KINETICS OF THE SUNFLOWER OIL ETHANOLYSIS USING CaO AS CATALYST

Article Highlights
- Ethanolysis of sunflower oil over CaO was studied
- Kinetics included the changing reaction mechanism with respect to triacylglycerols
- The kinetic parameters were correlated with the process variables
- A good agreement of the kinetic model with the experimental data was observed

Abstract
The ethanolysis of sunflower oil catalyzed by calcium oxide was studied in a wide range of reaction conditions: temperature 65-75 °C, ethanol-to-oil mole ratio 6:1-18:1 and catalyst loading 10-20% in order to determine the reaction kinetics. The proposed kinetic model of sunflower oil ethanolysis included the changing and first-order reaction mechanism with respect to triacylglycerols and fatty acid ethyl esters. The kinetic parameters were determined and correlated with the process variables. The Arrhenius equation could be applied to the reaction rate constant with the activation energy of 94.0 kJ/mol. The proposed kinetic model showed a good agreement with the experimental data with a mean relative percentage deviation of ±13% (based on 256 data points).

Keywords: biodiesel, ethanolysis, calcium oxide, kinetic modeling, sunflower oil.

Excessive utilization and non-renewability of crude oil leading to depletion of known crude oil reserves, together with increased concern for the environment, have encouraged recent interest in alternative fuels. In these circumstances, biodiesel has emerged as a potential substitute for diesel fuel. The main advantages of biodiesel, as an alternative fuel, are lower toxicity, biodegradability, higher oxygen content, less CO₂ emissions, almost zero CO and sulfur emissions, as well as better lubricating properties.

Biodiesel, a mixture of fatty acid alkyl esters (FAAE), is produced by transesterification (also known as alcoholysis), a reaction between renewable lipid feedstocks, such as vegetable oils or animal fats, and alcohols (most frequently methanol or ethanol) in the presence of a catalyst. However, the fossil sources (crude oil or natural gas) are mainly used in the production of methanol, hence methanolysis of vegetable oils or animal fats is not a completely renewable process. A possible way to overcome this limitation is to use ethanol that can be produced from renewable sources [1-4]. The main disadvantages of ethanol as a reactant in biodiesel production are its higher price [4] and lower reactivity [5] compared to methanol, as well as the formation of stable emulsion during ethanolysis process that make crude biodiesel separation from reaction mixture more difficult. Namely, one extra carbon atom of more nucleophile ethoxide ions causes their lower mobility and reactivity in comparison with methoxide ions [5].

Until recently, the main focus in biodiesel synthesis has been the use of homogeneous catalysts despite their obvious disadvantages, such as the side reaction (saponification), which consumes the catalyst and forms soaps making the separation of crude biodiesel much more difficult, and impossibility of their recuperation and reuse. Being less corrosive, more environmentally friendly, easily separable and potentially reusable, heterogeneous (solid) catalysts are more favorable than homogeneous ones. However, transesterification reactions over solid catalysts are usually more time consuming and require higher alcohol-to-oil mole ratio.

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Table 1 gives an overview of the applied kinetic models for alcoholysis of different feedstocks over solid catalysts. Heterogeneously catalyzed ethanolysis has rarely been studied compared to heterogeneously catalyzed methanolysis. In a few studies focused on the kinetics of ethanolysis over solid catalysts, only the pseudo-first order kinetic law has been applied. For instance, the ethanolysis of *Jatropha curcas* and waste cottonseed oils over Zr/CaO and Li/CaO catalysts, respectively, is a pseudo-first order reaction [6,7], while the ethanolysis of canola oil catalyzed by Mg₂CoAl is the a first order reaction [8]. The pseudo-first order reaction rate law has also been employed in kinetic modeling of methanolysis reactions over solid catalysts such as waste frying, yellow horn (*Xanthoceras sorbifolia* Bunge) seed and canola oils with calcinated snail shell [9], ion exchange resins [10] or Mg₂CoAl [8], respectively. Moreover, according to several research groups, methanolysis of various feedstocks over different solid catalysts, such as sunflower oil with CaO [11], Ca(OH)₂ [12] or CaO/ZnO [13], soybean oil with Ca-

