600 \text{ mg dm}^{-3}$  (or  $680 \text{ mg kg}^{-1}$ ) [45]. On the contrary, lower leaching was also reported, for example, for a  $\text{CaO/ZnFe}_2\text{O}_4$  hollow magnetic microspheres catalyst yielding the concentration of  $21.3 \text{ mg kg}^{-1}$  [43] or CaO prepared with pectin as a modifier amounting to  $0.7 \text{ mg kg}^{-1}$  [48]. Nevertheless, the leached amount of calcium ions can be considered as low and not sufficient to reduce the catalytic activity of the CaO-ZnO catalyst [46].

Since the reason for a decrease in activity could be a change in the catalyst structure, or adsorption of products formed during the transesterification process, the catalyst after methanolysis of the pretreated WCO was characterized by using FTIR and XRD analyses (Figure 7).

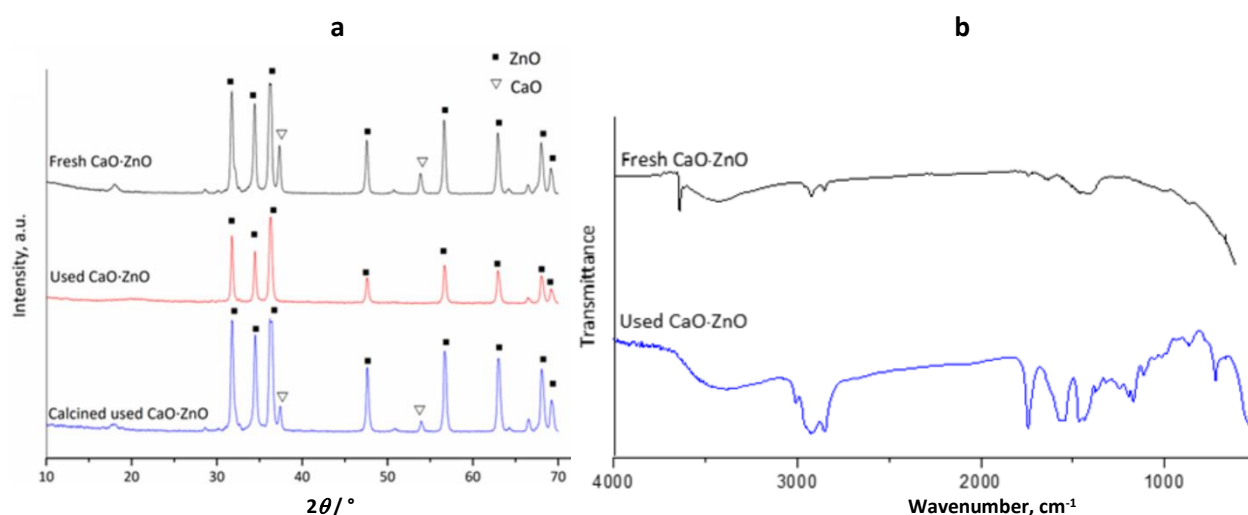


Figure 7. Analyses of the fresh CaO-ZnO catalyst and after methanolysis of the pretreated WCO: a) XRD patterns; b) FTIR spectra

Figure 7a shows diffractograms of the catalyst after the methanolysis reaction and after the reaction and calcination at  $700^\circ\text{C}$ . The XRD pattern of the used catalyst revealed only peaks characteristic for ZnO, while peaks corresponding to CaO were not observed neither the peaks of other Ca compounds that could have been formed in the reaction of Ca with glycerol or the mixture of glycerol and methanol (*e.g.* Ca glyceroxide). This means that there could have been either a change in the structure of the catalyst or "poisoning" of the active sites, in this case CaO, by various compounds present in the reaction mixture. Therefore, after the used catalyst was calcined at  $700^\circ\text{C}$ , peaks corresponding to CaO appeared in the XRD pattern, but of slightly lower intensity compared to the starting catalyst. This indicates that the active sites are probably blocked, and the FTIR spectra can provide more information about organic compounds that could have blocked the active centers of the catalyst.

The FTIR spectra of the used catalyst confirmed the presence of organic compounds on the catalyst surface (Fig. 7b). The intense band at  $1744 \text{ cm}^{-1}$  originates from the stretching vibration of the ester carbonyl functional group ( $\text{C}=\text{O}$ ), and at  $1171 \text{ cm}^{-1}$  from the stretching vibration of the  $\text{C}-\text{O}$  bond [49]. Bands at around  $1457$  and  $1568 \text{ cm}^{-1}$  when appearing together in the spectrum are attributed to the symmetric and asymmetric vibrations of carboxylate groups and may indicate that chemisorption of FAME molecules has occurred [49]. More intense bands at  $2922$  and  $2852 \text{ cm}^{-1}$  in the FTIR spectrum of the catalyst after transesterification is assigned to the asymmetric and symmetric stretching vibrations of methylene groups of the alkyl chain of FAME [49].

