Biodiesel synthesis and kinetic analysis based on MnCO₃/Na silicate as heterogeneous catalyst

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Abstract: The MnCO₃/Na silicate (Mn/Na/Si mole ratio of 4.65:1:1.65) catalyst in the form of solid particles with diameter of 0.99–1.99 mm was used as a catalyst for transesterification of soybean oil in batch autoclave at different conditions: 388–468 K, methanol-to-oil mole ratio 12:1–30:1, catalyst amount based on the mass of oil 0–12.5 %. The complete triacylglycerols (TAG) conversion and high yield of fatty acid methyl ester (FAME) was obtained after 1 h at 458 K, methanol-to-oil mole ratio 30:1 and 10 % of catalyst. Kinetics of transesterification process was analyzed by three models: the simple first order irreversible reaction rate, as well as two more complex models recently reported in literature. The catalyst reuse in transesterification process was tested and the average values of 99.0 % of TAG conversion and 97.5 % of FAME yield were obtained after 8 consecutive runs. Different techniques were used to characterize fresh and used MnCO₃/Na silicate catalyst. The determined amounts of leached Na (<500 ppm) and Mn (<20 ppm) in biodiesel phase implied that the homogeneous-heterogeneous process influences the catalyst selectivity, whereby leached Na enables the complete transformation of TAG to FAME.

Keywords: MnCO₃/Na-silicate; transesterification; kinetics; reusability.

INTRODUCTION

Biodiesel, consisting of fatty acid methyl esters (FAME) is usually produced by the transesterification of triacylglycerols (TAG), the main constituent of veg-

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etable oils, with alcohol such as methanol or ethanol, in the presence of a catalyst. The overall transesterification process occurs as a sequence of three reversible consecutive reactions, involving stepwise conversions of TAG to diacylglycerol (DAG), monoacylglycerol (MAG) and finally glycerol (GL), producing 1 mol of FAME in each step of the process. This complex reaction could be presented as one summarized reaction:

$$TG + 3MeOH \leftrightarrows 3FAME + GLY \qquad (1)$$

The current technology of catalyzed biodiesel synthesis applied in industry is designed, to use various bases or acids as homogeneous catalyst. In order to improve the technology of biodiesel synthesis, the heterogeneous (solid) catalysts have been thoroughly investigated in the last decade.[1–5] A simple procedures of biodiesel separation and purification process, without the aqueous treatment and the necessity to wash products in the case of homogeneous transesterification, are the main advantages of heterogeneously catalyzed transesterification.[5]

Some of the recently reported data have indicated that Mn-containing compounds could be used as effective catalysts for biodiesel synthesis. Transesterification at low temperatures was reported with commercial $MnCO_3$ (probably contained some other alkali metals as impurities),[6,7] while the application of synthesized and pure $MnCO_3$[8] showed the acceptable activity at higher temperature and pressure in batch autoclave and during 350 h of continuous process of transesterification performed in a small size HPLC column filled with $MnCO_3$. Furthermore, $MnCO_3/ZnO$[9] and $MnCO_3/Zn$-glycerolate[10] showed good activity even after 17 and 13 cycles reuse, respectively, in the transesterification of soybean oil in batch autoclave under subcritical conditions of methanol. However, all the mentioned catalysts containing $MnCO_3$ were used in powdered form and, although they showed good activity and stability, their application required the additional centrifugation step for separation of the solid catalyst powder from the products of transesterification (biodiesel and glycerol). Also, another disadvantage is the formation of a very dense packed bed inside small HPLC column that caused a very high pressure drop in a column at the end of the experiment.[8]

The practice in the industrial preparation of a solid catalyst in the form of particles is to add precursor to some support, which might be accomplished in different ways.[11–15] The research and development related to the granulation and the molding method of $MnCO_3$ was based on the use of hydrated sodium silicate $(Na_2O \cdot nSiO_2)$, which is one of the most popular and cheap inorganic adhesives.[16,17] Apart from its application as an adhesive, the Na-silicate has also been tested as catalyst for the biodiesel synthesis.[18–24]

The main goal of this study was to prepare $MnCO_3$ in the form of solid particles, which could be suitable for performing transesterification not only in batch, but also, more important, in the continuous process using a packed-bed of solid catalyst and to find the optimal ratio of $MnCO_3$ and $Na_2O \cdot nSiO_2$ in order to

produce the desired strength and size of MnCO$_3$/Na silicate particles (granules). The chemical and physical characteristics of granulated catalyst before and after usage in transesterification of soybean oil were analyzed.

