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Modeling the kinetics of calcium hydroxide catalyzed methanolysis of sunflower oil

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ABSTRACT

The kinetics of $\text{Ca}(\text{OH})_2$ -catalyzed methanolysis of sunflower oil was studied at a moderate temperature (60°C), a methanol-to-oil molar ratio (6:1) and different catalyst amounts (from 1% to 10% based on oil weight). The methanolysis process was shown to involve the initial triglyceride (TG) mass transfer controlled region, followed by the chemical reaction controlled region in the latter period. The TG mass transfer limitation was caused by the low available active specific catalyst surface due to the high adsorbed methanol concentration. Both the TG mass transfer and chemical reaction rates increased with increasing the catalyst amount.

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1. Introduction

The limited reserves of petroleum-based fuels and the scarcities of their use make renewable energy sources more attractive. An alternative diesel fuel is biodiesel, a biofuel defined as a mixture of monoalkyl esters of long chain fatty acids produced from triglycerides (TG) of fats and oils by alcoholysis with low molecular weight alcohols, primarily methanol, in the presence of a catalyst. Homogeneous base catalysts are commonly used for present industrial biodiesel production. These catalysts have to be removed from the final product with repeated washing with distilled water, which gives rise to generation of wastewaters. The drawbacks of homogeneous catalysts are overcome by using heterogeneous ones, which can be easily separated from the reaction mixtures and reused, have a less corrosive character and lead to safer, cheaper and more environment-friendly operations (Dossin et al., 2006a).

Many compounds have been checked as solid catalysts for the biodiesel synthesis such as metal oxides, hydroxides, and salts, zeolites, ion-exchanging resins, Mg–Al hydrotalcites, supported guanidines and metals. It is well known that basic catalysts are more active than acidic ones. Alkaline earth metal compounds have been reported in a number of studies as good heterogeneous cata-

lysts for the methanolysis reaction. Among them, calcium compounds such as CaO and $\text{Ca}(\text{OH})_2$ are inexpensive, less toxic and widely available (Arzamendi et al., 2008). CaO is shown to display a high catalytic activity for the methanolysis reaction (Arzamendi et al., 2008; Granados et al., 2007; Veljković et al., 2009). On the $\text{Ca}(\text{OH})_2$ catalytic activity there is no agreement among different investigators. According to Gryglewicz (1999), $\text{Ca}(\text{OH})_2$ does not catalyze the methanolysis reaction due to its weak base properties, while Arzamendi et al. (2008) and Kouzu et al. (2008) find out some catalytic activity of $\text{Ca}(\text{OH})_2$.

The kinetics of heterogeneously catalyzed methanolysis reaction has been rarely studied. The triolein methanolysis catalyzed by MgO was simulated by a three-step Eley–Rideal type of mechanism with the methanol adsorption on the catalyst active sites as the rate-determining step (Dossin et al., 2006a,b). The kinetics of metal oxide catalyzed soybean oil methanolysis at high temperatures was described by a simple first-order kinetic model with respect to TG (Wang and Yang, 2007) or methanol (Singh and Fernando, 2007). The order of the CaO - and $\text{Ca}(\text{OH})_2$ -catalyzed methanolysis with respect to TG changed from zero to one with the reaction progress (Kouzu et al., 2008). Veljković et al. (2009) reported a kinetic model of CaO -catalyzed methanolysis, which included the initial mass transfer controlled regime followed by the chemical reaction controlled regime close to the completion of the reaction.

In the present work the $\text{Ca}(\text{OH})_2$ -catalyzed methanolysis of sunflower oil was studied at the molar ratio of methanol to oil of 6:1 and 60°C . The methanolysis was catalyzed by the saturated methanolic $\text{Ca}(\text{OH})_2$ solution and solid $\text{Ca}(\text{OH})_2$ present in the

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Nomenclature

a_m	specific surface of catalyst (m^2/g)	TG	content of TG in the FAME/oil fraction of the reaction mixture (%)
A_1, A_2	parameters of Eq. (16)	TG_0	initial content of TG in the FAME/oil fraction (%)
c_A	concentration of TG in the oil phase (mol/dm^3)	Th	Thiele modulus, 1
c_{Ao}	initial concentration of TG (mol/dm^3)	V	volume of the reaction mixture volume, (cm^3)
c_B	concentration of methanol in liquid phase (mol/dm^3)	x_A	degree of TG conversion, 1
c_{cat}	catalyst amount based on the oil weight (%)	y	dependent variable in Eq. (16)
c_R	concentration of FAME (mol/dm^3)		
C	integration constant, 1		
k	effective pseudo-first-order reaction rate constant (min^{-1})	Greek symbols	
k_{app}	apparent process rate constant (min^{-1})	θ	fraction of the catalyst available active specific surface, 1
$k_{s,A}$	TG mass transfer coefficient towards catalyst surface active sites (m/min)	θ_0	fraction of the catalyst available active specific surface in the initial phase of the methanolysis process, 1
$k_{mt,A}$	volumetric TG mass transfer coefficient towards the catalyst surface ($= k_{s,A} \cdot \theta \cdot a_m \cdot \frac{m_{cat}}{V}$) (min^{-1})		
m_{cat}	mass of heterogeneous catalyst (g)	Abbreviations	
Q	the instantaneous concentration of adsorbed methanol (mol/g)	TG	triglycerides
t	time (min)	DG	diglycerides
t_0, t_1	parameters of Eq. (16) (min)	MG	monoglycerides
		FAME	fatty acid methyl esters

range from 1% to 10% (based on the oil weight). The main goals were to check the process mechanism, which was based on the mechanism of CaO-catalyzed methanolysis of sunflower oil reported by Veljković et al. (2009), and to model the methanolysis process kinetics using a simple model which did not require complex computations.