#### 4. CONCLUSION

High FAME yields could be achieved in methanolysis of WCO using CaO-ZnO catalyst under different reaction conditions. However, presence of FFA has a negative impact on the methanolysis rate so that the pretreatment of WCO using quicklime was proposed in the present work for the acid removal. The results showed that FFA from WCO could be successfully removed using quicklime as adsorbent at a lower temperature of 30 °C with the removal efficiency of 72 % and the equilibrium adsorption capacity of 910 mg g<sup>-1</sup>. When the pretreated oil was used as feedstock for methanolysis with a CaO·ZnO catalyst, a higher rate of transesterification was observed compared to methanolysis of untreated WCO, with over 96 % of FAME yield achieved after 15 min of the process. Based on the obtained results, it can be concluded that quicklime has considerable potential for the FFA removal from WCO, being cheap, available, and efficient. Besides, both adsorption and heterogeneously catalyzed methanolysis are environmentally and economically acceptable processes.

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#### REFERENCES

- [1] Enweremadu CC, Mbarawa MM, Technical aspects of production and analysis of biodiesel from used cooking oil—A review. *Renew Sust Energy Rev.* 2009; 13: 2205–2224. <https://doi.org/10.1016/j.rser.2009.06.007>
- [2] Maddikeri GL, Pandit AB, Gogate PR, Intensification Approaches for Biodiesel Synthesis from Waste Cooking Oil: A Review. *Ind Eng Chem Res.* 2012; 51: 14610–14628. <https://doi.org/10.1021/ie301675j>
- [3] Yaakob Z, Mohammad M, Alherbawi M, Alam Z, Sopian K, Overview of the production of biodiesel from waste cooking oil. *Renew Sust Energy Rev.* 2013; 18: 184–193. <https://doi.org/10.1016/j.rser.2012.10.016>
- [4] Refaat AA, Different techniques for the production of biodiesel from waste vegetable oil. *Int J Environ Sci Tech.* 2010; 7(1): 183–213. <https://doi.org/10.1007/BF03326130>
- [5] Çanakçı M, Van Gerpen J, A pilot plant to produce biodiesel from high free fatty acid feedstocks *Trans ASABE.* 2003; 46: 945–954. <https://doi.org/10.13031/2013.13949>
- [6] Corro G, Tellez N, Jimenez T, Tapia A, Banuelos F, Vazquez-Cuchillo O, Biodiesel from waste frying oil. Two step process using acidified SiO<sub>2</sub> for esterification step. *Catal Today* 2011; 166: 116–122. <https://doi.org/10.1016/j.cattod.2010.09.011>
- [7] Wang Y, Ou S, Liu P, Zhang Z, Preparation of biodiesel from waste cooking oil via two-step catalyzed process. *Energy Convers Manag.* 2007; 48: 184–188. <https://doi.org/10.1016/j.enconman.2006.04.016>
- [8] Cvangros J, Cvangrosova Z, Used Frying Oils and Fats and their Utilization in the Production of Methyl Esters of Higher Fatty Acids. *Biomass Bioenerg.* 2004; 27: 173–181. <https://doi.org/10.1016/j.biombioe.2003.11.006>
- [9] Díaz L, Brito A, FFA Adsorption from Waste Oils or Non-Edible Oils onto an Anion Exchange Resin as Alternative Method to Esterification Reaction Prior to Transesterification Reaction for Biodiesel Production. *J Adv Chem Eng.* 2014; 4: 105. <http://dx.doi.org/10.4172/2090-4568.1000105>
- [10] Demirbas A, Sari A, Isildak O, Adsorption thermodynamics of stearic acid onto bentonite. *J Hazard Mater.* 2006; 135: 226–231. <https://doi.org/10.1016/j.jhazmat.2005.11.056>
- [11] Sari A, İpýldak Ö, Adsorption properties of stearic acid onto untreated kaolinite. *Bull Chem Soc Ethiop.* 2006; 20(2): 259–267. <https://doi.org/10.1016/10.4314/bcse.v20i2.61410>
- [12] Bayrak Y, Application of Langmuir isotherm to saturated fatty acid adsorption. *Microporous and Mesoporous Mater.* 2006; 87: 203–206. <https://doi.org/10.1016/j.micromeso.2005.08.009>
- [13] Sari A, SoyLake M, Equilibrium and thermodynamic studies of stearic acid adsorption on Celtek clay. *J Serb Chem Soc.* 2007; 72(5): 485–494. <https://doi.org/10.2298/JSC0705485S>
- [14] İlgen O, Adsorption of oleic acid from sunflower oil on Amberlyst A26 (OH). *Fuel Process Technol.* 2014; 118: 69–74. <http://dx.doi.org/10.1016/j.fuproc.2013.08.012>
- [15] Maddikeri GL, Pandit AB, Gogate PR, Adsorptive Removal of Saturated and Unsaturated Fatty Acids Using Ion-Exchange Resins. *Ind Eng Chem Res.* 2012; 51: 6869–6876. <http://dx.doi.org/10.1021/ie3000562>
- [16] Jamal Y, Boulanger BO, Separation of oleic acid from soybean oil using mixed-bed resins. *J Chem Eng Data* 2010; 55: 2405–2409. <http://dx.doi.org/10.1021/ie900829c>
- [17] İlgen O, Dulger HS, Removal of oleic acid from sunflower oil on zeolite 13X: Kinetics, equilibrium and thermodynamic studies. *Ind Crops Prod.* 2016; 81: 66–71. <http://dx.doi.org/10.1016/j.indcrop.2015.11.050>
- [18] Pereira MRDN, Salviano AB, de Medeiros TPV, Santos MRD, Cibaka TE, de Andrade MHC, de Oliveira Porto A, Lago RM. Ca(OH)<sub>2</sub> nanoplates supported on activated carbon for the neutralization/removal of free fatty acids during biodiesel production. *Fuel* 2018; 221: 469–475. <http://dx.doi.org/10.1016/j.fuel.2018.01.123>





