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KINETICS OF HETEROGENEOUS METHANOLYSIS OF SUNFLOWER OIL WITH CaO·ZnO CATALYST: INFLUENCE OF DIFFERENT HYDRODYNAMIC CONDITIONS

Article Highlights
- Heterogeneous methanolysis of sunflower oil using CaO·ZnO catalyst
- Influence of different hydrodynamic conditions on overall rate of methanolysis
- Mathematical modeling of triglycerides methanolysis
- Resistance of mass transfer and chemical reaction at different hydrodynamic conditions
- Correlation defining interfacial area between oil and methanol for three-phase system

Abstract

The kinetics of heterogeneous methanolysis of sunflower oil was studied at 60 °C using mechanochemically synthesized CaO·ZnO as catalyst. The influence of agitation speed, catalyst amount, and methanol-to-oil molar ratio on the rate of reaction was analyzed. The rate of the process depends on the two resistances - mass transfer of triglycerides to the catalyst surface and chemical reaction on the catalyst surface, which are defined as the values of the overall triglyceride volumetric mass transfer coefficient, $k_{mt,TG}$, and the effective pseudo first-order reaction rate constant, k, respectively. These kinetic parameters actually determine the value of the apparent reaction rate constant, k_{app}, the time dependence of which is defined by the change of triglyceride (TG) conversion. A kinetic model is proposed and the model parameters are determined.

Keywords: biodiesel, heterogeneous catalyst, kinetics, model, CaO, ZnO.

Biodiesel consisting of fatty acid methyl esters (FAME) is considered to be a promising alternative fuel with properties similar to conventional diesel fuels. It is usually produced from renewable sources by methanolysis of vegetable oils or animal fats in a presence of a catalyst. Although homogeneous base catalysts are most commonly used for biodiesel synthesis, a heterogeneous catalyst could be a better choice since it is easily separated from the reaction mixture by filtration, regenerated, and has a less corrosive character, leading to safer, cheaper and more environment-friendly operation [1,2].

Among various heterogeneous catalysts, CaO is one of the most widely used in research [3-12]. Its properties regarding the leaching of the catalyst could be improved by fixing it to some support, e.g. silica [13] or alumina [14], or mixing with other oxides of which the mixture of CaO and ZnO oxides showed excellent activity under moderate reaction conditions [15-19].

The reaction kinetics of heterogeneous catalyzed methanolysis, as fundamental to reactor design, was the subject of several studies [20-26] and usually described by a first-order kinetic model. Heterogeneously catalyzed methanolysis reaction is very complex because it occurs in a three-phase system consisting of a solid (catalyst) and two immiscible liquid phases (oil and methanol), so combinations of different chemical and physical processes will affect its kinetics. The TG mass transfer resistances play important role at the beginning of the process, while in

the later stage the rate of process is governed by chemical reaction at catalyst surface.

Different variables influence the rate of reaction, and among them the amount of catalyst, the molar ratio of methanol to oil, the reaction temperature and the agitation intensity seem to be the most important. Agitation allows better contact between the reactants and contributes to the breakage of methanol drops thus causing the increase in the specific interfacial area between methanol and oil [27]. The agitation intensity influences only the initial step of methanolysis during which mass transfer conditions dominate the system and mass transfer limitation is effectively minimized at agitation speeds of 400−600 rpm [28] and is not significant using 600 rpm [29].

Stoichiometrically, the methanolysis of vegetable oil requires three moles of methanol (MeOH) for each mole of oil (TG). However, in practice a higher molar ratio is employed in order to shift the reaction equilibrium towards the products side and produce more methyl esters. Heterogeneously catalyzed methanolysis was studied in the wide range of molar ratio, from 4:1 to 50:1.

Since in the case of heterogeneous catalysis the reaction occurs at the active sites of the catalyst, the amount of the catalyst affects strongly the rate of reaction. With higher amount of the catalyst, the active specific catalyst surface where the reaction takes place is higher allowing faster reaction.

The present work investigates the effect of catalyst amount, stirring speed, and methanol:oil molar ratio on the rate of heterogeneous methanolysis of sunflower oil using mechanochemically synthesized CaO·ZnO as catalyst. The rate of methanolysis may be presented as irreversible pseudo-first order reaction with the variable apparent rate constant k_{app}, which takes into account the overall volumetric mass transfer coefficient, $k_{mt,TG}$, which is the function of triglycerides conversion, and the reaction rate constant, k. The change of k_{app} with time is defined with the change of FAME yield with time. A kinetic model is proposed and model parameters are determined for different working conditions.

Theoretical background

The overall reaction of triglycerides (TG) methanolysis occurs as a sequence of three reversible consecutive reactions where TG molecule converts into diglyceride (DG), monoglyceride (MG) and glycerol (GLY), while in each step one mole of FAME is produced.

$$TG + MeOH \rightarrow DG + FAME \qquad (1)$$

$$DG + MeOH \rightarrow MG + FAME \qquad (2)$$

$$MG + MeOH \rightarrow GLY + FAME \qquad (3)$$

When the concentrations of diglyceride and monoglyceride formed in complex series-parallel reactions, Eqs. (1)-(3) are negligible, this complex reaction could be represented as only one reaction with following equation:

$$TG + 3MeOH \rightarrow 3FAME + GLY \qquad (4)$$
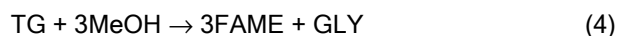
Due to the high molar ratio of methanol to oil the concentration of adsorbed methoxide ion at catalyst surface can be assumed constant and the rate of methanolysis may be presented as irreversible pseudo-first order reaction:

$$(-r_{TG}) = kc_{TG,v} \qquad (5)$$

where $c_{TG,v}$ is the triglyceride concentration very close to the active centers of catalyst (in methanol phase) and k is the reaction rate constant for pseudo-first kinetic model.

The molecules of triglycerides must be transferred from the liquid phase close to the active centers of catalyst, and the mass transfer rate must be equal to the reaction rate between TG and methanol at catalyst surface:

$$\Phi_{MT}a = (-r_{TG}) = k_{mt,TG}(c_{TG} - c_{TG,v}) \qquad (6)$$

After elimination of the unknown concentration $c_{TG,v}$ from Eqs. (5) and (6), it is possible to write the rate of triglyceride methanolysis in the simple form:

$$(-r_{TG}) = k_{app}c_{TG} \qquad (7)$$

The rate of the process depends on the two resistances - the resistance of mass transfer to the catalyst surface of TG and resistance of chemical reaction on the catalyst surface, which are defined as the values of the overall triglyceride volumetric mass transfer coefficient, $k_{mt,TG}$, and the effective pseudo first-order reaction rate constant, k, respectively. The mechanism of methanolysis process based on the use of CaO·ZnO as a heterogeneous catalyst is defined according to the Eley-Rideal model and has recently been reported in detail [30].

