Further Study on Kinetic Modeling of Sunflower Oil Methanolysis Catalyzed by Calcium-Based Catalysts

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Article Highlights
• Kinetics of methanolysis reaction catalyzed by calcium-based catalysts
• Kinetic model involves TAG mass transfer and chemically controlled regions
• Effects of reaction conditions on parameters of the kinetic models are analyzed

Abstract

The kinetic model, which was originally developed for sunflower oil methanolysis catalyzed by CaO·ZnO, was examined for several other calcium-based catalysts like neat CaO, quicklime and Ca(OH)2. This model including triacylglycerols mass transfer- and chemically-controlled regimes demonstrated a good agreement with the experimental data in terms of a high coefficient of determination (0.971±0.022) and acceptable mean relative percentage deviation (±15.9%). Hence, this model is recommended for modeling the kinetics of sunflower oil methanolysis over calcium-based catalysts under widely ranging reaction conditions.

Keywords: biodiesel; calcium-based catalysts; kinetics; methanolysis; modeling.

Biodiesel, which is commonly produced from plant oils and animal fats by alcoholysis (usually methanolysis), is an alternative fuel for diesel engines as being based on renewable raw materials, easily available, technically appropriate, economically competitive and environmentally beneficial. Although the current production of biodiesel is mainly carried out by homogeneous base-catalyzed methanolysis of edible vegetable oils, it is expected that it will soon be replaced by heterogeneous catalysis based on the use of basic solid metal oxides, hydroxides and complexes, zeolites, hydrotalcites or supported catalysts. Because of high basicity, mild reaction condition, high biodiesel yield, low cost and easy preparation, calcium compounds, such as oxide [1-3], hydroxide [4] or methoxide [5], are increasingly used in biodiesel production from various oily or fatty feedstocks. Calcium oxide (CaO) is used as neat [1-3,6], doped [7,8], supported [9] or mixed [10,11]. Its great advantage is the possibility of preparation from natural [12,13] or waste [14,15] sources.

The kinetic models that have been used so far for methanolysis reaction over calcium-based catalysts suppose zero [16,17] or first [2,3,5,10,11] order with respect to triacylglycerols (TAGs). Some researchers suppose [2,13] that the order of this reaction varies from the zeroth order in the beginning to the first one in the later period of methanolysis. Also, separate correlations for mass transfer- and reaction rate-controlled stages of the methanolysis reaction of the first order with respect to TAGs are reported [3,4]. Lukić et al. [10,11] have recently combined these two correlations into a single one that predicts the reaction rate during the whole course of methanolysis of refined and used sunflower oil over CaO·ZnO. Moreover, this model has successfully been employed by Sánchez et al. [15] for describing the kinetics of jojoba oil methanolysis over mussel shell-CaO. Hence, this model might be powerful for modeling the kinetics of methanolysis of different feedstocks over various calcium-based catalysts.

Therefore, the present work focuses on the adequacy, reliability and accuracy of the kinetic model of...
like neat CaO, quicklime and Ca(OH)₂. This work was catalyzed by several solid calcium-based catalysts esters (FAMEs), i.e., biodiesel and S is glycerol. In where A is TAG, B is methanol, R is fatty acid methyl esters reaction rate. The first order reaction rate law depends on the formation of fine emulsion of meth-oxide ions adsorbed on the active centers and TAG molecules in the liquid phase close to the active centers.

3. The rate of methanol mass transfer towards catalytically active sites, the reverse reaction rate as well as the adsorption/desorption rates of methanol, FAME and glycerol do not limit the overall process rate.

4. The methanolysis process is controlled by TAG mass transfer limitation in the initial reaction period and by the chemical reaction in the latter period. The mass transfer limitation, caused by the small available active specific catalyst surface [3,4], depends on the formation of fine emulsion of methanol into the oil. In addition, FAMEs act as a cosolvent, enhancing the miscibility of the reactants and increasing the TAG mass transfer rate and the methanolysis reaction rate. The first order reaction rate law with respect to TAG is adopted:

\[
\frac{dx_A}{dt} = k \left( \frac{k_{ml,A}}{x_A} \right) \left[ 1 + \alpha x_A^2 \right] \left[ 1 + \beta x_A^2 \right] (1 - x_A)
\]

where \(x_A\) is the TAG conversion degree, \(t\) is time, \(k\) is the pseudo first-order reaction rate constant, \((k_{ml,A})_0\) is the overall TAG volumetric mass transfer coefficient at the beginning of the process, and \(\alpha\) and \(\beta\) are fitting parameters. Thus, the model includes four parameters: \(\alpha, \beta, k\) and \((k_{ml,A})_0\). The detailed derivation of Eq. (2) can be found elsewhere [3,10].