2. Theoretical background

The vegetable oil methanolysis reaction can be showed by the following generalized stoichiometric equation:



where A is TG, B is methanol, R is fatty acid methyl esters (FAME) and S is glycerol.

In the presence of heterogeneous catalysts, the methanolysis reaction is very complex because the reaction mixture is a three-phase system (oil–methanol–catalyst). Besides methanolysis, some side reactions occur too, such as saponification of glycerides and methyl esters, as well as neutralization of free fatty acids by an alkaline catalyst. For the purpose of modeling the process of methanolysis, the following assumptions are introduced:

- (1) The methanolysis reaction occurs between methoxide ions and glycerides adsorbed on the catalyst surface.
- (2) The contribution of homogeneous catalysis is negligible because $\text{Ca}(\text{OH})_2$ is practically insoluble in methanol (Gryglewicz, 1999).
- (3) The methanol mass transfer rate toward catalyst particles and the methanol adsorption rate on the catalyst surface active sites do not limit the overall process rate.
- (4) The glyceride mass transfer rate towards the catalyst surface active sites can influence the overall process rate in the initial reaction period.
- (5) The glyceride adsorption rate on the catalyst surface in the initial reaction period is determined by the glyceride mass transfer rate towards the catalyst surface active sites.
- (6) Methanol adsorption follows the pseudo-first-order kinetics.
- (7) In the later reaction period where there is no external mass transfer limitation, the overall process rate is limited by the rate of the reaction between methoxide ions and TG.

- (8) The conversion of TG follows the pseudo-first-order reaction kinetics. The supercritical and subcritical methanolysis of soybean oil catalyzed by nano-MgO (Wang and Yang, 2007) and methanolysis of sunflower oil catalyzed by CaO (Veljković et al., 2009) were described by the pseudo-first-order reaction kinetics.
- (9) The internal diffusion rate does not influence the methanolysis reaction rate;
- (10) The desorption rate of methanolysis products from the catalyst surface and their mass transfer rates into the liquid reaction mixture do not limit the overall process rate.
- (11) Since the reaction is carried out in a batch reactor, the reaction mixture is perfectly mixed and its composition and the catalyst spatial distribution are uniform.
- (12) The neutralization of free fatty acids is ignorable because of their negligible content in the sunflower oil. The oil used in the present study had <0.15% of free fatty acids.
- (13) The saponification reaction is negligible and the catalyst concentration remains almost constant during the methanolysis. When CaO (1.5%) was used as catalyst for the coconut oil methanolysis under reflux, the soap formation degree was 2.28% (Hartman, 1956). As $\text{Ca}(\text{OH})_2$ is weaker base than CaO (Gryglewicz, 1999), the lower soap formation degree is expected in the case of $\text{Ca}(\text{OH})_2$ -catalyzed methanolysis.

The influence of the methanol mass transfer rate towards catalyst particles on the overall process rate is determined from the mass balance of methanol on the solid catalyst surface (Veljković et al., 2009):

$$\frac{dQ}{dt} = \left[\left(-\frac{dc_B}{dt} \right) - \frac{dc_R}{dt} \right] \frac{V}{m_{cat}} \quad (2)$$

where c_B and c_R are the methanol and FAME concentrations in the liquid phase, respectively, Q is the methanol concentration at the catalyst surface, m_{cat} is the catalyst mass, V is the reaction mixture volume and t is time.

According to the above assumptions, the conversion of TG follows the pseudo-first-order reaction kinetics:

$$-\frac{dc_A}{dt} = k_{app} \cdot c_A \quad (3)$$

where c_A is the TG concentration in the liquid phase and k_{app} is the apparent rate constant which takes into account both the mass transfer and the chemical reaction rate as follows (Veljković et al., 2009):

$$k_{app} = \frac{k \cdot k_{mt,A}}{k_{mt,A} + k} \quad (4)$$

where k is the effective pseudo first-order reaction rate constant and $k_{mt,A}$ is the volumetric TG mass transfer coefficient defined as follows:

$$k_{mt,A} = k_{s,A} \cdot \theta \cdot a_m \cdot \frac{m_{cat}}{V} \quad (5)$$

where $k_{s,A}$ is the TG mass transfer coefficient, a_m is the active specific catalyst surface and θ is the fraction of the available active specific catalyst surface. The reactant mass transfer coefficient depends on the reaction mixture composition, the reaction temperature and the agitation speed. The available active specific catalyst particle surface is dependent not only on the specific catalyst particle surface but also on the availability of the active sites for the reactant mass transfer (via the parameter θ).