The apparent reaction rate constant, k_{app}, depends on the value of the mass transfer coefficient of TG from oil to methanol phase, $k_{mt,TG}$, and on the reaction rate constant, k:

$$k_{app} = \frac{kk_{mt,TG}}{k_{mt,TG} + k} \qquad (8)$$

Very complex three-phase system (L-L-S), where the heterogeneously catalyzed methanolysis takes place, consists of a solid (catalyst) and two

immiscible liquid phases (oil and methanol). In such liquid-liquid-solid system the mass transfer resistance at the liquid-liquid interface, $1/(ak_{d,TG})$, bulk of liquid phase, $1/(am_{TG}k_{c,TG})$, and liquid-solid interface, $1/(a_s m_{TG} k_{s,TG})$ are connected in series. The overall volumetric mass transfer resistance represents the sum of all above mentioned resistances and the overall volumetric mass transfer coefficient can be calculated using Eqs. (9) and (10):

$$\frac{1}{k_{mt,TG}} = \frac{1}{a}\left(\frac{1}{k_{d,TG}} + \frac{1}{m_{TG}k_{c,TG}} + \frac{1}{a_s m_{TG} k_{s,TG}}\right) =$$
$$= \frac{1}{ak_{mt,TG}^s} \tag{9}$$

$$\frac{1}{(k_{mt,TG})_0} = \frac{1}{a_0 k_{mt,TG}^s} \tag{10}$$

By dividing Eq. (9) and (10) the following relation is valid:

$$\frac{1}{k_{mt,TG}} = \frac{a}{a_0 (k_{mt,TG})_0} \tag{11}$$

The overall volumetric mass transfer coefficient, $(k_{mt,TG})_0$, at the beginning of the process depends on interfacial area, a_0, between the oil and methanol. In this study, for the analysis of different working parameters, which define increase of interfacial area with conversion of triglycerides, a correlation proposed in a recently published paper [30] was used:

$$\left(\frac{a}{a_0}\right) = 1 + \alpha X_{TG}^{\beta} \tag{12}$$

Thus, the proposed correlation assumes that the overall volumetric mass transfer coefficient, $k_{mt,TG}$, is a function of triglycerides conversion [30]:

$$k_{mt,TG} = (k_{mt,TG})_0 (1 + \alpha X_{TG}^{\beta}) \tag{13}$$

The main idea of this study was to test this correlation and to investigate dependence of kinetic parameters, which define the rate of mass transfer ($(k_{mt,TG})_0$, α and β) on mixing intensity, the mass of catalyst, and ratio of methanol to oil used for methanolysis. Formation of even small amounts of MG and DG act as surface-active compounds and increase the rate of mass transfer from beginning of triglyceride conversion. The final or maximal value of mass transfer coefficient is for $X_{TG} = 1$, $(k_{mt,TG})_{max} = (k_{mt,TG})_0 (1 + \alpha)$. At the end of the methanolysis process, the formed glycerol and methanol are competitive compounds for creating at the active site of catalyst glyceroxide or methoxide ions. It means that

for theoretical analysis of mass transfer resistance it must be taken into account the mass transfer coefficient of TG through methanol as dispersed phase at the beginning of process and through the mixture of methanol and glycerol at the end of reaction. A creation of new type of dispersion (from methanol–oil to methanol/glycerol–FAME) will stabilize the interfacial area of the L-L system to the some new and finite value of average drop size.

The assumptions defined by Eqs. (12) and (13) indicate that for some conversion of triglycerides, X_{TG}, as a consequence of DG, MG, glycerol and FAME formation, the mass transfer rate (i.e. the volumetric mass transfer coefficient) starts to be equal or in some cases even higher than the chemical reaction at catalyst surface (i.e. the reaction rate constant, k), and then, the chemical reaction at catalyst surface start to control the overall process rate [30].

The goal of this study is to analyze the influence of different hydrodynamic conditions in batch process (mixing intensity, different molar ratio of methanol and oil, mass of used catalyst) to the value of apparent reaction rate constant. The value of initial mass transfer coefficient was calculated according to corresponding theory and correlations reported in literature and compared to the value determined after fitting experimental data of X_{TG} versus time by optimal simulation curves.

EXPERIMENTAL

Catalyst preparation

CaO (obtained by calcination of lime originated from southern part of Serbia) and ZnO (Kemika, Zagreb, Croatia) were used for catalyst synthesis. Mechanochemical treatment was carried out in the planetary ball mill Fritsch Pulverisette 5, in air atmosphere. Two zirconia vials of 500 cm^3 volume each charged with 500 g zirconia 10 mm diameter balls were used as milling medium. The balls to powder mass ratio was approximately 30. A powder mixture of CaO and ZnO, in the molar ratio of 1:2 with stoichiometrically required addition of water, was used as starting materials for mechanochemical treatment. Milling was done for 1 h and subsequently for 2 h with angular velocities of basic disc, measured by tachometer, of about 150 rpm (15.7 rad s^{-1}) and 250 rpm (26.2 rad s^{-1}), respectively.

Catalyst characterization

Catalyst was characterized by various analytical procedures. X-ray powder diffraction, XRD (Philips PW1710 diffractometer using CuKα graphite-mono-

chromatized radiation (λ = 1.5418 Å) in the 2θ range 4−65° (step-length: 0.02° 2θ, scan time: 5 s) was used to investigate phase composition of the samples after mechanochemical treatment and subsequent calcinations. Scanning electron microscopy/energy-dispersive spectroscopy, SEM/EDS (JEOL JSM-6610LV equipped with and energy dispersive X-ray spectrometer) was applied to analyze sample morphology and elemental chemical analysis. Particle size distribution was measured by particle size laser diffraction distribution, PSLD (Mastersizer 2000, Micro Precision Hydro 2000 µP sample dispersion unit, Malvern Instruments Ltd.). The base strength of the samples (H-) was determined using following Hammett indicators: phenolphthalein (H- = 9.3), thymolphthalein (H- = = 10.0), thymolviolet (H- = 11.0) and 4-nitroaniline (H- = 18.4). The solubility of the catalyst in methanol at 60 °C was determined by measuring the calcium(II) and zinc(II) concentration (HITACHI Z-2000 polarized atomic absorption spectrophotometer).

Methanolysis reaction

The catalytic activity was evaluated in the methanolysis of commercial edible sunflower oil (Dijamant, Zrenjanin, Serbia; acid value of 0.29 mg KOH g^{-1}) and methanol (99.5% purity, Fluka, Switzerland).

All the experiments were conducted in 1 liter jacketed glass reactor Series 5100 (Parr, USA) equipped with a heater and a mixer, as shown in Figure 1a. Heating of reaction mixture was achieved by a SE-6 heating circulator (Julabo, Germany) equipped with a PID controller and an external Pt100 sensor placed inside of reaction mixture. Recording of measured

temperature values was obtained trough a RS232 interface for PC connection. The pressure in the reactor was monitored by data acquisition system and computer using a Pressure Meter F-502C (Bronkhorst, Nederland). Stirrer speed was controlled by a 4836 Controller (Parr, USA).

Figure 1b shows a typical pressure and temperature heating profile in the reactor during the experiment. In the initial stage of heating, the stirrer speed was set to 100 rpm to ensure uniform heating of the reaction mixture and prevent possible hot spots on inner wall of the reactor. It might be seen that a temperature of 60 °C is reached in less than 40 min. The moment when the temperature of 60 °C in reactor is reached indicates the beginning of sunflower oil methanolysis (t = 0). The temperature in reactor slowly increased to 60.8 °C over the following 15 min, and after 10 min stabilized to 60 °C. For t = 0, the stirrer speed was also increased to the desired value (1000 or 300 rpm) and temperature and intensity of mixing were maintained at the same value until the end of the experiment.