- [19] Nor Shafizah I, Irmawati R, Omar H, Yahaya M, Alia Aina A, Removal of free fatty acid (FFA) in crude palm oil (CPO) using potassium oxide/dolomite as an adsorbent: Optimization by Taguchi method. *Food Chem.* 2022; 373: 131668. <https://doi.org/10.1016/j.foodchem.2021.131668>
- [20] Díaz L, Mertes L, Brito A, Rodríguez KE, Valorization of energy crop shells as potential green adsorbents for free fatty acid removal from oils for biodiesel production. *Biomass Convers Bioref.* 2022; 12: 655–668. <https://doi.org/10.1007/s13399-020-01089-y>
- [21] Cano M., Sbagoud K., Allard E., Larpent C, Magnetic separation of fatty acids with iron oxide nanoparticles and application to extractive deacidification of vegetable oils. *Green Chem.* 2012; 14: 1786–1795. <https://doi.org/10.1039/c2gc35270b>
- [22] Kalapathy U, Proctor A, New Method for Free Fatty Acid Reduction in Frying Oil Using Silicate Films Produced from Rice Hull Ash. *JAOCs.* 2000; 77(6): 593–598. <https://doi.org/10.1007/s11746-000-0095-4>
- [23] Clowutimon W, Kitchaiya P, Assawasaengrat P, Adsorption of Free Fatty Acid from Crude Palm Oil on Magnesium Silicate Derived From Rice Husk. *Eng J.* 15 2011; 15(3):15–25. <https://doi.org/10.4186/ej.2011.15.3.15>
- [24] Kim M, Yoon SH, Choi E, Gil B, Comparison of the adsorbent performance between rice hull ash and rice hull silica gel according to their structural differences. *LWT-Food Sci Technol.* 2008; 41: 701–706. <https://doi.org/10.1016/j.lwt.2007.04.006>
- [25] Topallar H, Bayrak Y, Investigation of Adsorption Isotherms of Myristic, Palmitic and Stearic Acids on Rice Hull Ash. *Turk J Chem.* 1999; 23: 193–198.
- [26] Adam F, Chua JH, The adsorption of palmitic acid on rice husk ash chemically modified with Al(III) ion using the sol–gel technique. *J Colloid Interface Sci.* 2004; 280: 55–61. <https://doi.org/10.1016/j.jcis.2004.07.006>
- [27] Bao Y, Zhou Q, Zhang M, Zhang H, Luan Q, Zhou W, Tang H, Huang F, Wet-spun nanoTiO<sub>2</sub>/chitosan nanocomposite fibers as efficient and retrievable absorbent for the removal of free fatty acids from edible oil. *Carbohydr Polym* 2019; 210: 119–126. <https://doi.org/10.1016/j.carbpol.2019.01.035>
- [28] Adewuyi A, Ogagbalo AI, Lau WJ, Oderinde RA, Synthesis of spinel ferrite and its role in the removal of free fatty acids from deteriorated vegetable oil. *Chinese Journal of Chemical Engineering* 2021; 40: 78–87. <https://doi.org/10.1016/j.cjche.2020.08.054>
- [29] Lukić I, Kesić Ž, Maksimović S, Zdujić M, Liu H, Krstić J, Skala D, Kinetics of sunflower and used vegetable oil methanolysis catalyzed by CaO-ZnO. *Fuel* 2013; 113: 367–78. <https://doi.org/10.1016/j.fuel.2013.05.093>
- [30] Kesić Ž, Lukić I, Brkić D, Rogan J, Zdujić M, Liu H, Skala D, Mechanochemical preparation and characterization of CaO-ZnO used as catalyst for biodiesel synthesis. *Appl Catal A* 2012; 427–428: 58–65. <https://doi.org/10.1016/j.apcata.2012.03.032>
- [31] Miladinović MR, Krstić JB, Tasić MB, Stamenković OS, Veljković VB, A kinetic study of quicklime-catalyzed sunflower oil methanolysis. *Chem Eng Res Des.* 2014; 92(9) 1740–1752. <https://doi.org/10.1016/j.cherd.2013.11.023>
- [32] Lukić I, Kesić Ž, Maksimović S, Zdujić M, Krstić J, Skala D. Kinetics of heterogeneous methanolysis of sunflower oil with CaO-ZnO catalyst: Influence of different hydrodynamic conditions. *Chem. Ind. Chem. Eng. Q.* 2014; 20: 425–439. <https://doi.org/10.2298/CICEQ130514025L>
- [33] Qiu H, Lv L, Pan B, Zhang Q, Zhang W, Zhang Q, Critical review in adsorption kinetic models. *J Zhejiang Univ Sci A* 2009; 10(5)716–724. <https://doi.org/10.1631/jzus.A0820524>
- [34] Song G, Zhu X, Chen R, Liao Q, Ding Y, Chen L, An investigation of CO<sub>2</sub> adsorption kinetics on porous magnesium oxide. *Chem Eng J.* 2016; 283: 175–183.
- [35] Ho YS, McKay G, Pseudo-second order model for sorption processes. *Process Biochem.* 1999; 34(5): 451–465. [https://doi.org/10.1016/S0032-9592\(98\)00112-5](https://doi.org/10.1016/S0032-9592(98)00112-5)
- [36] Filopoulou A, Vlachou S, Boyatzis SC, Fatty Acids and Their Metal Salts: A Review of Their Infrared Spectra in Light of Their Presence in Cultural Heritage. *Molecules* 2021; 26(19): 6005. <https://doi.org/10.3390/molecules26196005>
- [37] Lu Y, Miller JD, Carboxyl Stretching Vibrations of Spontaneously Adsorbed and LB-Transferred Calcium Carboxylates as Determined by FTIR Internal Reflection Spectroscopy. *J Colloid Interface Sci.* 2002; 256: 41–52. <https://doi.org/doi:10.1006/jcis.2001.8112>
- [38] Zul NA, Ganesan S, Hamidon TS, Oh W-D, Hussin MH, A review on the utilization of calcium oxide as a base catalyst in biodiesel production. *J Environ Chem Eng* 2021; 9(4): <https://doi.org/10.1016/j.jece.2021.105741>
- [39] Lin Y-C, Amesho KTT, Chen C-E, Cheng P-C, Chou F-C, A cleaner process for green biodiesel synthesis from waste cooking oil using recycled waste oyster shells as a sustainable base heterogeneous catalyst under the microwave heating system. *Sustain Chem Pharm* 2020; 17: 100310 <https://doi.org/10.1016/j.scp.2020.100310>
- [40] Aghel B, Mohadesi M, Ansari A, Maleki M, Pilot-scale production of biodiesel from waste cooking oil using kettle limescale as a heterogeneous catalyst. *Renew Energy* 2019; 142: 207–214. <https://doi.org/10.1016/j.renene.2019.04.100>
- [41] Yusuff AS, Gbadamosi AI, Atray N, Development of a zeolite supported CaO derived from chicken eggshell as active base catalyst for used cooking oil biodiesel production. *Renew Energy* 2022; 197: 1151–1162. <https://doi.org/10.1016/j.renene.2022.08.032>
- [42] Borah MJ, Das A, Das V, Bhuyan N, Deka D, Transesterification of waste cooking oil for biodiesel production catalyzed by Zn substituted waste egg shell derived CaO nanocatalyst. *Fuel* 2019; 242: 345–354. <https://doi.org/10.1016/j.fuel.2019.01.060>