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*Microwave irradiation. ‡Ultrasound irradiation*
metoxide [14] and waste cooking oil with CaO/ZnO [15], includes two pseudo-first order steps, i.e., the mass-transfer controlled regime, followed by the chemically controlled regime. Some of these researchers use two independent correlations, both based on a pseudo-first order model, which express a shift in the rate-controlling step [11,12,14]. Other researchers use more complex models including the mass transfer limitation that describe the conversion during the whole reaction time by only one kinetic expression [13,15,16]. These complex models have been recently shown to be better approaches in describing the kinetics of sunflower oil methanolysis over calcium-based solid catalysts [17,18]. Another more complex model involving the Eley-Rideal mechanism describes the kinetics of methanolysis of canola oil and trilinolein over KOH/MgO [19] and MgO [20], respectively. As an exception, ultrasonic-assisted methanolysis of palm, corn, canola, sunflower and used vegetable oils using SrO is satisfactorily described by a second-order kinetic model [21].

The influence of catalyst loading, ethanol-to-oil molar ratio and reaction temperature on the kinetics of fatty acid ethyl ester (FAEE) formation in the ethanolysis of sunflower oil catalyzed by CaO was investigated in this study. The main goal was to test if the kinetic model reported in literature [16], originally developed for the sunflower oil methanolysis catalyzed by quicklime, could also be used for the ethanolysis of the same oil. The developed model was validated by simulating the variations of triacylglycerols (TAGs) and FAEE concentrations with the progress of the ethanolysis reaction. To the authors’ best knowledge, there have been yet no published results regarding the kinetics of CaO-catalyzed ethanolysis of sunflower oil.

**Kinetic modeling**

The overall ethanolysis reaction can be shown by the following stoichiometric reaction:

\[
A + 3B \rightarrow 3R + S
\]

where A is TAGs, B is ethanol, R is FAEEs and S is glycerol. Formally, the reaction between TAG and ethanol includes three consecutive reversible reactions during which the FAEEs, monoacylglycerols (MAGs), diacylglycerols (DAGs) and glycerol are formed. As it can be seen in Figure 1, the concentrations of MAGs and DAGs, especially in the first 6 h and in the last period of the ethanolysis, are very small (DAG up to 2.3% and MAG up to 14.5%) because of their much faster consumption rates, compared to that of TAGs (up to 50.7% in the first six hours of the reaction). Thus, Eq. (1) can be used as the overall stoichiometric equation to represent the complex ethanolysis reaction.

In order to model the kinetics of CaO-catalyzed ethanolysis of sunflower oil, the following assumptions were used:

1) The initial reaction mixture is a three-phase system consisting of a solid (CaO) and two immiscible liquids (ethanol and sunflower oil). During the reaction, FAEEs, MAGs, DAGs and glycerol are formed, making the reaction mixture even more complex. Acting as emulsifiers, MAGs and DAGs stabilize the emulsion of fine dispersed droplets (mainly ethanol and glycerol) into the continuous phase (mainly oil and FAEEs).

2) Composition of the liquid phase and the catalyst particles distribution are uniform due to perfect mixing of the reaction mixture.

3) Ethanolysis occurs on the solid catalyst surface, similarly to methanolysis reaction [11,22].

4) The ethanol mass transfer rate toward solid particles and the ethanol adsorption rate on the solid surface active sites do not limit the overall process rate [6].

5) The kinetics of ethanolysis reaction depends on the mass transfer limitation in the initial stage, similar to methanolysis reaction [11,16]. This type of the kinetics can successfully be described by the model of Miladinović et al. [16]:

\[
-\frac{dc_A}{dt} = k_o \frac{c_A}{K + c_A}(c_{R0} + c_R)
\]

where \(c_A\) is the concentration of TAGs, \(c_R\) and \(c_{R0}\) represent the FAEE concentration and the hypothetical initial FAEE concentration corresponding to the initial available active catalyst surface, respectively, \(k_o\) is the apparent reaction rate constant and \(K\) is the parameter which refers to the affinity of TAGs for the catalyst active sites. The model parameter \(c_{R0}\) is taken into consideration in order to avoid that the initial TAG consumption rate equals to zero at \(t = 0\) when \(c_A = 0\). Thus, this kinetic model combines the changing reaction mechanism with respect to TAG (zero- and first order during the initial and the later period of the reaction, respectively) and the first order reaction rate law regarding to FAEE. Also, it assumes the autocatalytic behavior of ethanolysis reaction, similarly to the methanolysis reaction, caused by increasing the FAEE concentration with time. The formed FAEEs act as a cosolvent, enhancing the miscibility of sunflower oil to ethanol, the interfacial area, i.e., the TAG mass transfer toward the catalyst active sites, and consequently the overall process rate. The kinetic
model has recently been shown to successfully predict the reaction rate during the whole course of the sunflower oil methanolysis over quicklime, neat CaO, Ca(OH)₂ and mixed oxide CaO/ZnO [18].