The following standard conditions (S.C.) for analysis influence of different hydrodynamic conditions were used in this study: 60 °C, 2 wt.% of CaO·ZnO catalyst based on oil, 300 rpm stirring intensity in batch reactor, and molar ratio of methanol to sunflower oil of 10:1. Methanolysis of sunflower oil at 60 °C was performed to find the effect if higher mixing intensity (1000 rpm), the smaller mass of catalyst (1 and 0.5 wt.%) or lower molar ratio od reactant (6:1) is used for FAME synthesis.
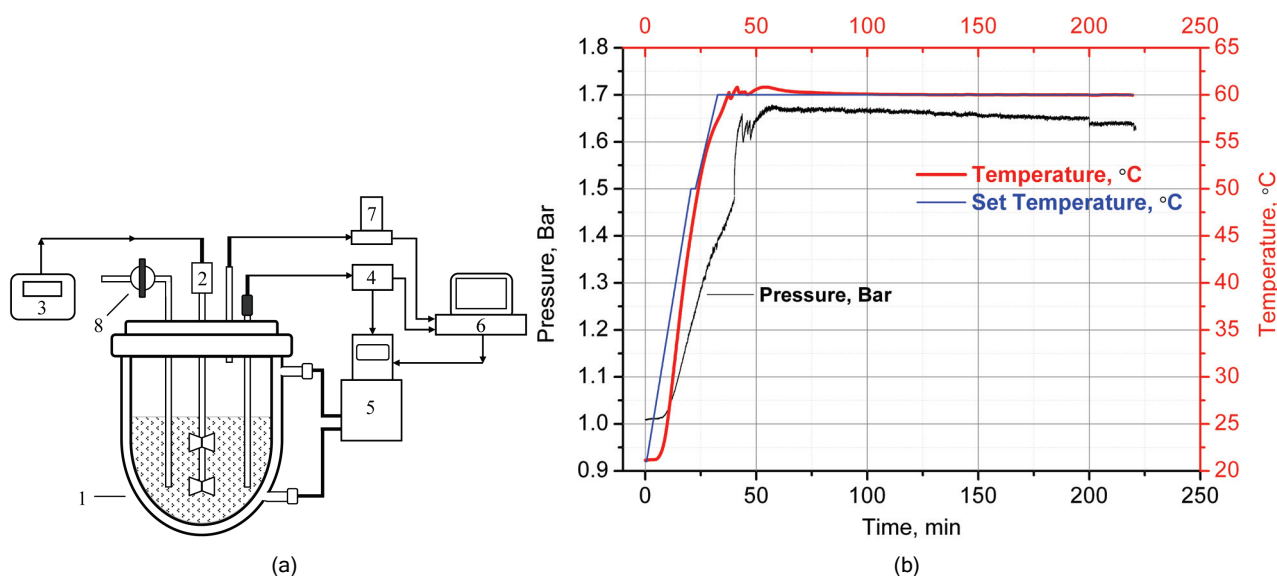

Figure 1. a) Experimental set-up: 1. jacketed glass reactor; 2. stirrer; 3 stirrer controller; 4. PC interface; 5. Heating unit; 6. PC; 7. pressure transducer; 8. valve for sample withdrow from reactor. b) Control of temperature and pressure in reactor.

The samples were taken out of the reactor at different reaction times, and after filtration, analyzed by gas chromatography (Varian 3400) equipped with an FID detector, on-column injector and MET-Bio-diesel capillary GC column (14 m×0.53 m, film thickness 0.16 μm).

RESULTS AND DISCUSSION

Catalyst characterization

Detailed characterization of prepared catalyst has recently been reported [30] and only a short overview of these results is reported in this paper.

The XRD analysis indicated that the bulk composition of mechanochemically prepared catalyst consisted of calcium zinc hydroxide hydrate (CaZn$_2$(OH)$_6$·2H$_2$O) and some amount of ZnO phases. It was concluded that about 20% of ZnO remained as unreacted, while corresponding CaO or Ca(OH)$_2$ are dispersed into the powder matrix. After calcination at 700 °C only CaO and ZnO phases were revealed. The SEM images of CaO·ZnO catalyst indicated the existence of the agglomeration of small round-shape particles, including nanoparticles. The small particles were merged together giving large agglomerates. The atomic Zn/Ca ratios detected using EDS are around 2.2, which is close to the theoretical values suggesting very fine CaO·ZnO composite powder.

The particle size distribution of the catalyst is within the size range of 0.2-3 μm and the rest is within the range of 3-100 μm. The median particle size decreased from 6.9 to 4.3 μm after calcination at 700 °C and the specific surface area increased from 1.97 to 3.1 m² g^{-1}.

The result of Hammet titration (basic strength of 9.3-10) also suggested that the catalyst contains different types of surface basic sites.

The amount of Ca^{2+} present in methanol has been investigated after the contact of catalyst with methanol at 60 °C for 2 h and catalyst removal. The result showed that the concentration in methanol of dissolved Ca^{2+} was 62 mg L^{-1}. To compare this value to the leaching of pure CaO, the same analysis has been done with the pure CaO used for catalyst synthesis. In this case, concentration of dissolved Ca^{2+} was 91 mg L^{-1}. Other authors [12] reported that the solubility of Ca^{2+} was 96 and 121 mg L^{-1} after 1 and 3 h contact time of Ca^{2+} and methanol, respectively. Very fine composite powder is most likely the reason for the lower solubility of the obtained catalyst in methanol.

Analysis of the reaction mixture composition

Results of the reaction mixture composition analysis showed that in all cases the amount of formed MG was minimal, while the identified amount of DG was up to 12% (Figure 2). Data presented in Table 1 indicate time necessary to obtain complete conversion of TG (depending on the working conditions) and time when amount of MG and DG reached their maximal value in reaction mixture.

Influence of stirring intensity on the methanolysis of sunflower oil

The reaction rate in initial stage of the process is controlled by the mass transfer of the reactant from the bulk liquid phase to the surface of the catalyst particles [30]. The role of the mass transfer is usually studied through the effect of agitation speed on the reaction rate of TG conversion under the same other reaction parameters.

The *S*-shape of the curve representing the variations of TG conversion versus time for methanolysis of sunflower oil (SO) at 60 °C with different agitation speed (Figure 3) indicate that the change of mechanisms which determine the rate of process obviously exists. For the purpose of simulation and modeling of X_{TG} versus time the Matlab software package was used, and the values of the model parameters based on the complex process mechanism were optimized. Model parameters α, β, k and $k_{mt,0}$ (*i.e.*, $(k_{mt,TG})_0$) for methanolysis of SO at S.C. are given in Table 2 and corresponding simulation curves (solid lines) are shown in Figure 3.

In the initial phase of the process at S.C., the immiscibility of methanol and vegetable oil causes slow mass transfer and represents important resistance in the overall rate of vegetable oil transesterification. The mass transfer of TG from the oil phase towards the methanol/oil interface limits the rate of methanolysis reaction and controls the kinetics at the beginning of the reaction. Moreover, the mass transfer in liquid-liquid system (methanol-oil) is related to the drop size of the dispersed phase, which is rapidly reduced with the progress of the methanolysis reaction. The size of drops are stabilized to the final minimum value by creating even small amounts of surface active compounds (MG and DG) and causing the increase of the interfacial area available for mass transfer. Finally, after a certain degree of TG conversion the fast increase of the overall process rate is usually detected.