Since the TG concentration is related to the conversion degree of TG, x_A :

$$c_A = c_{A0}(1 - x_A) \quad (6)$$

Eq. (3) can be transformed into the following one:

$$\frac{dx_A}{dt} = k_{app}(1 - x_A) \quad (7)$$

The following equation is obtained by the integration of Eq. (7):

$$-\ln(1 - x_A) = k_{app}t + C \quad (8)$$

where C is the integration constant. The apparent rate constant and the integration constant can be calculated from the linear dependence of $-\ln(1 - x_A)$ on time as its slope and intercept, respectively.

The model of the methanolysis process applied involves two limiting situations as possible to happen. If $k_{mt,A} \ll k$, then:

$$k_{app} = k_{mt,A} \quad (9)$$

and

$$\frac{dx_A}{dt} = k_{mt,A}(1 - x_A) \quad (10)$$

Since for $t = 0$, $x_A = 0$, the following equation is obtained by integration of Eq. (10):

$$-\ln(1 - x_A) = k_{mt,A}t \quad (11)$$

This means that the overall methanolysis process rate is limited by TG mass transfer to active sites on the catalyst surface and, in accordance with Eq. (5), depends on the total amount of the catalyst.

When $k_{mt,A} \gg k$, then

$$k_{app} = k \quad (12)$$

and the chemical reaction between the adsorbed molecules of TG and methanol controls the overall process rate:

$$\frac{dx_A}{dt} = k(1 - x_A) \quad (13)$$

or upon integration

$$-\ln(1 - x_A) = k \cdot t + C \quad (14)$$

3. Methods

3.1. Materials

Refined, edible sunflower oil (Plima, Kruševac, Serbia) was used. The acid, saponification and iodine values of the oil were 0.29 mg

KOH/g, 190 mg KOH/g and 139 g I₂/100 g, respectively, determined by the AOCS official methods (AOCS, 1980). Certified methanol of 99.8% purity and Ca(OH)₂ of 96% purity were purchased from (Lachema, Neratovice, Czech Republic) and (Kemika, Zagreb, Croatia), respectively. Methanol, 2-propanol and *n*-hexane, all of HPLC grade, were obtained from LAB-SCAN (Dublin, Ireland). The HPLC standards for FAME containing methyl esters of palmitic, stearic, oleic, linolenic and linoleic acids (20% of each ester) as well as triolein, diolein and monoolein were purchased from Sigma Aldrich (Sent Luis, USA).

3.2. Catalyst preparation

Before use, Ca(OH)₂ was ground (3 × 3 min) in an electrical domestic grinder (PS-299, Elite). The average particle size of Ca(OH)₂ was 2.0 μm. The catalyst powder was stored in a dark, well closed, glass bottle in a desiccator containing calcium chloride and potassium hydroxide pellets.

3.3. Equipment

The reaction was carried out in a 250 mL three-neck glass flask fitted with a condenser and a two flat-blade paddle agitator, placed centrally close to the bottom. The impeller diameter was 30 mm. The flask was immersed in a glass chamber filled with water circulating from a thermostated bath by means of a pump.

3.4. Reaction conditions

The 6:1 molar ratio of methanol to sunflower oil was used in all experiments. The amount of Ca(OH)₂ (suspended into methanol before use) was in the range from 1% to 10% (based on the oil weight). The experiments were carried out at 60 °C and under the atmospheric pressure. The impeller speed of 900 rpm was applied to produce a uniform suspension of Ca(OH)₂. The homogeneously catalyzed reaction was carried out with the saturated methanolic Ca(OH)₂ solution. All experiments were carried in duplicates.

3.5. Experimental procedure

The suspension of methanol (10.14 g) and a desired amount of Ca(OH)₂ was first poured into the reactor and then placed in the glass chamber thermostated at 60 °C. The oil (45.96 g) which was thermostated separately was added to the reactor. As soon as the mechanical stirrer was turned on, the reaction was timed. For kinetic studies, the samples (1 mL) were taken out from the reaction mixture during the progress of the reaction, immediately quenched by adding an aqueous hydrochloric acid solution containing the stoichiometric amount required to neutralize Ca(OH)₂ and centrifuged (5000 rpm for 10 min). The upper layer was withdrawn, dissolved in 2-propanol/*n*-hexane (5:4 v/v) in an appropriate ratio (1:200) and filtered through a 0.45 μm Millipore filter. The resulting filtrate was used for HPLC analysis.

3.6. Internal and external mass transfer limitations

Due to a very small average particle size, the internal diffusion limitation was checked by a theoretical calculation based on the Thiele modulus value, using the experimentally determined value of the reaction rate constant. The external mass transfer limitation was studied at agitation speeds of 700, 900 and 1100 rpm using 10% of Ca(OH)₂ (based on the oil weight). The reaction temperature and the methanol to oil molar ratio were 60 °C and 6:1, respectively.