The homogeneous catalyzed methanolysis reaction is ignorable due to negligible leaching of the catalyst. This is experimentally verified for neat CaO [19], a CaO-based catalyst [20] and Ca(OH)₂ [4] in batch stirred reactors. Since CaO·ZnO is practically insoluble in methanol, homogeneous catalysis is also considered as negligible [10]. According to Granados et al. [1], the contribution of the homogeneous methanolysis arising from the leached calcium species is negligible if the catalyst loading is larger than 1% to the oil, this condition being fulfilled in the above-mentioned studies.

The internal diffusion rate inside catalyst particles does not influence the methanolysis reaction rate. This assumption is verified for neat CaO [3] and Ca(OH)₂ [4]. Also, powdered quicklime is a mesoporous material with pores significantly greater than the diameter of a typical TAG molecule which minimizes internal diffusion limitations [13]. In addition, CaO·ZnO is characterized as a catalyst with small surface area and low porosity [10].

The neutralization of free fatty acids is negligible because of their very small content in the oil used (acid value of 0.24-0.29 mg KOH/g) [3,4,10,13]. Also, the saponification reaction is ignorable and consequently, the catalyst amount remains constant during the methanolysis.

**EXPERIMENTAL**

**Experimental data**

The experimental data for the sunflower oil methanolysis reactions catalyzed by neat CaO [3], quicklime [13], Ca(OH)₂ [4] and CaO·ZnO [10] in batch stirred reactors were taken from the earlier investigations. Median particle size, median pore diameter, specific surface area, basic strength and basicity of the used catalysts are presented in Table 1. The reaction conditions (type and volume of reactor, methanol-to-oil mole ratio, catalyst loading, temperature and stirring speed) applied in the above-mentioned studies are given in Table 2.
Modeling techniques and computer software

Kinetic parameters of Eq. (2) were obtained by fitting the sets of experimental data using the Mathematica™ v.9 (trial version). A demonstration [22] which generated realistic-looking curves was modified and rewritten using Eq. (2) in order to provide both good initial value guessing and computing of each kinetic parameter.

TAG and FAME concentrations, \(c_A\) and \(c_R\), were calculated from values of TAG conversion degree as follows:

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

\[
c_R = 3c_{A0}x_A \tag{4}
\]

Statistical estimation of kinetic models

The significance of the models was statistically evaluated from the coefficient of determination \(R^2\) and the mean relative percent deviation (MRPD), respectively:

\[
R^2 = \frac{\sum_{i=1}^{n} (y_{p,i} - y_{a,i})^2}{\sum_{i=1}^{n} (y_{p,i} - y_{m})^2} \tag{5}
\]

\[
MRPD = \frac{100}{n} \sum_{i=1}^{n} \left| \frac{y_{p,i} - y_{a,i}}{y_{a,i}} \right| \tag{6}
\]

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

RESULTS AND DISCUSSION

Kinetic modeling of sunflower oil methanolysis

Predicted values of parameters of the kinetic model, Eq. (2), as well as \(R^2\)- and MRPD-values as the statistical measures of their adequacy, reliability and accuracy, are presented in Table 3. The kinetic model shows very high \(R^2\) (0.971±0.022) for all four catalysts, showing that it predicts the time variation of TAG conversion degree within the ranges of the reaction conditions applied reliably. In addition, the MRPD of ±15.9% (based on a set of 240 data) shows a good agreement between the predicted and experimental values of TAG conversion degree. Thus, the kinetic model is reliable and accurate not only for CaO⋅ZnO but also for neat CaO, quicklime and Ca(OH)\(_2\).