The data presented in Figure 2 prove conclusion that formation of even small quantities of DG and MG are crucial for creation a large interfacial area between
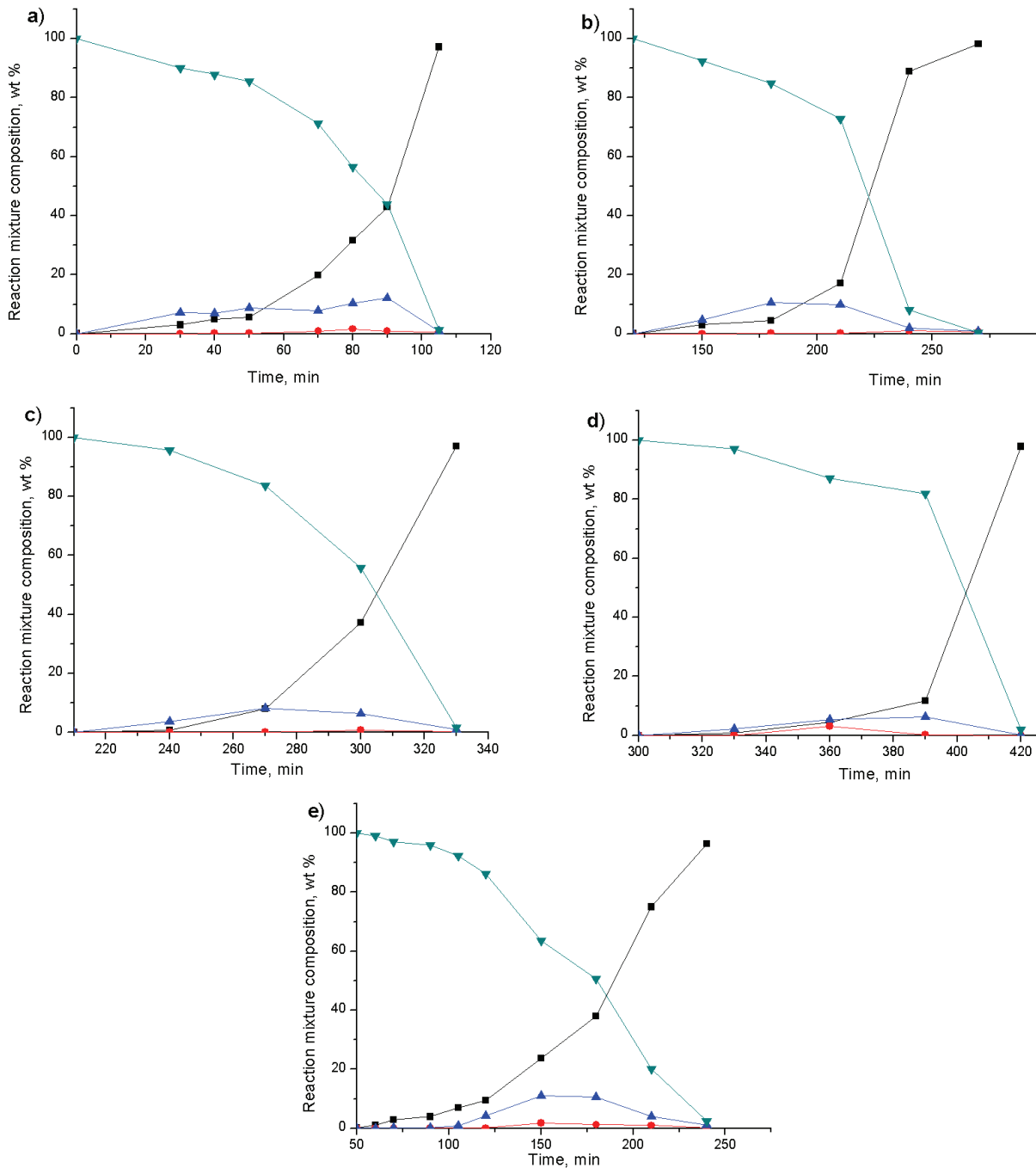
Figure 2. The variation of the reaction mixture composition with time; a) methanol:oil = 10:1, 2 wt.% of catalyst, 1000rpm; b) methanol:oil = 6:1, 2 wt.% of catalyst, 1000 rpm; c) methanol:oil = 10:1, 1 wt.% of catalyst, 1000 rpm; d) methanol:oil = 10:1, 0.5 wt.% of catalyst, 1000 rpm; e) S.C. - methanol:oil = 10:1, 2 wt.% of catalyst, 300 rpm; Used symbols: ■ - FAME; ● - MG; ▲ - DG; ▼ - TG.

Table 1. Methanolysis of sunflower at 60 °C - working conditions

Experiment	Methanol:oil mole ratio	Mass of used catalyst, wt.%	Stirring intensity, rpm	DG,max time, min	MG,max time, min	Maximal yield of FAME time, min
1	10:1	2	1000	12.1/90	1.55/80	97.2/105
2	6:1	2	1000	10.5/180	0.97/240	98.2/270
3	10:1	1	1000	8.2/270	0.76/300	97.1/330
4	10:1	0.5	1000	6.3/390	3.11/360	97.9/420
5 (S.C.)	10:1	2	300	11.1/150	1.7/150	96.5/240

Table 2. Determined reaction rate constants for methanolysis of sunflower oil

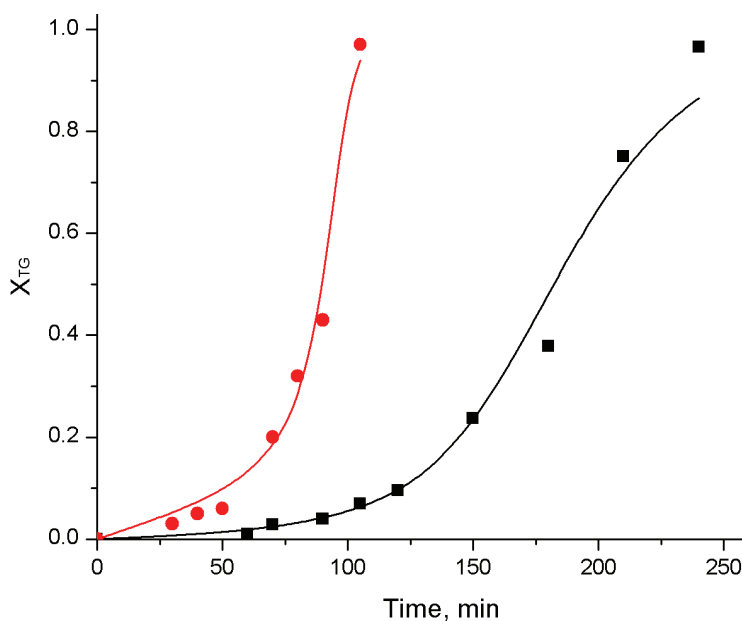| Kinetic parameter	Mixing intensity	
	1000	300 (S.C.) [30]
k / min^{-1}	0.530	0.043
α	210	378
β	2.35	1.37
$k_{mt,0}$ / min^{-1}	0.0017	0.000205
Standard deviation, σ	0.0481	0.0419

Figure 3. Triglyceride conversion vs. time as a function of agitation speed at 60 °C, methanol:oil molar ratio 10:1, catalyst amount 2 wt.%. Legend: solid lines - simulation curve calculated using optimal values of kinetic parameters; ● – 1000; ■ – 300 rpm.

oil and methanol. Experimental data and performed calculation of mass transfer resistances (Appendix) also indicated that at 1000 rpm the methanol–oil dispersion is stabilized by formation of very fine drops of dispersed (methanol) phase. At higher agitation speeds (1000 rpm) breakage is more rapid than coalescence of drops causing decrease of average drop size. The Sauter mean drop diameter d_{32} could be calculated according to the equation proposed by Stamenkovic *et al.* [36]: $d_{32} = 4782n^{-1.825}$ (Appendix) indicating that its decrease is from 0.144 to 0.016 mm. However, theoretical analysis and calculation showed that the Sauter mean size of 0.144 mm must result in almost 2.5 times larger value of $k_{mt,0}$ (0.0038 instead 0.0017 min^{-1}, determined from simulation curve). It must be noted that the equation given by Stamenkovic *et al.* [36] was derived for an L-L system (homogeneous methanolysis); however, this study concerns an L-L-S system, which could be the main reason for the observed difference.