- [43] Torkezaban S, Feyzi M, Norouzi L, A novel robust CaO/ZnFe<sub>2</sub>O<sub>4</sub> hollow magnetic microspheres heterogenous catalyst for synthesis biodiesel from waste frying sunflower oil, *Renew Energy* 2022; 200: 996–1007. <https://doi.org/10.1016/j.renene.2022.09.077>.
- [44] Foroutan R, Mohammadi R, Razeghi J, Ramavandi B, Biodiesel production from edible oils using algal biochar/CaO/K<sub>2</sub>CO<sub>3</sub> as a heterogeneous and recyclable catalyst. *Renew Energy* 2021; 168: 1207–1216. <https://doi.org/10.1016/j.renene.2020.12.094>
- [45] López Granados M, Martín Alonso D, Sádaba I, Mariscal R, Ocón P, Leaching and homogeneous contribution in liquid phase reaction catalysed by solids: the case of triglycerides methanolysis using CaO. *Appl Catal B* 2009; 89: 265–272. <https://doi.org/10.1016/j.apcatb.2009.02.014>
- [46] Pavlović SM, Marinković DM, Kostić MD, Janković-Častvan IM, Mojović LjV, Stanković MV, Veljković VB, A CaO/zeolite-based catalyst obtained from waste chicken eggshell and coal fly ash for biodiesel production. *Fuel* 2020; 267: 117171. <https://doi.org/10.1016/j.fuel.2020.117171>.
- [47] Kostić MD, Bazargan A, Stamenković OS, Veljković VB, McKay G, Optimization and kinetics of sunflower oil methanolysis catalyzed by calcium oxide-based catalyst derived from palm kernel shell biochar. *Fuel* 2016; 163: 304–313. [10.1016/j.fuel.2015.09.042](https://doi.org/10.1016/j.fuel.2015.09.042).
- [48] Acosta PI, Campedelli RR, Correa EL, Bazani HAG, Nishida EN, Souza BS, Mora JR, Efficient production of biodiesel by using a highly active calcium oxide prepared in presence of pectin as heterogeneous catalyst. *Fuel* 2020; 271: 117651. <https://doi.org/10.1016/j.fuel.2020.117651>.
- [49] López Granados M, Martín Alonso D, Sádaba I, Mariscal R, Ocón P, Surface chemical promotion of Ca oxide catalysts in biodiesel production reaction by the addition of monoglycerides, diglycerides and glycerol. *J Catal* 2010; 276: 229–236. <https://doi.org/10.1016/j.jcat.2010.09.016>