The kinetic models proposed by Lukić *et al.*[25] and Miladinović *et al.*[26] deserve considerable attention among various models used to describe the kinetics of heterogeneously catalyzed transesterification, from the most commonly used simple pseudo-first order model,[11,27,28] to more complex models.[29–32] It was shown that both of them are suitable for describing the kinetics of transesterification over various calcium-based catalysts at low temperature,[33,34] but they are also capable to predict correctly the reaction rate of transesterification process at high temperature using different catalysts (La/Mn, Ce/Mn, Sr/cinder, Fe–Zn double-metal cyanide complex, La$_2$O$_3$/ZrO$_2$ and MnCO$_3$).[8,35]

The prepared samples of MnCO$_3$/Na-silicate particles were used in soybean oil transesterification at different working parameters: the catalyst amount, the methanol-to-oil mole ratio, the reaction temperature and the duration of transesterification process. The reusability of the prepared solid particles of catalyst was also studied in batch autoclave and the deactivation of the catalyst was discussed.

The experimental data of the soybean oil transesterification obtained in the batch autoclave were used to define the kinetic model which might be used for the design of a larger size of a tubular reactor packed with MnCO$_3$/Na silicate as catalyst. Three models were tested: a) the first-order irreversible kinetic model, b) the model developed by Lukić *et al.*[25], signed as the IL model, based on the simultaneous influence of the mass transfer and the chemical reaction rate on the overall process rate and c) the model proposed by Miladinović *et al.*[26], *i.e.*, MM model, which include a changing reaction mechanism with respect to TAG concentration.

EXPERIMENTAL

Materials

The reagents used in this study, MnCO$_3$ (99%) and methanol (99.5%) of analytical grade, and the 27 % aqueous solution of Na$_2$O·nSiO$_2$ (n = 3.3),were obtained from Aopu Chemical Company (Wuhan, China). Raw soybean oil was purchased from Baifu Oils & Fat Co. Limited (Wuhan, China). Methanol and acetone of HPLC grade were purchased from Tedia Company Inc. (Fairfield, OH, USA) and Mallinckrodt Baker, Inc. (Phillipsburg, NJ, USA), respectively.

Catalyst preparation

The granular MnCO$_3$/Na silicate catalyst was manufactured by means of simple mixing, kneading, extruding, granulating, drying and sieving.[36] The mixture of MnCO$_3$ and hydrated Na-silicate was first thoroughly stirred in a beaker for 10 min, and then heated in an oven at 333 K for about 20 min; afterwards, the wet mixture was added in rotary granulator.[36] In order to produce the granules with the desired strength, the mass ratio (δ) of initial components, the hydrated Na silicate and MnCO$_3$, was varied in the range of 0:1 to 1:1.The rotation speed of

impeller has been kept constant at 60 rpm during granulation.[36] The samples were subsequently dried in an oven at 333 K for 24 h, and then particles within the range between 0.99 and 1.99 mm were selected by the sieving. For comparison, the starting materials, hydrated Na silicate and $MnCO_3$, were also dried at 333 K for 24 h, grinded and subjected to characterization.

Transesterification of soybean oil

The transesterification of soybean oil was conducted in a 500 mL autoclave (PCF0.5-10 Jian Bang Chemical Machinery Co. Limited, China) made of stainless steel and equipped with a stirrer, an internal cooling pipe and an external heating jacket. The pressure and temperature were monitored during transesterification up to the maximum values of 10 MPa and 573 K, respectively. In each batch, soybean oil, methanol and the catalyst particles (0.99–1.99 mm) were placed in the reactor at the ambient temperature and pressure. The reaction was conducted at pre-set temperature and under the vapour pressure of methanol depending on the reaction temperature (<3.5 MPa), and stirred at a constant speed of 200 rpm. The reaction time was recorded from the moment when temperature in the autoclave reached the pre-set value. After a given time, the reaction was stopped by the rapid cooling of the reaction mixture, and the product was removed from the autoclave and analyzed using the HPLC.