The value of apparent reaction rate of methanolysis process is thus affected by the presence of

formed surface-active compounds by TG methanolysis (DG and MG). Also, it depends on transferred energy into reaction mixture by mixing, which plays an important role in breakage of dispersed phase drops. However, the obtained results showed that agitation speed also significantly affects the slope of the curve which represent the TG conversion versus time (Figure 3). It means that increasing stirring intensity from 300 to 1000 rpm is important for better utilization of available catalyst surface. It was found that for S.C. (300 rpm) some amount of catalyst remained at the bottom of the reactor but such situation was not detected in the case of higher stirring intensity (1000 rpm).

Calculation of mass transfer coefficient at beginning of methanolysis is shown in the Appendix. According to theory, at 1000 rpm, calculated volumetric mass transfer coefficient at beginning of process is 0.0038 min^{-1}, and at 300 rpm only 0.000174 min^{-1}. The volumetric mass transfer coefficient at 1000 rpm is almost 20 times higher compared to the mass transfer at S.C. Simulation curves show the best agreement with experimental data only for 8.3 times

higher ratio (0.0017/0.000205). Analyzing the ratio between the volumetric mass transfer calculated according to theory and experimentally determined ($k_{mt,0}$) at same mixing intensity one can conclude that at lower mixing intensity it is in a range of 15% difference (Appendix and Table 3), while at 1000 rpm, such difference is more than 200%. Because the main resistance for mass transfer exists in disperse (methanol) phase the difference between theory and experimental data could be a consequence of used equation for calculation the Sauter mean drops diameter (disperse phase). Experiments indicated that Sauter mean diameter must be slightly larger than the value determined using correlation from literature [36], which is possible taking into account that the proposed equation was derived for an L-L and not for an L-L-S system used in this study.

Table 3. Determined model parameters for methanolysis of SO used for simulation process of FAME synthesis performed with different amount of catalyst

Parameter	Catalyst amount, wt.%		
	2	1	0.5
k	0.53	0.53	0.53
α	210	1300	3600
β	2.35	2.01	2.28
$k_{mt,0}$	0.00170	0.00015	0.00010
k_{mt} for $X = 0.1$	0.0033	0.0021	0.0020
a/a_0 for $X = 0.1$	2	14	20
$k_{app,0}$	0.0017	0.00015	0.00010
k_{app} for $X = 0.1$	0.0033	0.00210	0.0020
k_{app} for $X = 0.9$	0.183	0.122	0.185

Influence of catalyst amount on the methanolysis of sunflower oil

TG conversion *versus* time is shown in Figure 4 for different initial amount of catalyst (0.5; 1 and 2 wt.% based on oil).

It can be observed that in all cases there is a characteristic period of time for which TG conversion in reaction mixture reaches 10−15%, after which very fast methanolysis begins. For reaction mixture containing 2 wt.% of catalyst based on oil, this characteristic time is 50−60 min, with 1% about 270 min and for 0.5% 380 min. Furthermore, duration of fast process of methanolysis is approximately the same either 0.5 wt.% of catalyst or more (1 or 2 wt.%) was used. Namely, the TG conversion reached from 10−15% conversion to approx. 97% for 40−50 min for different amount of catalyst at 60 °C, 1000 rpm and 10:1 mole ratio of methanol and oil. Since the agitation speed is the same for all cases, these results could be explained by taking into account two effects. The first one is that the presence of larger amount of solid catalyst particles causes faster droplet diameter decrease, and the second is that the total surface of the catalyst at which the reaction takes place during the period of fast methanolysis, does not affect the rate of the process. Practically the rate of methanolysis is only defined by achieved interfacial area between the oil and methanol.

The optimal values of kinetic parameters were defined to give the minimal value of standard deviation between simulation curve and experimental data, and shown in Table 3.
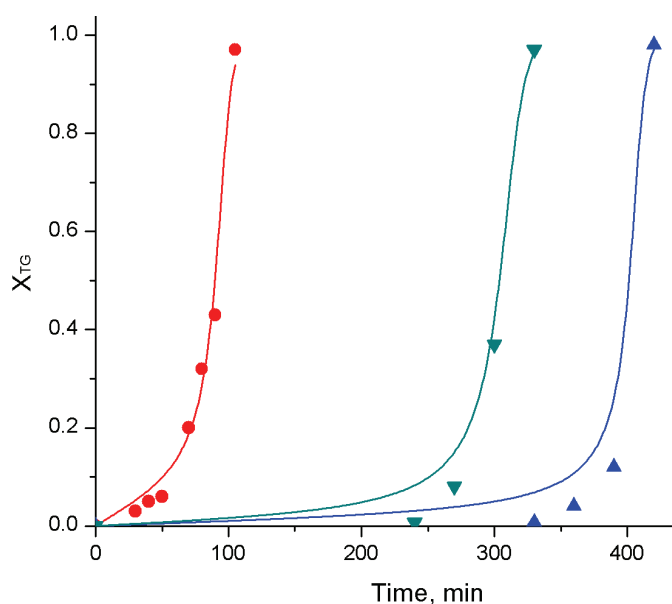

Figure 4. Influence of the catalyst amount on triglyceride conversion at 60 °C, methanol:oil molar ratio 10:1, agitation speed 1000 rpm. Legend: solid lines - simulation curve calculated using optimal values of kinetic parameters; ● - 2; ▼ - 1; ▲ - 0.5 wt.%.

The apparent reaction rate constant, k_{app}, depends on mass transfer resistance in the L-L-S system and on chemical reaction at the surface of the catalyst. The proposed model assumed that only parameters $k_{mt,0}$, α and β could be dependent on used amount of the catalyst. The best agreement of simulation with experimental data are obtained if $k_{mt,0}$ decreases by decrease of used amount of catalyst, while α increases and β practically remains its value. Decrease of $k_{mt,0}$ for smaller amount of catalyst is a result of smaller value of oil–methanol interfacial area at a beginning of process. More time is necessary for the formation of critical amount of DG and MG (Table 1), which are responsible for creation a large interfacial area important for higher mass transfer of TG from oil into methanol phase. It might be seen that kinetic parameter α is in a direct correlation to time of critical DG and MG formation. A lower amount of catalyst leads to higher value of α, and if 10–15% conversion of TG is used as critical, the difference between the value of mass transfer coefficient k_{mt} is much smaller then difference between the $k_{mt,0}$ values (Table 3). It might be concluded that the presence of smaller amount of catalyst needs more time for reaching critical conversion of TG but also that delayed initial period of methanolysis is followed by larger increase of oil--methanol interfacial area (a/a_0 for $X = 0.1$; Table 3).

According to experimental data as well as from results of performed simulation, the reaction rate constant, k, have the same value in all cases since the slope for all experimental curves TG conversion *versus* time is practically identical. Experimental data shows that change in TG conversion from 10% to 97–98% is realized within 60–65 min when methanolysis was performed with 2, 1 and 0.5 wt.% of catalyst. The results indicate that almost same value of the apparent reaction rate constant, k_{app}, has to be achieved before the period of fast methanolysis starts (Table 3).

All of above comments and calculation prove original assumption that in order to obtain so-called "autocatalytic" effect of methanolysis process and very high increase of overall rate of methanolysis for a short period of time, the reaction mixture has to contain small amounts of MG and DG which promote the increase of the interfacial area between methanol and oil at the beginning of process. The combination of α and β parameters, more precise an enlargement mainly and only of α parameter (β parameter could be assumed as constant), as well as decrease of parameter $k_{mt,0}$ may result in the same value of apparent reaction rate constant for experiments performed with 0.5, 1 or 2 wt.% of catalyst. Modeling of X_{TG} conversion with time shows that the same sigmoid change of the apparent reaction rate constant with time exists, but is shifted to longer time if smaller amount of catalyst used for methanolysis.