TAG and FAEE concentrations can be related to the TAG conversion degree, \( x_A \), respectively as follows:

\[
c_A = c_{A0}(1-x_A) \quad (3)
\]

and

\[
c_R = 3c_{A0}x_A \quad (4)
\]

where \( c_{A0} \) is the initial TAG concentration.

Combining Eqs. (2)-(4), the following kinetic expression is obtained:

\[
\frac{-dx_A}{dt} = k_m \frac{(1-x_A)(c_{G0} + 3c_{A0}x_A)}{K + c_{A0}(1-x_A)} \quad (5)
\]

which can be used for determining the kinetics parameters \( k_m \), \( K \) and \( c_{G0} \).

6) The internal diffusion rate has no influence on the ethanolysis reaction rate. The highest values of the Thiele modulus were calculated to be 0.009 or 0.003 for the diffusion of TAGs through sunflower oil and ethanol, respectively which were much smaller than the limit value (0.4), thus confirming the negligible internal diffusion resistance under all reaction conditions applied [23].

7) The external diffusion rate does not influence the ethanolysis reaction rate because the applied agitation speed of 900 rpm is higher than the minimum one needed for perfect mixing of the multiphase system, complete suspension of catalyst particles and no external mass transfer limitation [23].

8) The rate of products desorption from the catalyst surface and their mass transfer rates into the liquid reaction mixture do not limit the overall process rate, similar to the methanolysis products [16].

9) The neutralization reaction is negligible due to the very low content of free fatty acids in the used sunflower oil [16]. The saponification reaction could also be negligible since the formation of soap was not observed and the concentrations of calcium in both FAEE and glycerol phases at the end of the ethanolysis were very low.

**Experimental**

**Materials**

Refined, edible sunflower oil (Sunce, Sombor, Serbia) was used. Its physico-chemical properties can be found elsewhere [16]. Ethanol, absolute (99%) and calcium oxide (CaO, min. 96% purity) were obtained from Fisher Chemical (Leicestershire, UK) and Lachema (Neratovice, Czech Republic), respectively. Hydrochloric acid, conc., was from Centrohem (Belgrade, Serbia), while methanol, 2-propanol and \( \pi \)-hexane (HPLC grade) were purchased from Lab-Scan (Dublin, Ireland). The HPLC standards for ethyl esters of palmitic, stearic, oleic and linoleic acids, triolein, diolein and monoolein were obtained from Sigma-Aldrich.

**Catalyst preparation**

For obtaining the highest catalytic activity the CaO was calcined at 550 °C for 2 h under atmospheric pressure [11]. After transferring and cooling in a desiccator containing calcium chloride and potassium hydroxide pellets, the CaO was stored in a dark, well-closed glass bottle, which was kept in the desiccator. The size and specific surface area of calcined catalyst particles were less than 15 μm and 13.7 m²/g [24], respectively. The basic strength and total basicity of calcined CaO were 15 < H_ < 18.4 [24] and 2.46 mmol/g [25], respectively.

**Equipment and experimental procedure**

The ethanolysis reaction was carried out in a 250 mL glass three-neck, round-bottom flask equipped with a condenser and a two flat-blade paddle agitator. The agitation intensity, measured with an optoelectronic counter, was 900 rpm in all experiments. The temperature was kept constant by circulating water from a thermostated bath (Dema, Ilirska Bistrica, Slovenia) into the chamber with the emerged reaction flask by means of a pump. The ethanolysis of sunflower oil was carried out under the atmospheric pressure at 6:1, 12:1 or 18:1 mole ratios of ethanol-to-oil, CaO loadings of 10, 15 or 20% (based on the oil weight) and temperatures 65, 70 and 75 °C.