3.7. Analytical methods

3.7.1. Composition of the reaction mixture

The composition of the reaction mixture samples was determined by HPLC, as described elsewhere (Stamenković et al., 2007). The conversion degree of TG was calculated from the content of TG (in%) in the FAME/oil fraction of the reaction mixture, by the following equation:

$$x_A = 1 - TG/TG_0 \quad (15)$$

where TG_0 and TG are the initial and actual mass percentage of TG in the FAME/oil fraction, respectively.

3.7.2. Particle size measurements

The mean catalyst particle diameter was determined microphotographically. $\text{Ca}(\text{OH})_2$ powder (0.025 g) was suspended in paraffin oil (1 g) by a vortex agitator for 3 min. The microphotography was taken by a microscope equipped with a digital camera (Motic Digital Microscope DMB3-223ASC; magnification: 400 times). The mean catalyst particle diameter was calculated from the mean particle perimeter which was measured using the image software (Motic Images Plus v.2.0. Software).

4. Results and discussion

4.1. Methanolysis reaction analysis

The variations of the reaction mixture composition with the progress of the sunflower oil methanolysis reaction in the presence of different catalyst amounts are shown in Fig. 1. The shape of the curves representing the variations of FAME concentration in time was sigmoidal indicating three periods of the reaction. The sigmoidal shape of the FAME concentration in time has been already observed for homogeneously (Noureddini and Zhu, 1997; Stamenković et al., 2007, 2008; Vicente et al., 2005) and heterogeneously (Veljković et al., 2009) base-catalyzed methanolysis. In the initial stage of the process the formation of FAME was slow, then it increased in the medium stage and was getting slower as the reaction approached the completion. This shape indicated that the reaction was limited in the initial period, compared to the middle region. It is clear from Fig. 1 that the initial limitation was less emphasized at higher catalyst amounts. The FAME production rate increased and the initial slow period shortened with increasing the $\text{Ca}(\text{OH})_2$ amount, indicating that the methanolysis reaction took place on basic active sites on the solid catalyst surface. Also, during the homogeneously $\text{Ca}(\text{OH})_2$ -catalyzed methanolysis the increase of FAME content was negligible (confirming the assumption 2) because the calcium methoxide concentration in the reaction mixture was very small due to the very low solubility of $\text{Ca}(\text{OH})_2$ in methanol. Consequently, we assumed that $\text{Ca}(\text{OH})_2$ -catalyzed methanolysis occurred between methanol and glyceride molecules adsorbed on the surface catalyst active sites (assumption 1).

The TG concentration decreased and the FAME concentration increased with time in all experiments. The concentrations of intermediate products, monoglycerides (MG) and diglycerides (DG), increased at the beginning of the reaction achieving the maximum, then decreased and finally stayed nearly constant until the end of the reaction. Independently of the catalyst amount used for alcoholysis the final methyl esters yield was higher than 98%.

4.2. Internal and external mass transfer limitations

Both the intraparticle diffusion and external liquid–solid mass transfer limitations were checked before a true kinetic model

was assigned using the same procedure as before (Veljković et al., 2009).

If the internal mass transfer limitations exist, the diffusion of the reactants from the surface to the active sites within the catalyst particles controls the reaction rate. The presence of internal mass transfer limitations defines the effectiveness factor, which can be estimated from the Thiele modulus. In the present work, the values of the average particle size and the pseudo-first-order reaction rate constant for the catalyst amount of 10% were determined to be $2.0 \mu\text{m}$ and 0.070 min^{-1} , respectively. The effective diffusion coefficient was determined from the molecular diffusion coefficient and the porosity and the tortuosity of the catalyst particle. The values of the molecular diffusion coefficient of TG through methanol and TG were estimated by the Wilke and Chang correlation (Poling et al., 2004) to be 7.8×10^{-10} and $6.1 \times 10^{-11} \text{ m}^2/\text{s}$, respectively. For typical values for the porosity (~ 0.4) and the tortuosity (~ 3) of catalyst particle, the Thiele modulus value was calculated to be 0.001 or 0.004 for the diffusion of TG through methanol and TG, respectively. Due to very small Thiele modulus values (i.e. $Th \ll 0.4$) internal diffusion resistance was negligible, thus verifying the assumption 9.

If external liquid–solid mass transfer limitations exist, the reaction rate is controlled by the mass transfer of the reactant from the bulk liquid phase to the surface of the catalyst particles. The presence of external mass transfer limitation can be verified experimentally by studying the effect of agitation speed on the reaction rate under the same reaction conditions. The reaction was carried out at 700, 900 and 1100 rpm, which were higher than the minimum agitation speed providing perfect mixing and complete suspension of catalyst particles of 520 rpm as calculated by the correlation of Dossin et al. (2006b) for the amount of the catalyst of 10%. Fig. 2, where the conversion degree of TG is plotted as a function of time, indicates that both the reaction rate and the final reactant conversion degree were not influenced by the agitation speed, signifying the absence of external mass transfer resistance. The agitation speed of 900 rpm was chosen in order to compare the kinetics of methanolysis reactions catalyzed by $\text{Ca}(\text{OH})_2$ and CaO (Veljković et al., 2009).