# Adsorpcioni predtretman otpadnog jestivog ulja primenom kreča za sintezu metil estara masnih kiselina

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## (NAUČNI RAD)

### Izvod

Sinteza biodizela iz različitih biljnih ulja ostvaruje se transesterifikacijom triglicerida sa metanolom ili reakcijom koja se obično definiše kao metanoliza. Korišćenje ulja lošijeg kvaliteta, kao što je otpadno jestivo ulje (engl. *waste cooking oil*, WCO), prate neželjene sporedne reakcije kao posledica povećanog sadržaja slobodnih masnih kiselina (engl. *free fatty acids*, FFA) i vode. Prisustvo FFA u tim uljima obično zahteva fazu prethodne obrade pre nego što se ulje podvrgne procesu transesterifikacije. U ovom radu istražena je heterogeno kanalizovana metanoliza WCO sa i bez predtretmana. Uklanjanje FFA iz WCO obavljeno je korišćenjem samo kreča ili uz dodatak male količine metanola (molarni odnos FFA prema metanolu = 1:3). Dobijeni rezultati su pokazali da se u predtretmanu WCO krečom na 30 °C nakon 1 h može smanjiti sadržaj FFA za 72%, dok je određeno da je ravnotežni kapacitet adsorpcije 910 mg g<sup>-1</sup>. Predtretman adsorpcijom, kao jednostavnom operacijom, korišćenjem jeftinog kreča pod blagim uslovima, pozitivno je uticao na brzinu reakcije transesterifikacije s CaO·ZnO kao katalizatorom, omogućujući postizanje preko 96 % prinosa biodizela za samo 15 min, u poređenju sa potrebnim vremenskim periodom od 1 h za postizanje istog prinosa iz ulja bez predtretmana. Nadalje, prethodno tretirano WCO omogućuje povećan broj ciklusa ponovne upotrebe katalizatora i ukupnu uštedu potrebne količine katalizatora. Ova studija je pokazala da je kreč ekonomičan, ekološki prihvatljiv i održiv materijal za uklanjanje FFA iz WCO.

*Ključne reči:* biodizel; adsorpcija; CaO·ZnO; metanoliza