Recently, Tasić et al. [16] have recommended the kinetic model of Miladinović et al. [13] as general for describing the kinetics of sunflower oil methanolysis over calcium-based catalyst. This is a three-parameter model:

\[
\frac{dx_A}{dt} = k_m \frac{(1 - x_A)(c_{O} + 3c_{A0}x_A)}{K + c_{A0}(1 - x_A)} \tag{7}
\]

where \(x_A\) is the conversion degree of TAG, \(t\) is time, \(c_{O}\) is the initial TAG concentration, \(K\) is the model parameter defining the TAG affinity for the catalyst active sites, \(c_{O}\) is the hypothetic initial FAME concentration corresponding to the initial available active catalyst surface and \(k_m\) is the apparent reaction rate constant.

Table 1. Textural properties, basic strength and basicity of used catalyst; \(D_{\text{med, particle}}\) - median particle size, \(D_{\text{med, pore}}\) - median pore diameter and \(S_{\text{BET}}\) - specific surface area

<table>
<thead>
<tr>
<th>Sample</th>
<th>(D_{\text{med, particle}} / \mu m)</th>
<th>(D_{\text{med, pore}} / \text{nm})</th>
<th>(S_{\text{BET}} / \text{m}^2 \text{g}^{-1})</th>
<th>Basic strength (H)</th>
<th>Basicity, mmol/g</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaO</td>
<td>2.8</td>
<td>15.2</td>
<td>13.7</td>
<td>15&lt;H&lt;18.4</td>
<td>2.46</td>
<td>[21]</td>
</tr>
<tr>
<td>Quicklime</td>
<td>&lt;500</td>
<td>18.8</td>
<td>9.5</td>
<td>15&lt;H&lt;18.4</td>
<td>2.16</td>
<td>[13]</td>
</tr>
<tr>
<td>Ca(OH)(_2)</td>
<td>2.0</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>[4]</td>
</tr>
<tr>
<td>CaO⋅ZnO</td>
<td>4.3</td>
<td>-</td>
<td>3.1</td>
<td>9.3&lt;H&lt;10</td>
<td>0.58</td>
<td>[11]</td>
</tr>
</tbody>
</table>

Table 2. Reaction conditions (type and volume of reactor, methanol-to-oil molar ratio, catalyst loading, temperature and stirring speed) applied in the studies of sunflower oil methanolysis catalyzed by the calcium compounds; BSR - batch stirred reactor

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Catalyst amount</th>
<th>Temperature °C</th>
<th>MeOH/oil mole ratio</th>
<th>Stirring intensity rpm</th>
<th>Reactor type</th>
<th>Reactor volume mL</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaO</td>
<td>1-10</td>
<td>60</td>
<td>6:1</td>
<td>900</td>
<td>BSR</td>
<td>250</td>
<td>[3]</td>
</tr>
<tr>
<td>Quicklime</td>
<td>1-10</td>
<td>60</td>
<td>6:1 - 18:1</td>
<td>900</td>
<td></td>
<td>250</td>
<td>[13]</td>
</tr>
<tr>
<td>Ca(OH)(_2)</td>
<td>1-10</td>
<td>60</td>
<td>6:1</td>
<td>900</td>
<td></td>
<td>250</td>
<td>[4]</td>
</tr>
<tr>
<td>CaO⋅ZnO</td>
<td>2</td>
<td>60-96</td>
<td>10:1</td>
<td>300</td>
<td></td>
<td>300</td>
<td>[10]</td>
</tr>
<tr>
<td></td>
<td>0.5, 1, 2</td>
<td>60</td>
<td>6:1, 10:1</td>
<td>300, 1000</td>
<td></td>
<td>1000</td>
<td>[11]</td>
</tr>
</tbody>
</table>
where \( k \) is the actual reaction rate constant, while \( c_{B0} \) and \( c_{cat} \) are initial concentrations of methanol and catalyst, respectively. Equation (7) is shown as a reliable predictor of the time variation of TAG conversion degree in the sunflower oil methanolysis over the same calcium-based catalysts used in the present study within the ranges of the reaction conditions applied as indicated by high coefficient of determination \((R^2 > 0.93)\) and relatively small MRPD (±9.1%) [18]. Based on the MRPD, the model of Miladinović et al., Eq. (7), is better for CaO, quicklime and CaO-ZnO, while the model of Lukić et al., Eq. (2), is more adequate for Ca(OH)\(_2\). The kinetic model of Lukić et al., Eq. (2), was used for calculation of TAG and FAME concentrations during the sunflower oil methanolysis over the calcium-based catalysts. The accuracy of the kinetic models was examined by comparing the predicted and experimental values of FAME and TAG concentrations. Figures 1 and 2 show the variation of TAG and FAME concentrations with the progress of the sunflower oil methanolysis catalyzed by neat CaO, quicklime and Ca(OH)\(_2\). As it can be seen, the calculation of FAME and TAG concentrations obtained by Eq. (2) agree quite well with the experimental concentrations independently of methanol-to-oil molar ratio and catalyst amount.