The phenomena that occurred in the initial region of the $\text{Ca}(\text{OH})_2$ -methanolysis of sunflower oil have been already observed in the reaction catalyzed by CaO (Veljković et al., 2009). Initially, the catalyst surface active sites were occupied by methanol (see Section 4.4) which reduced the available active specific catalyst surface area. Therefore, the volumetric TG mass transfer coefficient was small (due to very small θ) and the TG mass transfer rate limited the overall reaction rate (the assumption 4). The breakage of methanol drops and their stabilization by surface active compounds formed in the reaction occurred. Because of the drop breakage process intensification, the frequency of the catalyst particle passage through the surface of the dispersed methanol drops increased. Because of four times larger volume of the oil than that of methanol, the residence time of catalyst particles in the oil phase was approximately four times longer. The higher frequency of the catalyst particle passage through the liquid–liquid interface and the longer residence time of the catalyst particles in the oil phase would cause the increase of the available active specific catalyst surface for the TG mass transfer towards the catalyst active sites with the progress of the methanolysis reaction. As the available active specific catalyst surface and the TG mass transfer rate increased, the importance of the external mass transfer limitation was reduced to nothing with the progress of the methanolysis process.

4.3. Kinetics of the methanolysis reaction

The time variation of the methanol concentration on the catalyst surface was calculated from the rates of methanol and the

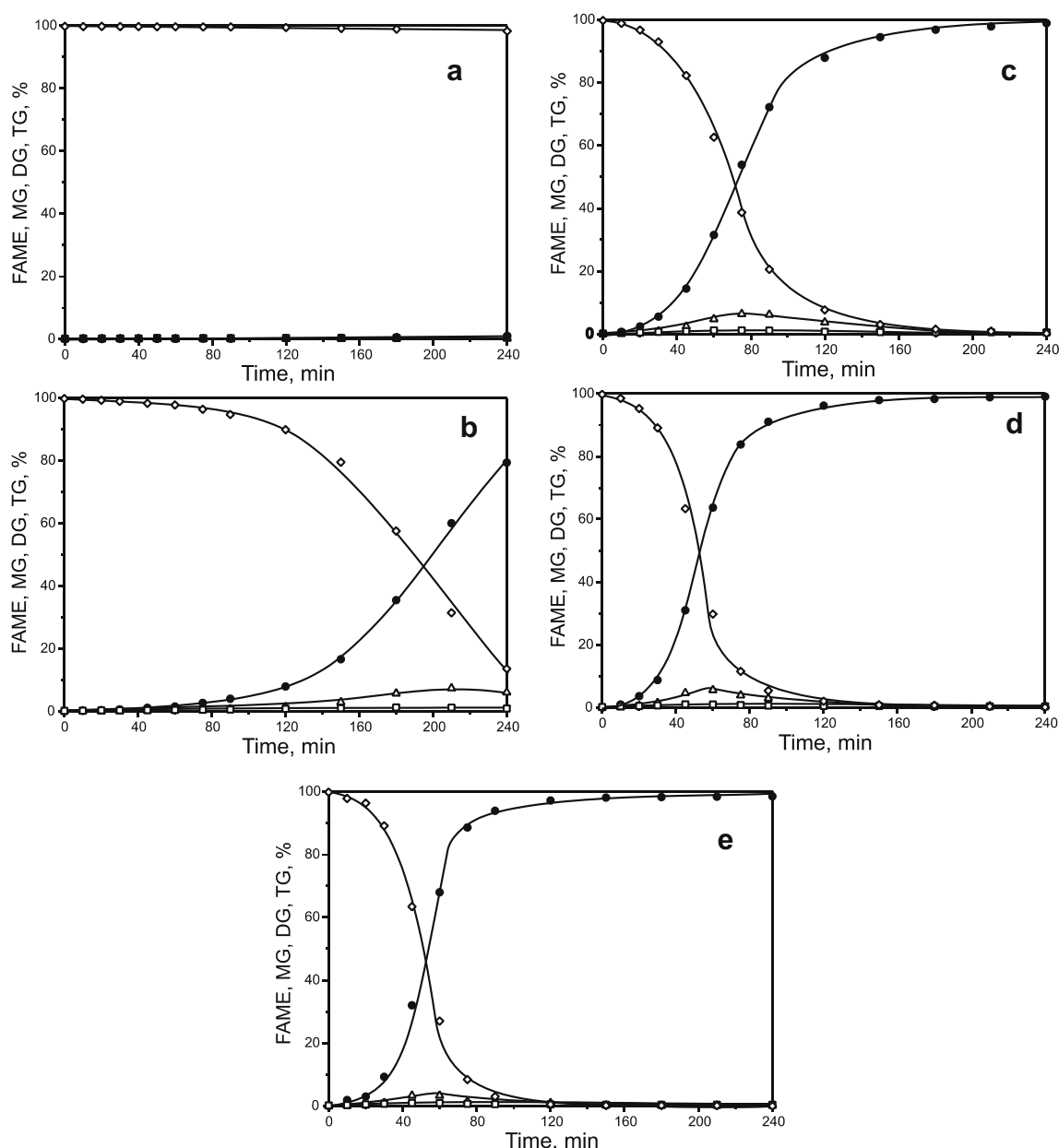


Fig. 1. The variations of the reaction mixture composition with the progress of $\text{Ca}(\text{OH})_2$ -catalyzed methanolysis of sunflower oil; catalyst amount, based on the oil weight, %: 0 (a); 1 (b); 2.5 (c); 5 (d) and 10 (e) (FAME (●); MG (Δ); DG (□) TG (◇)).