Ethanol and CaO were agitated in the reaction flask at the desired temperature for about 30 min. Meanwhile, sunflower oil was thermostated separately. After achieving the desired temperature, the agitator was turned off, and the oil was added to the ethanol-catalyst suspension. As soon as the agitator was turned on, the reaction was timed. During the ethanolysis reaction, the samples (0.5 mL) were withdrawn and immediately quenched by adding a required amount of the aqueous hydrochloric acid solution (5 mol/L) and centrifuged at 3.500 rpm for 10 min. The FAEE-oil layer was separated, dissolved in a solution of a mixture of 2-propanol and \( \pi \)-hexane (5/4 ml/ml) in a ratio 1:200, filtered through a Millipore filter (0.45 μm) and analyzed by the HPLC method described elsewhere [26].
Computer software

Kinetic parameters of Eq. (5) were calculated using the experimental data on TAG conversion determined at various reaction times. Nonlinear least squares regression analysis was performed using the Polymath, v. 6.10, software. Then, using these kinetic parameters, the values of the TAG conversion predicted by the model were calculated using the same software. The statistical evaluation of the model was based on the mean relative percent deviation (MRPD) and the coefficient of determination ($R^2$) calculated by Eqs. (6) and (7), respectively:

$$
MRPD = \frac{100}{n} \sum_{i=1}^{n} \left| \frac{y_{p,i} - y_{a,i}}{y_{a,i}} \right|
$$

$$
R^2 = 1 - \frac{\sum_{i=1}^{n} (y_{p,i} - y_{a,i})^2}{\sum_{i=1}^{n} (y_{p,i} - y_m)^2}
$$

where $y_a$ and $y_p$ are the predicted and experimental values of the TAG conversion (%), $y_m$ is the mean value of the TAG conversion (%), and $n$ is the number of experimental runs.

RESULTS AND DISCUSSION

Analysis of sunflower oil ethanolysis performed at different reaction conditions

Figure 1, which represents the change of the reaction mixture composition with time, shows the sigmoidal variation of the TAG and FAEE contents. On the other side, the concentrations of MAGs and DAGs in the reaction mixture pass through a maximum (less than 20% for MAGs and several percentages for DAGs). During the initial stage of the reaction (approximately the first five hours), the FAEE content increases slowly on account of the slow TAG conversion. Then, in the next two hours, the FAEE content rapidly increases while the TAG content rapidly decreases. Finally, the rate of FAEE formation slows down, while almost the complete TAG conversion is achieved in about seven hours. The TAG formation in the last three hours of reaction is almost on account of the MAG conversion. The DAG concentration is very small during the whole course of the reaction, while the MAG concentration passes through a maximum (about 20%) at the seventh hour of the reaction.

Effect of catalyst loading on the FAEE formation

Figure 2 shows the influence of catalyst loading in the range between 10 and 20% on the FAEE formation during the ethanolysis reaction at 65 °C and the ethanol-to-oil mole ratios of 6:1, 12:1 and 18:1. At the mole ratios of 6:1 and 12:1, the increase of the catalyst loading from 10 to 20% accelerates the FAEE formation (Figure 2a and b), shortening the initial lag reaction period due to the increase of the total number of acid sites available for the reaction. Similarly, Kaur and Ali [6,7] observed the increase of FAEE formation with the increase of the Li/CaO or Zr/CaO catalyst amount only in the range from 1 to 5%, while a further increase in the catalyst amount did not either reduce the reaction time or enhance the conversion significantly. Contrary to these findings, some researchers have reported that the TAG conversion either not depends or even decreases with increasing the catalyst amount above a certain level for transesterification with zinc oxide modified with alkali earth metals [27] and CaO-based catalysts [16,25,28,29], respectively. The adverse influence of higher catalyst amount might be attributed to enhanced viscosity of the three-phase reaction mixture creating the mixing problem and increasing the mass transfer resistance in the system [27,29] and to the reduced available catalytically active surface sites due to the clustering of catalyst particles under the mentioned mixing problem [25]. However, at the ethanol-to-oil mole ratio of 18:1, the increase of the catalyst amount to 20% adversely affects the FAEE formation (Figure 2c) probably because of the lower catalyst concentration in the reaction mixture ($0.0015 \text{ mol/dm}^3$), compared to molar ratios of 12:1 ($0.0018 \text{ mol/dm}^3$) and 6:1 ($0.0023 \text{ mol/dm}^3$). The opposite results of different research groups imply that an optimal catalyst concentration in
the reaction mixture depends on the ethanol-to-oil mole ratio. Indeed, for the CaO-catalyzed ethanolysis of sunflower oil the optimal catalyst loading of 17% (in the range between 10 and 20%) was found at the optimal ethanol-to-oil mole ratio of 14:1 (in the range of 6:1 to 18:1) at the reaction temperature of 72 °C [23].