So far, different mechanisms of methanolysis reaction catalyzed by calcium-based catalysts have been proposed in the literature [2,3,23], but the exact nature of any of them has not been confirmed yet. The results of the present kinetic analysis might indicate the possible reaction mechanism of methanolysis reaction catalyzed by calcium-based catalysts. Probably, methanolysis reaction proceeds through the simplified Eley-Rideal mechanism when the chemical reaction at the catalyst surface controls the reaction rate [10].

### Table 3. Parameters and statistical estimation of kinetic models for methanolysis of sunflower oil

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Temperature °C</th>
<th>Methanol-to-oil mole ratio</th>
<th>Parameters</th>
<th>Statistical evaluation</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>( \beta )</td>
<td>( k / \text{min}^{-1} )</td>
</tr>
<tr>
<td>CaO</td>
<td>1.0</td>
<td>60</td>
<td>1.00</td>
<td>0.067</td>
</tr>
<tr>
<td></td>
<td>2.5</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>5.0</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>10.0</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Quicklime</td>
<td>1.0</td>
<td>60</td>
<td>1.00</td>
<td>0.042</td>
</tr>
<tr>
<td></td>
<td>2.5</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>5.0</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>10.0</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ca(OH)(_2)</td>
<td>1.0</td>
<td>60</td>
<td>1.00</td>
<td>0.021</td>
</tr>
<tr>
<td></td>
<td>2.5</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>5.0</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>10.0</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CaO-ZnO(_a)</td>
<td>2.0</td>
<td>60</td>
<td>10:1</td>
<td>1.37</td>
</tr>
<tr>
<td></td>
<td>70</td>
<td></td>
<td>1.75</td>
<td>0.051</td>
</tr>
<tr>
<td></td>
<td>84</td>
<td></td>
<td>1.27</td>
<td>0.083</td>
</tr>
<tr>
<td></td>
<td>96</td>
<td></td>
<td>2.90</td>
<td>0.120</td>
</tr>
<tr>
<td>Mussel shell CaO(_b)</td>
<td>6-10</td>
<td>45-65</td>
<td>6:1-12:1</td>
<td>0.23</td>
</tr>
</tbody>
</table>

\( k_{\text{m}} = k c_{\text{B0}} c_{\text{cat}} \)

\(^a\)Values of parameters were taken from Lukić et al[10]; \(^b\)values of parameters were taken Sánchez et al. [15] for the jojoba oil methanolysis; \(^c\)the parameter is a function of methanol concentration; \(^d\)not available
located near the catalyst surface. In the initial reaction period the overall methanolysis process rate is limited by the TAG mass transfer to active sites on the catalyst surface. In the later period of reaction, the reaction rate at the catalyst surface becomes slower than the TAG mass transfer rate toward the catalyst surface as a consequence of FAME formation and better oil dispersion, so TAG consumption at catalyst surface begins to control the overall rate of reaction.

**Influence of reaction conditions on kinetic parameters**

Values of the parameters of Eq. (2), $\beta$, $\alpha$, $k$ and $(k_{mt,A})_0$, for the methanolysis reaction over CaO-ZnO were taken from the works of Lukeć et al. [10], while values for the catalytic reaction systems using neat CaO, quicklime and Ca(OH)$_2$ were calculated by fitting the experimental data (20 data sets).