FAME concentration variation in the liquid phase by using Eq. (2). The experimental data on methanol and FAME concentrations in the liquid phase were firstly fitted using the following equation:

$$y = \frac{A_1}{1 + \exp\left(\frac{t-t_0}{t_1}\right)} + A_2 \quad (16)$$

where y is the methanol or FAME concentration and A_1 , A_2 , t_0 and t_1 are parameters calculated by a computer program. Then, the rates of methanol and FAME concentration variation, dc_B/dt and dc_R/dt , respectively were calculated from Eq. (16) by the same computer program. The variations of the concentration of methanol adsorbed on the catalyst surface active sites with the progress of the methanolysis reaction for different catalyst amount are shown in Fig. 3. The variation of dQ/dt with time was the same as that observed for the CaO -catalyzed methanolysis reaction (Veljković et al., 2009). Initially, the catalyst was saturated by methanol. After the addition

of oil to the catalyst-methanol mixture the conditions for the methanolysis reaction were made and the decrease in the concentration of the adsorbed methanol could be expected. In this period $dQ/dt \approx 0$ meaning that the chemical reaction was very slow. With the progress of the reaction $dQ/dt < 0$, indicating that the adsorbed methanol concentration decreased. The decrease of the methoxide ion concentration also indicated that the methanol adsorption was slower than the chemical reaction even though the methanol adsorption on liberated sites proceeded. However, the methanol adsorption did not limit the overall process because of the high adsorbed methanol concentration on the catalyst surface. On the basis of dQ/dt variation in this period, the kinetic regime change was assumed. The value of dQ/dt decreased in the initial phase, achieved the minimum and then increased. The slower decrease of the adsorbed methanol concentration in the initial period indicated a slow chemical reaction rate. Significantly, a faster decrease of the adsorbed methanol concentration in the next, relatively short phase

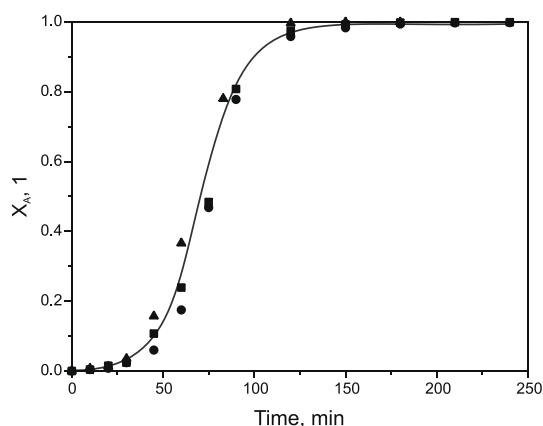


Fig. 2. The influence of the agitation speed on the conversion degree of TG (60 °C; methanol to oil ratio: 6:1; 10% of the catalyst based on the oil amount; agitation speed, rpm: 700 (●); 900 (▲) and 1100 (■)).

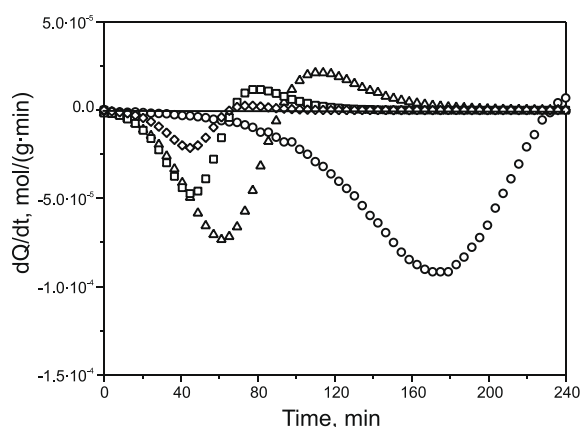


Fig. 3. The rate of the adsorbed methanol concentration variations on the catalyst active sites with the progress of $\text{Ca}(\text{OH})_2$ -catalyzed methanolysis (catalyst amount, based on the oil weight, %: 1 (○); 2.5 (Δ); 5 (□) and 10 (◇)).

denoted that the chemical reaction became faster. Therefore, we assumed that the kinetic regime changed at the moment when dQ/dt reached the minimum. In the further reaction progress $dQ/dt > 0$ considering that the methanol adsorption rate was faster than the chemical reaction. As a consequence, the mass transfer and the adsorption of methanol did not limit the methanolysis process at all, confirming the assumption 3. Finally, $dQ/dt = 0$, i.e. $Q = \text{const}$, indicating the reaction completion.

To analyze the kinetics of $\text{Ca}(\text{OH})_2$ -catalyzed methanolysis, the dependence $-\ln(1 - x_A)$ versus time is shown in Fig. 4. At different catalytic conditions, the dependences could be approximated with two line curves having a different slope in the initial and later reaction periods where the overall process, as proposed, was limited by TG mass transfer and by chemical reaction, respectively. The volumetric TG mass transfer coefficient ($k_{mt,A}$) and the effective pseudo-first-order reaction rate constant were calculated from the slope of linear curves in the initial and later reaction period, respectively.