Product analysis

The determination of TAG, FAME and the intermediate products, *i.e.*, the monoacylglycerols (MAG) and diacylglycerols (DAG) in the product was performed using the HPLC combined with the internal standard analysis. The ester phase was diluted using the HPLC grade acetone, and then 5 μL of sample was analyzed by the HPLC Shimadzu chromatograph at 313 K. For the separation and the identification of acylglycerols (FAME, TAG, DAG and MAG) and acetone, the C18 column with particle size 5 μm, 200 mm×4.6 mm I.D., and UV detector (205 nm) was used. Methanol was used as the mobile phase with a flow rate of 1.0 mL/min.

The FAME yield (Y_{FAME}) and TAG conversion (x_{TAG}) were determined from HPLC peak areas and internal standards using equations:

$$Y_{FAME} = 100\frac{FAME'_{es}}{FAME_A} \tag{2a}$$

$$FAME'_{es} = \alpha_{FAME} \times FAME_{es} \tag{2b}$$

$$x_{TAG} = 100\frac{TAG_{oil} - TAG'_{es}}{TAG_{oil}} \tag{3a}$$

$$TAG'_{es} = \alpha_{TAG} \times TAG_{es} \tag{3b}$$

where $FAME_A$ and $FAME_{es}$ refer to the sum of the areas of all FAME peaks of the sample prepared by the complete conversion of TAG (defined as sample A) and of the ester phase, *i.e.*, biodiesel, respectively, and TAG_{oil} and TAG_{es} are the areas of TAG peaks determined in the sample of soybean oil and ester phase, respectively. The areas of acetone HPLC peaks of esters phase (P_{es}), sample *A* (P_A) and sample of soybean oil (P_{oil}) were used as the internal standard:

$$\alpha_{FAME} = \frac{P_A}{P_{es}} \tag{4}$$

$$\alpha_{\text{TAG}} = \frac{P_{\text{oil}}}{P_{\text{es}}} \tag{5}$$

The significance of the kinetic model was statistically evaluated using the mean relative percent deviation (*MRPD*) between the calculated and the experimentally determined TAG conversion degree according to the equation:

$$MRPD = \frac{100}{n} \sum_{1}^{n} \left| \frac{x_{\text{TAG}_{\text{mod}}} - x_{\text{TAG}_{\text{exp}}}}{x_{\text{TAG}_{\text{exp}}}} \right| \tag{6}$$

Catalyst characterization

The morphology and the composition of different elements at some specific and arbitrary chosen points of catalyst sample, were determined by the scanning electron microscopy (SEM) using Quanta 200 SEM system equipped with EDS detector (FEI company, Netherlands).

The surface area of the catalysts sample was determined by SSA-4200 Surface Area & pore size analyzer (Beijing Builder Electronic Technology Co., Ltd., China) using the multipoint N_2 adsorption–desorption method. Before the measurements, the samples were degassed under vacuum overnight at 373 K.

The Hammett indicator method was used for determining the basic strength of the samples (*H_*). Approximately 100 mg of the sample was shaken with 5 mL cyclohexane and 1 mL of Hammett indicators–benzene solution (0.1 mass%,) and then left to equilibrate for 2 h until no further colour changes were observed. The Hammett indicators used were as follows: 4-nitroaniline (*H_* = 18.4), 2,4-dinitroaniline (*H_* = 15.0), phenolphthalein (*H_* = 9.8). The base strength of the samples was defined as being stronger than the Hammett indicator if there was a colour change, but weaker if it showed no colour change.

The STA 409 PC (NETZSCH Co., Ltd., Germany) was used for the thermal analysis of samples in the temperature range from 303 to 1173 K (10 K/min; in N_2).