Effect of ethanol-to-oil mole ratio on the FAEE formation

The influence of the ethanol-to-oil mole ratio on the FAEE formation at 75 °C and various catalyst loadings in the range of 10 to 20% is shown in Figure 3. At the catalyst loadings of 10 and 15%, the FAEE formation is accelerated with the increase of the etha-

Figure 2. The influence of the catalyst loading on the FAEE formation at 65 °C and the ethanol-to-oil mole ratios of: a) 6:1, b) 12:1 and c) 18:1 (catalyst loading, %: 10 – ○, 15 – △ and 20 – □).

Figure 3. The influence of the ethanol-to-oil mole ratio on the FAEE formation at the reaction temperature of 75 °C and the catalyst amounts of: a) 10, b) 15 and c) 20% (ethanol-to-oil mole ratio: 6:1 - ○, 12:1 - △ and 18:1 - □).
nol-to-oil mole ratio from 6:1 to 12:1, but further increasing the ethanol-to-oil mole ratio to 18:1 has a negative influence on the FAEE formation (Figure 3a and b). As already explained, this adverse effect of the ethanol-to-oil molar ratio can probably be attributed to the reduced catalyst concentration. On the other hand, at the catalyst loading of 20% (Figure 3c), the increase of the ethanol-to-oil mole ratio from 6:1 to 12:1 leads to a slight increase in the FAEE formation, but its further increase to 18:1 has almost no influence on it. The positive effect of increased number of active sites on the surface of the catalyst particles is suppressed by the negative effect of catalyst dilution at higher ethanol amount. Also, Kostić et al. [30] have recently reported the same effect for the sunflower oil methanolysis over a CaO-based catalyst with increasing the methanol-to-oil mole ratio from 9:1 to 15:1. Some researchers concluded the same for the ethanolysis of jatropha oil with Zr/CaO [6] and waste cotton seed oil with Li/CaO [7], where increasing the ethanol-to-oil mole ratio above 21:1 and 12:1, respectively had no influence on the FAEE yield. However, Li et al. [8] observed only the increase of FAEE yield in the ethanolysis of canola with Mg2CoAl with increasing the ethanol-to-oil mole ratio from 7:1 to 16:1.

Effect of reaction temperature on the FAEE formation

Figure 4 represents the influence of temperature on the FAEE formation at the ethanol-to-oil mole ratio of 12:1 and catalyst amounts in the range of 10 to 20%. Generally, the combined effect of catalyst loading and temperature is observed at all ethanol-to-oil mole ratios. At the catalyst loadings of 10 and 15% (Figure 4a and b), the FAEE formation speeds up with increasing the reaction temperature as expected. However, at the maximum catalyst loading (20%), temperature over 70°C does not influence significantly the FAEE formation (Figure 4c). Generally, the same influence of temperature is observed at the ethanol-to-oil mole ratios of 6:1 and 18:1 (not shown).

Kinetics of CaO catalyzed sunflower oil ethanolysis

The kinetic parameters $k_m$ and $K$ depend on the initial ethanol-to-oil mole ratio, the catalyst loading and the reaction temperature. The value of $c_{R0}$ was calculated to be 0.021 mol/dm$^3$ for all reaction conditions, which agreed with previously reported for the quicklime-catalyzed sunflower oil methanolysis [16]. Figure 5 represents $k_m$ and $K$ as functions of the catalyst loading at the reaction temperature of 70°C and ethanol-to-oil mole ratios of 6:1, 12:1 and 18:1. Both $k_m$ and $K$ increase linearly with increasing the catalyst loading as represented by three separate straight lines whereby their slopes enhance with increasing the initial ethanol-to-oil mole ratio. Taking into account the report of Miladinović et al. [16], it was accepted that $k_m$ and $K$ depend on both catalyst loading and initial ethanol-to-oil molar ratio as follows:

$$k_m = k c_{R0} c_{cat}$$  \hspace{1cm} (8)

and

$$K = K' c_{R0} c_{cat}$$  \hspace{1cm} (9)
where $c_{B0}$ is the initial ethanol concentration and $c_{\text{cat}}$ is the catalyst concentration. To check Eqs. (8) and (9), $k_m/c_{B0}$ and $K/c_{B0}$ were correlated with $c_{\text{cat}}$ as shown in Figure 5. The linear dependences at three different reaction temperatures confirm the validity of Eqs. (8) and (9).