The reaction period where TG mass transfer limited the overall process rate significantly shortened with increasing the catalyst amount. According to Eq. (5), this is the result of the TG mass transfer increase due to the increase of the active catalyst surface in the presence of a higher catalyst amount. The volumetric TG mass transfer coefficient increased with the reaction progress due to the increase of the available active catalyst surface (Eq. (5)) and the dependence $-\ln(1 - x_A)$ on time became nonlinear after a

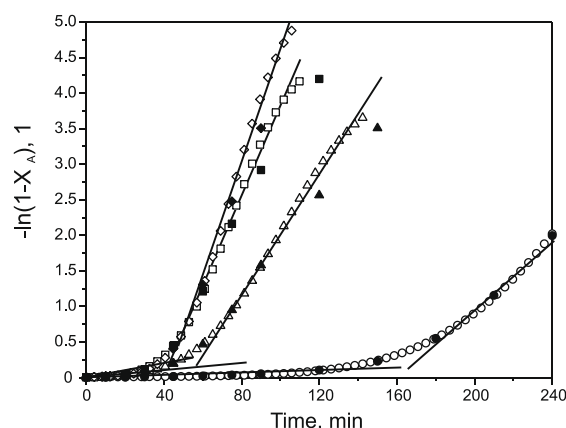


Fig. 4. Dependence $-\ln(1 - x_A)$ versus t during methanolysis (catalyst amount, based on the oil weight, %: 1 (○); 2.5 (Δ); 5 (□) and 10 (◇); irreversible pseudo-first-order reaction – straight lines; experimental data – solid symbols and sigmoidal fit – open symbols).

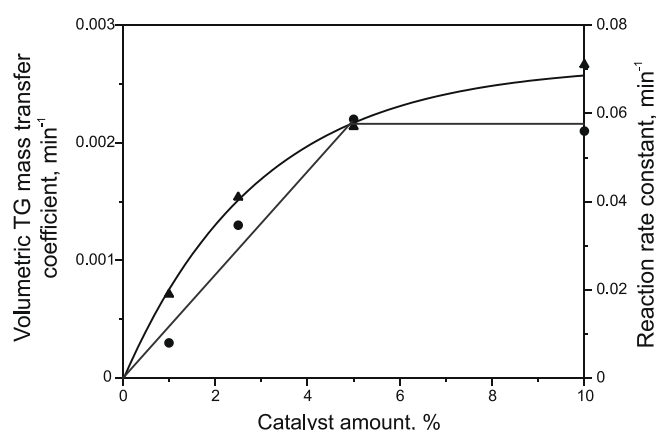


Fig. 5. The volumetric TG mass transfer coefficient (●) and the effective reaction rate constant (▲) at various catalyst amounts.

short period of time. At the moment corresponding to the minimum of dQ/dt , the volumetric TG mass transfer coefficient became higher than the chemical reaction constant, so in the final reaction period the chemical reaction controlled the overall process rate.

The volumetric TG mass transfer coefficient increased nearly proportionally with increasing the catalyst amount up to 5% of $\text{Ca}(\text{OH})_2$ and stayed constant at higher catalyst amounts (Fig. 5). The conclusion was drawn that in the presence of 10% of $\text{Ca}(\text{OH})_2$ the total active catalyst surface was not available for catalysis. It follows from Eq. (5) that the lumped parameter $k_{s,A} \cdot \theta_0 \cdot a_m$, as well as the value of θ_0 in the initial phase of the methanolysis process, was independent of the catalyst amount in the range from 1% to 5%. Based on Eq. (5) the values of $k_{s,A} \cdot \theta_0 \cdot a_m$ at different catalyst amount can be compared using the following equation:

$$k_{s,A} \cdot \theta_0 \cdot a_m = \frac{k_{mt,A} \cdot V}{m_{cat}} \quad (17)$$

The value of $k_{s,A} \cdot \theta_0 \cdot a_m$ was twice lower in the presence of 10% of the catalyst than in the presence of smaller catalyst amounts, meaning that the value of θ_0 at the highest catalyst amount was only 50% of that for the catalyst amount in the range from 1% to 5%. This decrease of the fraction of the available active specific catalyst surface in the initial phase of the methanolysis process was the result of the catalyst particles agglomeration in the higher catalyst amount, which was visually observed. Recently, Vujicic et al.

(2009) have shown by scanning electron microscopy pictures of fresh and used CaO catalyst that particle agglomeration really occurs during vegetable oil methanolysis.

The effective pseudo-first-order reaction rate constants were calculated from the slope of relation $-\ln(1-x_A)$ on time in the final process period. As can be seen in Fig. 5, the effective reaction rate constants are increased exponentially as the catalyst amount is increased from 1% to 10% (based on the oil weight). This observation practically meant that all adsorbed glycerides and methanol molecules did not react, and that with increasing the catalyst amount, the possibility of adsorbed molecules for the reaction enhanced. The dependence on the effective rate constant of the catalyst amount was described by the following equation:

$$k = 0.07 \left[1 - \exp \left(-\frac{C_{cat}}{2.86} \right) \right] \quad (18)$$

where C_{cat} is the catalyst amount (in% based on the oil weight).