In general, the reaction rate constant, $k$, seems to depend on type and amount of catalyst, methanol-to-oil molar ratio and reaction temperature, as it can be concluded from Table 3. The catalyst amount does not affect the reaction rate constant in the case of neat CaO and quicklime, as well as CaO-ZnO [11]. However, in the case of Ca(OH)$_2$ it increases exponentially with increasing the catalyst amount, which is attributed to the enhanced possibility of adsorbed molecules for the reaction at higher catalyst amount [4]. For three CaO-based catalysts the reaction rate constant $k$ reduces with decreasing their basicity in the following order: neat CaO > quicklime > CaO-ZnO. It seems that the methanol-to-oil molar ratio does not or very slightly affect the reaction rate constant for quicklime (Table 3) and CaO-ZnO [11]. As expected, the reaction rate constant increases with increasing the reaction temperature in the CaO-ZnO reaction system [10]. The $k$-value depends on temperature in accordance to the Arrhenius equation, as shown by Sánchez et al. [15] for the jojoba oil methanolysis over mussel shell CaO with the activation energy of 55.09 J/mol. However, the $k$-value for this process is much lower than those for the sunflower oil methanolysis, as it can be seen in Table 3, because of the difference in the chemical composition of the two oils. While sunflower oil consists of TAGs predominantly, jojoba oil has no TAGs in their structure but long straight ester chains [15], which slows down the methanolysis reaction.

$\beta$-Values for the CaO-ZnO reaction system range between 1.37 and 2.90 [10], and no obvious dependence on temperature is observed. However, the constant $\beta$-value of 1.00±0.01 is determined for other three reaction systems using neat CaO, quicklime and Ca(OH)$_2$ at a constant temperature (60 °C). Sánchez et al. [15] reported much lower $\beta$-value (0.23) for the jojoba oil methanolysis over mussel shell CaO that was not dependent on reaction temperature and methanol-to-oil molar ration in the ranges of 45 to 65 °C and 6:1 to 12:1, respectively.

The fitting parameter $\alpha$ appears to depend on the type and amount of catalyst. For the same other conditions, its value increases in the following order: CaO-ZnO, then Ca(OH)$_2$ and finally neat CaO and quicklime that have the same $\alpha$-value. The $\alpha$-value of...
59.7 for mussel shell CaO in the range of catalyst amount of 6 to 10% \cite{15} is close to those for neat CaO and quicklime in the range of catalyst amount of 5 to 10%. For CaO\(\cdot\)ZnO \cite{11}, neat CaO, quicklime and Ca(OH)\(_2\) the parameter \(\alpha\) decreases with increasing the catalyst amount according to a power law function. The value of this parameter depends on the time when the critical TAG conversion is achieved and the change of the limiting reaction regime occurs \cite{11}. At lower catalyst amounts a longer reaction time is required for achieving the critical TAG conversion at which the reaction rate is enhanced. For the catalyst amount of 1%, the \(\alpha\)-value is 1300 for CaO\(\cdot\)ZnO \cite{11}, while only 200-213 for neat CaO, quicklime and Ca(OH)\(_2\). This difference could be attributed to different values of \(\beta\)-parameter for CaO\(\cdot\)ZnO \((\beta = 2.01)\), on one hand and neat CaO, quicklime and Ca(OH)\(_2\) \((\beta = 1.00)\), on the other hand. Methanol-to-oil mole ratio does not influence the \(\alpha\)-value in the quicklime reaction system. In the case of CaO\(\cdot\)ZnO, the dependence of \(\alpha\) on reaction temperature is not obvious.

The mass transfer coefficient, \((k_{mt,A})_0\), is dependent on the type and amount of catalyst, methanol-to-oil mole ratio and reaction temperature. Figure 3 shows the dependence of \((k_{mt,A})_0\) on the amount of various catalysts. The same value of \((k_{mt,A})_0\) is observed for the neat CaO and quicklime reaction systems, which is higher than that for the Ca(OH)\(_2\) reaction system. For all reaction systems, \((k_{mt,A})_0\) increases with increasing the catalyst amount, reaching a plateau approximately at the catalyst amount of 5%. This means that the increase of the catalyst amount above 5% had no significant effect on the overall process rate in the initial reaction period. For the CaO\(\cdot\)ZnO reaction system, \((k_{mt,A})_0\) increases with increasing the catalyst amount in the range from 0.5 to 2.0% \cite{11}.