X-ray analysis were applied for the structure identification using D/MAX-RB powder X-ray diffractometer (Rigaku Corporation, Japan) with CuKα (λ = 0.15418 nm) as the radiation source at room temperature ($\Delta(2\theta)$ = 0.01° from 5 to 90° at a scanning speed of 10 °/min).

FTIR analysis was done by Nicolet FTIR 5700 spectrometer (Thermo Electron Corporation, USA) with a scanning range of 4000–400 cm^{-1}. The sample was prepared for analysis by the KBr pressed disc method. All measurements were conducted at room temperature.

The amount of Mn and Na dissolved in esters (biodiesel) and glycerol phases was analyzed with an atomic absorption spectrophotometer (AAS, Z-2000, Hitachi, Japan).

RESULTS AND DISCUSSION

Optimization of catalyst preparation

The optimization of the catalyst preparation by varying the mass ratio (δ) of the initial components revealed that the mixture could not be granulated for values of δ < 0.6. For δ between 0.6:1 and 0.7:1, it was possible to granulate mixture of Na silicate and MnCO₃, but the granules were fragile, while for δ = = 0.8:1 they were very hard. Furthermore, the crashing and settling of the prepared particles in a centrifuge indicated that some precipitate existed at the bot-

tom of the centrifuge tube, but not if larger ratio ($\delta > 0.9:1$) was used. Thus, the particles of MnCO$_3$/Na silicate catalyst were prepared using $\delta = 0.9:1$, or the mole ratio of Mn/Na/Si equal to 4.65:1:1.65. After drying and sieving, the particle fraction with size 0.99 mm $< d <$ 1.99 mm was used in the transesterification of soybean oil with methanol.

Analysis of different conditions used for transesterification of soybean oil

Influence of temperature. The reaction temperature is an important parameter that affects the conversion of TAG to FAME as shown in Fig. 1. The transesterification was performed for 1 h using 5 mass% of MnCO$_3$/Na silicate catalyst based on mass of oil (*i.e.*, about 2.4 % MnCO$_3$ and 2.6 % of Na silicate) and methanol-to-oil mole ratio 18:1. With the increase of the reaction temperature from 388 to 438 K, the TAG conversion increased from 68.2 to 95%, and the FAME yield from 70.6 to 85 %. Furthermore, it is evident that the TAG conversion was almost complete at temperatures higher than 438 K, while the FAME yield was practically the same or even slightly less than 85 %. The similar results were found, although at slightly different conditions (2 mass% of catalyst, molar ratio of methanol to oil 21:1) when the transesterification of soybean oil was performed at high temperature (>430 K) using the MnCO$_3$ as a catalyst.[8] The main difference between the activity of MnCO$_3$ and MnCO$_3$/Na silicate used as catalyst in this study was noted for the transesterification performed at lower temperature (<423 K). While the TAG conversion was only about 20 % at 392 K
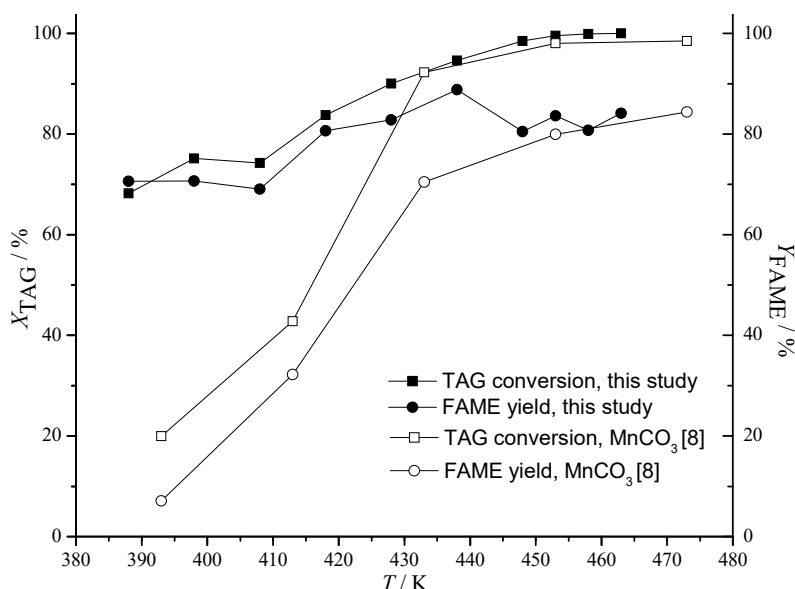