Such a phenomenon was previously observed for homogeneous (Vicente et al., 2005) and heterogeneous (Wang and Yang, 2007) catalyzed methanolysis of different vegetable oils. In the case of homogeneous methanolysis, the effective rate constant increased linearly with the catalyst concentration (Vicente et al., 2005, 2006). Wang and Yang (2007) showed that the rate constants of the heterogeneous supercritical and subcritical methanolysis of soybean oil catalyzed by nano-MgO were improved as the content of nano-MgO increased from 0.5% to 3% and remained almost identical when the catalyst content was further enhanced to 5%. On the other hand, the reaction rate constant in the case of CaO-catalyzed methanolysis practically did not depend on the catalyst amount in the same range (Veljković et al., 2009).

4.4. Simulation of the methanolysis reaction

The variations of the TG conversion degree with the reaction time were satisfactorily described by the sigmoidal fit of the same form as Eq. (16). The relative deviations of calculated (based on the sigmoidal fit) and experimental TG conversion degree were ± 13.9 , ± 2.1 , ± 2.0 and 4.5% in the methanolysis reaction catalyzed by $\text{Ca}(\text{OH})_2$ amounts of 1%, 2.5%, 5% and 10%, respectively.

The applicability of the kinetic model was verified by comparison on the experimental and calculated values of the TG conversion degree. Based on the kinetic model, the TG conversion degree was calculated from the following equations:

- for TG mass transfer controlled regime ($k_{mt,A} = \text{const}$)

$$x_A = 1 - \exp(-k_{mt,A}t) \quad (19)$$

- for chemical reaction controlled regime

$$x_A = 1 - \exp(-kt - C) \quad (20)$$

The relative deviations of the calculated TG conversion degree, based on the kinetic model in the reaction period when it was applicable, and the experimental values were ± 13.0 , ± 11.0 , ± 7.1 and $\pm 6.0\%$ at $\text{Ca}(\text{OH})_2$ amounts of 1%, 2.5%, 5% and 10%, respectively.

Fig. 6 shows the comparison of the experimental data and the kinetic model via the variations of the molar concentrations of TG and FAME. The molar TG concentration was calculated by Eq. (6) and the molar FAME concentration was calculated using the TG conversion degree corrected for the MG and DG formation. As can be seen from Fig. 6, the kinetic model agrees well with the experimental data in the initial and later reaction periods but not in the period when FAME formation rate rapidly increased, indicat-

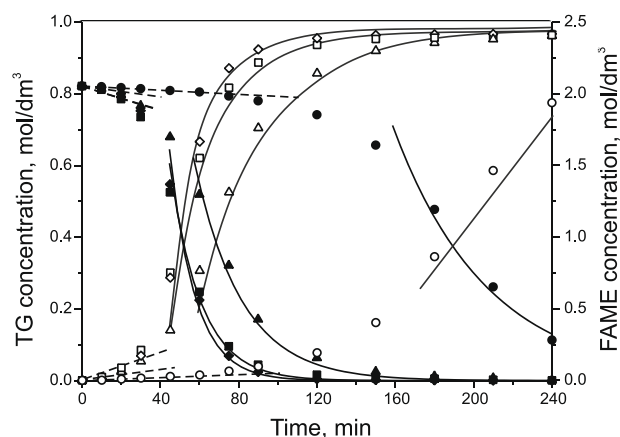


Fig. 6. The comparison of TG and FAME concentrations calculated by the kinetic model (mass transfer: —, chemical reaction: ---) with the experimental data (TG – solid symbols and FAME – open symbols) during the methanolysis (catalyst amount, based on the oil weight, %: 1 (○); 2.5 (Δ); 5 (□) and 10 (◇)).

ing that in this reaction period both the TG mass transfer and the chemical reaction control the overall process kinetics. Such results were previously obtained for CaO-catalyzed sunflower oil methanolysis (Veljković et al., 2009).

5. Conclusions

The methanolysis of sunflower oil catalyzed by $\text{Ca}(\text{OH})_2$ was studied in order to model the methanolysis reaction kinetics and to check the reaction mechanism. Based on the mechanism of the reaction, which occurred on the surface catalyst active sites between adsorbed methanol and glyceride molecules, the reaction kinetics was modeled using a simple model. The overall chemical reaction followed the pseudo-first-order reaction kinetics. The kinetics of methanolysis process was described by initial TG mass transfer limitations, followed by the kinetically controlled region in the latter reaction period. The TG mass transfer limitations were related to the small available active specific catalyst surface, which was mainly covered by adsorbed molecules of methanol in the initial reaction period. Thus, the mass transfer limitation was important at the lower catalyst amount (1% and 2.5% based on the oil weight) while it significantly decreased at the higher catalyst amount. At the highest catalyst amount (10% based on the oil weight) the TG mass transfer was also limited by agglomeration of the catalyst particles.

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