According to equations for k_c and k_d calculations (Appendix), the catalyst amount does not influence any of both parameters, but it does influence k_s, the mass transfer resistance through parameter a_s (liquid-solid interfacial area). Namely, the mass transfer resistance from the liquid (methanol) to solid phase (catalyst) is slightly higher when a smaller amount of the catalyst is used due to lower available surface, but optimization of kinetic parameters showed a larger difference mainly caused by initial value of interfacial methanol–oil area (Table 3). It might be concluded that according to the value of determined k_c and thus $k_{mt,0}$ parameter the presence of 2% of catalyst will cause a smaller initial value of interfacial methanol–oil area than expected according to correlation proposed in literature. Thus, the following correction of correlation proposed for Sauter mean drop value calculation (L-L system) is used in the case of L-L-S system:

$$d_{32} = (69490 - 29760m)n^{-1.825} \qquad (14)$$

where m is mass percent of catalyst used for oil methanolysis (valid for $0.5 \leq m \leq 2$).

The resistances for mass transfer of TG to catalyst surface are calculated using the proposed correlation and shown in Table 4.

As can be seen, calculated value of $k_{mt,0}$ (Table 4) and that obtained using simulation curve (Table 3) are identical supporting the assumption that initial interfacial area (*i.e.*, the $d_{3/2}$ - Sauter mean size drop diameter) between methanol and oil calculated using correlation from literature [36] must be corrected by Eq. (14) which takes into account the presence of solid phase in reaction mixture.

Table 4. Calculation of $k_{mt,0}$ for experiments performed with different amount of catalyst (MeOH:oil molar ratio 10:1; mixing intensity 1000 rpm; 60 °C)

Mass of catalyst, wt.%	a_0 m^{-1}	$k_c \times 10^6$ m min^{-1}	k_d m min^{-1}	k_s m min^{-1}	$10^4/a_0k_d$	$1/m_{TG}a_0k_c$	$1/m_{TG}a_sk_s$	$k_{mt,0} \times 10^4$ min^{-1}
2	50330	8.04	0.019	0.022	10.3	588.3	0.269	17.0
1	4441	8.04	0.019	0.022	116.5	6667.4	0.54	1.5
0.5	2960	8.04	0.019	0.022	174.8	10003.3	1.08	1.0

Influence of methanol to oil molar ratio on the methanolysis of sunflower oil

The rate of the methanolysis is higher when molar ratio of methanol to oil is higher. However, there is a characteristic period until the critical conversion of TG is achieved (TG conversion of about 10%), after which the rates of methanolysis become similar. It was determined that when methanol to oil molar ratio is 10:1 the moment when fast methanolysis begins is about 50–60 min after commencement of methanolysis, and almost complete TG conversion was finished after 40–45 min. When the molar ratio is 6:1, intense methanolysis begins after 200 min and finishes after 60–70 min (Figure 5).

Molar ratio methanol:oil affects the mass transfer rate since fraction of dispersed phase in the reaction mixture is changed, and thus the specific interfacial area between oil and methanol. Assuming that the drop size is the same (agitation speed is the same) in both experiments calculated by Eq. (14), the total surface for mass transfer, defined by the expression: $a = 6\varphi/d_{32}$, is directly proportional to the fraction of dispersed phase in the reaction mixture. Fractions of dispersed phase when molar ratio is 10:1 and 6:1 are 30 and 18%, respectively. It is reasonable to assume that methanol to oil molar ratio mass affects mainly the mass transfer rate and only minor the chemical reaction rate at catalyst surface. Based on that assumption, simulation using Matlab software was performed, and optimal parameters defined for molar ratio 6:1 (1000 rpm; 2 wt% of catalyst, 60 °C) was determined: $k = 0.53$ min^{-1}, $k_{mt,0} = 0.00036$ min^{-1}, $\alpha = 1175$ and $\beta = 2.49$.

Standard deviation between simulated curve (solid line, Figure 5) and experimental data for mole ratio 6:1 is 0.0343.

Calculated values $k_{mt,0}$ after using Eq. (14) and volume fraction of methanol $\varphi = 0.18$ is even 2.7 times higher, and with equation proposed in literature [36] it is only 7 times higher (Appendix) then the experimentally determined value. Knowing that resistance of mass transfer through the methanol phase again control the overall rate of mass transfer it seems that correction which take into account the volume of methanol in reaction mixture must be included into equation (14):

$$d_{32} = M_c(69490 - 29760m)n^{-1.825} \tag{15}$$

$$M_c = M_{max}^{1.2\left(\frac{M_{max} - M}{M_{max}}\right)} \tag{16}$$

where M_{max} is maximal and minimal mole ratio of methanol and oil, and for $M = 6$ (*i.e.*, $M = 6:1$), $M_{max} = 10$ (*i.e.*, 10:1), the correction factor is 3.02, while for $M = 10$ it is equal 1. Calculated value of Sauter mean diameter is for $M = 6:1$, 0.107 mm, the interfacial area between oil and methanol at beginning of methanolysis 10110 m^{-1}, and resistance of mass transfer in methanol phase 2929 min. It is much larger than resistances of TG through the oil phase and near the solid phase surface and determine the overall mass transfer coefficient. Finally, difference between calculated (0.00034 min^{-1}) and experimentally determined $k_{mt,0}$ (0.00036 min^{-1}) is only 2.6%.

Simulation and calculation results show that when methanolysis start with molar ratio of methanol
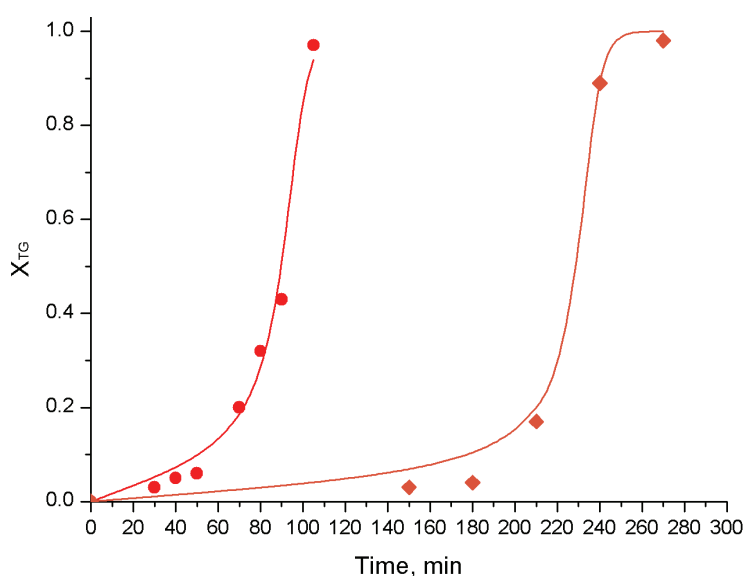

Figure 5. Influence of molar ratio of methanol and oil on triglyceride conversion at 60 °C. Legend: solid lines - simulation curve calculated using optimal values of kinetic parameters; ● - 10:1; ♦ - 6:1.

to oil 6:1, 2mas% catalyst and 1000 rpm at 60 °C, a lower TG mass transfer rate to the catalyst surface, $k_{mt,0}$, is obtained in the initial phase compared to the same condition but with higher molar ratio of methanol to oil (10:1). The overall surface of the dispersed phase is 5.5 times smaller for 6:1 compared to that when molar ratio is 10:1. Although the energy that is transferred to the reaction mixture by mixing in both cases is the same (the same agitation speed), the specific energy consumption based on the volume of dispersed phase is higher when molar ratio of methanol to oil is lower. This means that just at the beginning of the process the energy consumed for phase mixing is not sufficient for creating fine dispersion of methanol into oil phase. A difference of drop sizes causes also difference in initial rate of methanolysis and it will be continued till small amounts of MG and DG are created, acting as surface-active compounds. It must be pointed out that practically very similar value of apparent reaction rate constants could be detected for TG conversion of approx. 10%, either 6:1 or 10:1 molar ratio of methanol and oil are used. However, at 6:1 mole ratio, as a consequence of initially formed smaller interfacial area, the longer process is necessary for achieving 10% conversion of TG.