In the quicklime reaction system at a constant catalyst amount, \((k_{mt,A})_0\) decreases with the increase of methanol-to-oil molar ratio from 6:1 to 12:1, but it remains almost constant with further increase of methanol-to-oil mole ratio (Table 3). This observation
means that the mass transfer rate is enhanced at higher methanol amount due to higher oil-methanol interfacial area because of the lower density of the reaction mixture enabling more efficient mixing. As expected, \((k_{mt,A})_0\) increases with increasing the reaction temperature in the CaO\(\cdot\)ZnO reaction system probably because of a faster formation of emulsifying agents stabilizing the emulsion [10]. However, Sánchez et al. [15] noticed no effect of catalyst amount and reaction temperature on the \((k_{mt,A})_0\) for mussel shell CaO and its increase with increasing the methanol concentration in the range of methanol-to-jojoba oil molar ratio from 6:1 to 12:1.

CONCLUSIONS

The kinetics of sunflower oil methanolysis catalyzed by neat CaO, quicklime, Ca(OH)\(_2\) and CaO\(\cdot\)ZnO was tested using the recently reported kinetic model involving the initial region controlled by the TAG mass transfer followed by the chemically controlled region. This model adopts the pseudo-first order reaction rate law or both the mass transfer and the chemical reaction. The model demonstrates a good agreement with the experimental data and can be recommended for describing the time variations of TAG and FAME concentrations during methanolysis of sunflower, used vegetable and jojoba oil. However, its generalization capability could be verified entirely after the analysis of experimental data obtained with other solid base catalysts and vegetable oils as it has been done for calcium-based catalysts in the present study.

Acknowledgments

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Nomenclature

- \(c_A\): Concentration of TAG, mol/dm\(^3\)
- \(c_{A0}\): Initial concentration of TAG, mol/dm\(^3\)
- \(c_{R0}\): Initial concentration of TAG, mol/dm\(^3\)
- \(c_R\): Concentration of FAME, mol/dm\(^3\)
- \(k\): Reaction rate constant, Eq. (2), min\(^{-1}\)
- \((k_{mt,A})_0\): Overall TAG volumetric mass transfer coefficient at the beginning of the process, min\(^{-1}\)
- \(MRPD\): Mean relative percent deviation, %
- \(n\): Number of experimental runs
- \(R^2\): Coefficient of determination
- \(t\): Time, min
- \(\alpha\): Degree of TAG conversion
- \(\eta_0\): Experimental values of the TAG conversion degree, %
- \(\eta_m\): Mean value of the TAG conversion degree, %
- \(\eta_p\): Predicted values of the TAG conversion degree, %

Greek symbols

- \(\alpha, \beta\): Fitting parameters

REFERENCES

DALJE PROUČAVANJE KINETIČKOG MODELOVANJA METANOLIZE SUNCOKRETOVOG ULJA KATALIZOVANE NEKIM KALCIJUMOVIM JEDINJENJIMA

Kinetički model, koji je prvobitno razvijen za metanolizu suncokretovog ulja katalizovanog CaO·ZnO, primenjen je na nekoliko drugih katalizatora na bazi kalcijuma, kao što su čist CaO, negašeni kreč i Ca(OH)₂. Ovaj model, koji uključuje režime kontrolisane prenosom mase triacilglicerola i hemijskom reakcijom, pokazao je dobro slaganje sa eksperimentalnim podacima, što je potvrđeno visokim koeficijentom determinacije (0,971±0,022) i prihvatljivim srednjim relativnim procentnim odstupanjem (±15,9%). Stoga se ovaj model preporučuje za modelovanje kinetike metanolize suncokretovog ulja u prisustvu katalizatora na bazi kalcijuma u širokom opsegu reakcionih uslova.

Ključne reči: biodizel, katalizatori na bazi kalcijuma, kinetika, metanoliza, modelovanje