![Figure 5. The changes of $k_m$ (a) and $K$ (b) with the catalyst concentration at the reaction temperature of 70 °C at different ethanol-to-oil mole ratios (6:1 - ○, 12:1 - △ and 18:1 - ●).](image)

The slopes of the linear dependence of $k_m/c_{B0}$ on $c_{\text{cat}}$ at 65, 70 and 75 °C, representing the reaction rate constant $k$, were calculated to be 0.0118, 0.0173 and 0.0310 dm$^6$/mol$^2$ min, with the $R^2$ values of 0.974, 0.976 and 0.920, respectively. The slopes of the linear dependence of $K/c_{B0}$ on $c_{\text{cat}}$ at three different reaction temperatures represent the TAG affinity for the catalyst active sites (1.088, 1.416 and 1.952 dm$^3$/mol with the $R^2$ values of 0.982, 0.975 and 0.979, respectively).

The linear dependence of $\ln k$ on $1/T$ confirms that the Arrhenius equation could be applied for the ethanolysis reactions ($R^2 = 0.983$). The activation energy of 94.0 kJ/mol was calculated from the slope of the linear dependence. This value is higher than the activation energies reported for the ethanolysis of waste cottonseed oil with Li/CaO [7], canola oil with MgCoAl-LDH [8], Jatropha oil with Zr/CaO [6] (70.0, 60.5 and 42.5 kJ/mol, respectively). In addition, the linear dependence of $K'$ on temperature was found ($R^2 = 0.981$):

$$K' = 0.0867 - 4.5636$$  \hspace{1cm} (10)

Simulation of sunflower oil ethanolysis

The TAG conversion degree was calculated using Eq. (5), for the purpose of verifying the proposed kinetic model by comparing it with experimental data points. In this computation, the values of the kinetic parameters, namely $k$ and $K$, were calculated from corresponding values of the initial ethanol concentration and the reaction temperature, while $q_{\text{in}} = 0.0021$ mol/dm$^3$. The variation of the TAG conversion degree during the ethanolysis reaction at the optimal reaction conditions (the ethanol-to-oil mole ratio of 12:1, the reaction temperature of 75 °C and the catalyst loading of 15%) [23] is shown in Figure 6a. The TAG conversion degree was calculated by

![Figure 6. Comparison of: a) the predicted $x_A$ values with the experimental data (● - experimental data; straight line - kinetic model) and b) the experimental TAG and FAEE concentrations and the corresponding ones calculated by the kinetic model (experimental data: TAG - ● and FAEE - ○; kinetic model - straight line) at the ethanol/oil mole ratio of 12:1, the reaction temperature of 75 °C and the catalyst loading of 15%.](image)
the proposed kinetic model, Eq. (5). It is obvious that the model underestimates the TAG conversion degree, but the model curve follows the experimental points. Figure 6b compares the experimental and calculated values of the TAG and FAEE concentrations corresponding to the optimal reaction conditions. The TAG and FAEE concentrations were calculated from the corresponding values of the TAG conversion degree using Eqs. (3) and (4), respectively. A satisfactory agreement between the predicted FAEE concentration ($c_{ee}$) and the experimental data is observed. Moreover, the validity of the kinetic model was also confirmed for all other reaction conditions applied where the acceptable MRPD value of ±13.0% (based on 256 data points) was observed for the TAG conversion degree higher than 10%.

CONCLUSION

The kinetics of the sunflower oil ethanolysis over calcium oxide was described by the kinetic model that includes the changing and first-order reaction mechanism with respect to TAGs and FAEEs, respectively. The TAG and FAEE contents calculated by the proposed kinetic model agreed quite well with the experimentally determined contents (MRPD = ±13% based on 256 data points) in the applied ranges of the operating conditions (temperature of 65–75 °C; catalyst loading of 10-20% based on oil; ethanol-to-oil mole ratio of 6:1-18:1). Since this model has already been employed successfully for the sunflower oil methanolysis over Ca-based catalysts, the present result demonstrates its general applicability. The activation energy of 94.0 kJ/mol found for the sunflower oil ethanolysis over CaO is higher than those reported for other vegetable oils and solid catalysts. Hence, the ethanolysis of sunflower oil catalyzed by CaO is very sensitive to the applied temperature, so the reaction could occur much faster at temperatures higher than 75 °C.

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REFERENCES

KINETIKA ETANOLIZE SUNCOKRETOVOG ULJA U PRISUSTVU CAO KAO KATALIZATORA


Ključne reči: biodizel, etanoliza, kalcijum-oksid, kinetičko modelovanje, suncokretovo ulje.