Comparison between experimentally determined and calculated TG conversion

Correlation between experimentally determined and calculated values of TG conversion for different hydrodynamic conditions used in this study is shown in Figure 6. The calculated standard deviation for all the experimental data is:

$$\sigma = \sqrt{\frac{\sum_{1}^{p}\left(X_{TGexp} - X_{TGmod}\right)^2}{p}} = 0.049$$

CONCLUSION

The agitation speed, added amount of catalyst and used methanol-to-oil molar ratio affect the overall rate of sunflower methanolysis. The proposed kinetic model, which takes into account the chemical reaction between methanol and triglyceride and mass transfer of triglyceride into methanol phase was checked and the model parameters were determined. The model assumed that the reaction rate constant, k, is not influenced neither by the value of the methanol-to-oil molar ratio nor the used amount of catalyst, but depends on the stirring intensity. It was shown that the rate of sunflower methanolysis depends greatly on the mass transfer rate defined by $k_{mt} = k_{mt,0}$
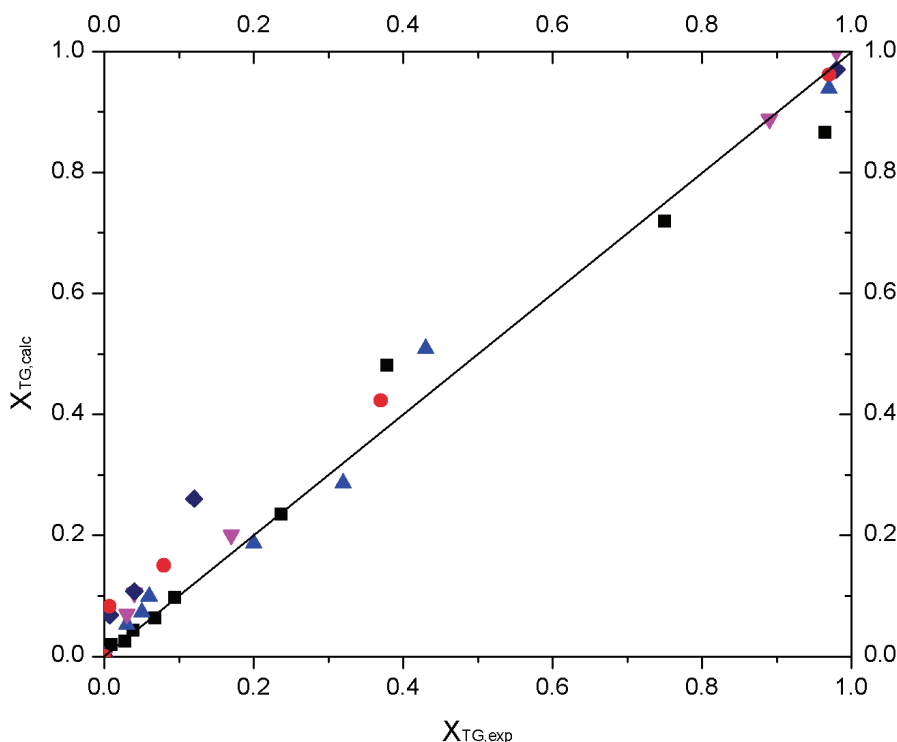

Figure 6. Comparison of experimentally determined and calculated triglyceride conversion using model equation at different hydrodynamic condition. Used symbols: ■ - 300 rpm, 2 wt.% cat., 10:1; ▲ - 1000 rpm, 2 wt.% cat., 10:1; ▼ - 1000 rpm, 2 wt.% cat., 6:1; ● - 1000 rpm, 1 wt.% cat., 10:1; ◆ - 1000 rpm, 0.5 wt.% cat., 10:1.

$(1+\alpha X_{TG}{}^{\beta})$. Parameters $k_{mt,0}$, α and β are influenced by different hydrodynamic conditions which is explained using the corresponding theory.

The proposed model suggests that the rate of the process depends greatly on the mass transfer rate at the beginning of the process and for a longer period of time until certain amounts of diglyceride and monoglyceride are formed.

The main resistance of mass transfer exists in the methanol phase and it is higher for a larger value of the Sauter mean drop diameter of the dispersed phase (methanol). This study proposed a correction of the correlation derived in literature for the calculation of the Sauter mean drop diameter, taking into account different values of the methanol:oil molar ratio as well as different initial mass of catalyst used for methanolysis of triglycerides.

Acknowledgements

Nomenclature

a specific interfacial area, m^{-1}

a_0 specific interfacial area at the beginning of the process, m^{-1}

a_m active specific catalyst surface, $m^2\ g^{-1}$

a_s liquid-solid interfacial area, m^{-1}

c_{TG} triglyceride concentration in the liquid phase, $mol\ dm^{-3}$

$c_{TG,v}$ triglyceride concentration close to the active centers of catalyst, $mol\ dm^{-3}$

d_p particle diameter, m

d_{32} Sauter mean drop diameter, mm

D diffusion coefficient, $m^2\ s^{-1}$

D_i impeller diameter, m

g gravity constant, $m\ s^{-2}$

k pseudo first-order reaction rate constant, min^{-1}

k_{app} apparent rate constant, min^{-1}

$k_{app,0}$ initial value of apparent rate constant, min^{-1}

$k_{c,TG}$ mass transfer coefficient for the continuous phase, $m\ min^{-1}$

k_c mass transfer coefficient for the continuous phase, $m\ min^{-1}$

$k_{d,TG}$ mass transfer coefficient for the dispersed phase, $m\ min^{-1}$

k_d mass transfer coefficient for the dispersed phase, $m\ min^{-1}$

$(k_{mt,TG})_0$ overall triglyceride volumetric mass transfer coefficient at the beginning of the process (experimentally determined), min^{-1}

$k_{mt,0}$ overall triglyceride volumetric mass transfer coefficient at the beginning of the process (experimentally determined), min^{-1}

$k_{mt,TG}$ overall triglyceride volumetric mass transfer coefficient, min^{-1}

k_{mt} overall triglyceride volumetric mass transfer coefficient, min^{-1}

$k^s_{mt,TG}$ overall triglyceride mass transfer coefficient, $m\ min^{-1}$

k^s_{mt} overall triglyceride mass transfer coefficient, $m\ min^{-1}$

$k_{s,TG}$ mass transfer coefficient for the solid phase, $m\ min^{-1}$

k_s mass transfer coefficient for the solid phase, $m\ min^{-1}$

m mass percent of catalyst on the basis of oil

M mole ratio of methanol and oil

M_c correction parameter defined by equation (16)

M_{max} 10:1 maximal molar ratio of methanol and oil used in this study

M_{min} 6:1 minimal molar ratio of methanol and oil used in this study

m_{cat} mass of catalyst, g

m_{TG} distribution coefficient of triglyceride between the methanol phase and the oil phase

n stirring velocity, rpm

P power dissipated by the agitator, $kg\ m^2\ s^{-3}$

$(-r_{TG})$ rate of methanolysis, $mol\ dm^{-3}\ min^{-1}$

t time, min

V reaction mixture volume, m^3

V_c volume of the continuous phase, m^3

X_{TG} conversion of triglyceride

Greek symbols

α fitting parameter

β fitting parameter

φ the dispersed phase holdup

μ_c viscosity of the continuous phase, Pa s

ρ_c density of the continuous phase, $kg\ m^{-3}$

ρ_d density of the dispersed phase, $kg\ m^{-3}$

ρ_p density of catalysts particle, $kg\ m^{-3}$

ρ_{mix} density of the mixture, $kg\ m^{-3}$

σ standard deviation

ψ agitator power consumption number equal to 1.5

Φ_{MT} rate of mass transfer, $mol\ dm^{-2}\ min^{-1}$

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APPENDIX

Calculation of mass transfer coefficient

a. The mass transfer coefficient in the continuous phase [31,32]:

$$k_c = 1.3 \times 10^{-3} \left[\frac{P\mu_c}{V_c \rho_c} \right]^{1/4} \left[\frac{\mu_c}{D\rho_c} \right]^{2/3} \tag{A.1}$$

The diffusion coefficient of TG through methanol and TG estimated by the Wilke and Chang correlation [35] are 7.8×10^{-10} and 6.1×10^{-11} m^2 s^{-1}, respectively. The factor P is equal to $\psi \rho_{mix} n^3 D_i^5$, where ψ is the agitator power consumption number equal to 1.5 [31], ρ_{mix} (kg m^{-3}) is the density of the mixture equal to $\rho_{mix} = \varphi \rho_d + (1-\varphi)\rho_c$ [36]. The dispersed phase holdup, φ, was estimated as the volume fraction of methanol in the reaction mixture at the

beginning of reaction. For the molar ratio of methanol to oil 10 to 1 the volume fraction of the methanol in the reaction mixture was 0.3. Using values for density of oil and methanol at 60 °C [35], ρ_{mix}, was calculated.

$$P = \psi \rho_{mix} n^3 D_i^5 \ P \tag{A1.1}$$

$\psi = 1.5$

$n = 300$ rpm or 1000rpm

$D_i = 0.05$ m

$$\rho_{mix} = \varphi \rho_d + (1 - \varphi)\rho_c \tag{A 1.2}$$

ρ_c (60 °C) = 891 kg m^{-3}

μ_c (60 °C) = 17.2 mPa s

$V_c = 2.76 \times 10^{-4}$ m^3

$D = 6.1 \times 10^{-11}$ m^2 s^{-1}

b. The mass transfer coefficient in the disperse phase [31,32]:

$$k_d = \frac{2\pi^2 D}{3 d_{32}} \tag{A 2}$$

The Sauter mean drop diameter, d_{32}, was calculated from the correlation given by Kolmogorov's theory of homogeneous isotropic turbulence and according to the equation proposed by Stamenkovic *et al.* [36]. The following correlation between the Sauter mean drop diameter (in mm) and the agitation speed (in rpm) was derived for L–L system (methanol–oil):

$$d_{32} = 4782 n^{-1.825} \tag{A 2.1}$$

$D = 7.8 \times 10^{-10}$ m^2 s^{-1}

c. The mass transfer coefficient near the solid surface [31,32]:

$$k_s = \frac{D}{d_p}\left(2 + 0.31 \frac{d_p^3 g (\rho_p - \rho_c)}{\mu_c D}\right) \tag{A 3}$$

$d_p = 4.3$ μm

$g = 9.81$ m^2 s^{-1}

$\rho_p = 3350$ kg m^{-3}

d. The overall volumetric mass transfer coefficient:

$$\frac{1}{k_{mt,TG}} = \frac{1}{a}\left(\frac{1}{k_{d,TG}} + \frac{1}{m_{TG} k_{c,TG}} + \frac{1}{a_s m_{TG} k_{s,TG}}\right) = = \frac{1}{a k_{mt,TG}^s} \tag{A 4}$$

At the beginning of the process:

$$\frac{1}{(k_{mt,TG})_0} = \frac{1}{a_0 k_{mt,TG}^s} \tag{A 4.1}$$

$$d_{32} = 4782 n^{-1.825}$$

$$a_0 = \frac{6\varphi}{d_{32}}$$

$$a_s = \frac{a_m m_{cat}}{V} \tag{A 4.2}$$

$m_{TG} = 0.0042$

Experiment	Methanol:oil mole ratio	Mass of catalyst, wt.%	Stirring intensity, rpm	V_c / 10^{-4} m^3	φ	ρ_{mix} kg m^{-3}	d_{32} mm	a_0 / m^{-1}	a_s / m^{-1}
1	10:1	2	1000	6.52	0.3	850	0.016	112500	40300
2	6:1	2	1000	6.52	0.2	864	0.016	75000	45421
3	10:1	1	1000	6.52	0.3	850	0.016	112500	20043
4	10:1	0.5	1000	6.52	0.3	850	0.016	112500	10021
5	10:1	2	300	6.52	0.3	850	0.144	12500	40300

Experiment	MeOH:oil mole ratio	Mass of catalyst, wt.%	Stirring intensity, rpm	$k_c \times 10^6$ m min^{-1}	k_d, m min^{-1}	k_s, m min^{-1}	$10^4/a_0 k_d$	$1/m_{TG} a_0 k_c$	$1/m_{TG} a_s k_s$	$(k_{mt,TG})_0 \times 10^3$ min^{-1}
1	10:1	2	1000	8.04	0.019	0.022	4.6	263.2	0.269	3.8
2	6:1	2	1000	8.22	0.019	0.022	6.9	386.2	0.238	2.6
3	10:1	1	1000	8.04	0.019	0.022	4.6	263.2	0.54	3.8
4	10:1	0.5	1000	8.04	0.019	0.022	4.6	263.2	1.08	3.8
5 S.C..	10:1	2	300	3.32	0.0021	0.022	380	5737	0.269	0.174

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NAUČNI RAD

KINETIKA HETEROGENE METANOLIZE SUNCOKRETOVOG ULJA SA CaO·ZnO KAO KATALIZATOROM: UTICAJ RAZLIČITIH HIDRODINAMIČKIH USLOVA

Kinetika heterogene metanolize suncokretovog ulja je ispitivana na 60 °C korišćenjem CaO·ZnO katalizatora koji je sintetizovan mehanohemijskim putem. Analiziran je uticaj intenziteta mešanja, mase korišćenog katalizatora u sintezi i različitog molskog odnosa metanola i ulja na brzinu metanolize. Brzina procesa metanolize zavisi od dva otpora - otpora prenosu mase triglicerida do površine katalizatora i otpora brzini hemijske reakcije na površini katalizatora. Oba otpora određuju vrednost ukupnog zapreminskog koeficijenta prenosa mase triglicerida, $k_{mt,TG}$, odnosno efektivne vrednosti konstante brzine hemijske reakcije pseudo-prvog reda, k. Ovi kinetički parametri određuju vrednost prividne kons- tante brzine procesa metanolize, k_{app}, koja se menja sa vremenom u zavisnosti od ostva- renog stepena konverzije triglicerida (TG). Predložen je odgovarajući model kojim je moguće definisati brzinu metanolize i određeni su odgovarajući parametri ovog modela.

Ključne reči: biodizel, heterogena kataliza, kinetika, model, CaO, ZnO.