Fig. 1. The effect of reaction temperature on TAG conversion and FAME yield using MnCO$_3$/Na-silicate in comparison to MnCO$_3$ as catalyst.

when pure $MnCO_3$ was used,[8] the $MnCO_3$/Na silicate showed higher activity with 68.2% of the TAG conversion at 388 K, as a consequence of the influence of Na silicate, which displays activity even at lower temperature.[18] Compared to $MnCO_3$ catalyst,[8] the yield of FAME could be further increased using higher amount of $MnCO_3$/Na silicate catalyst, enabling the complete conversion of TAG followed with very high yield of FAME.

Based on the experimentally determined TAG conversion degree and the first-order reaction kinetic assumption[35], the apparent reaction rate constant was determined; the obtained results are presented in the form of the Arrhenius plot (Fig. 2), showing that the slope of straight lines changes around 423 K. This was attributed to the catalytic effect of two different constituents, namely Na silicate, which is active in the whole analyzed range of temperature, and $MnCO_3$, more active at higher temperatures (433–458 K).[8]
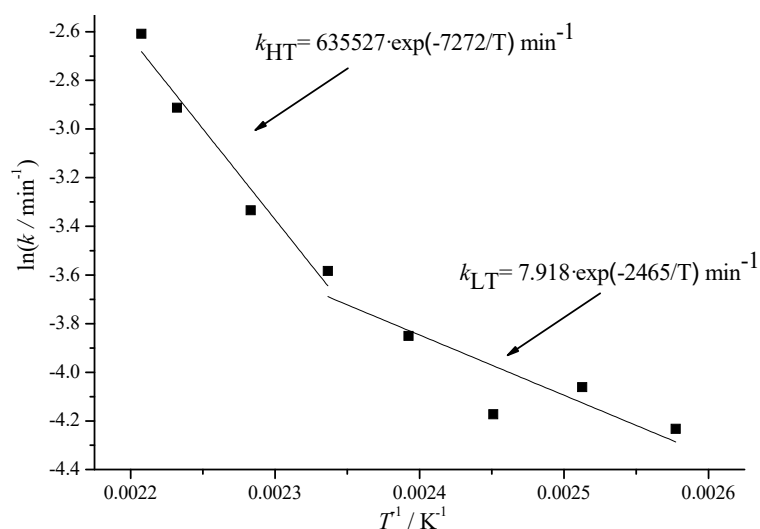

Fig. 2. The Arrhenius plot for the transesterification of soybean oil with $MnCO_3$/Na silicate catalyst performed at different temperature.

Both components, as stated above, influenced the rate of transesterification at high temperature. Hence, in the present study, the transesterification of TAG could be analyzed as a process occurring at low temperature (T < 423 K, designated by the subscript LT), where the Na-silicate mainly catalyzes the transesterification of TAG and at the high temperature (T > 423 K, designated by the subscript HT), where both components influence the transesterification process. Na is probably more soluble in methanol phase than Mn, and could be detected either as the main constituent of the catalyst, or present in the methanol phase to a certain amount.[19] Thus, it might be assumed that the transesterification of soybean oil was governed by the heterogeneous effect of both components ($MnCO_3$

and Na silicate) and the homogeneous process catalyzed by Na dissolved in the reaction mixture, where heterogeneous and homogeneous processes occurred concurrently. The apparent reaction rates (k_{app}) were simply determined by the corresponding reaction rate constants, k_{LT} ($T < 423$ K) and k_{HT} ($T > 423$ K), from the experimental data of TAG conversion degree, according to the Arrhenius plot (Fig. 2) assuming the first-order irreversible reaction kinetics.

The determined values of the apparent reaction rate constants were used for calculating the TAG conversion degree (x_{TAG}) in the batch reactor according to the first-order kinetic model:

$$\frac{dx_{TAG}}{dt} = \frac{(-r_{TAG})}{c_{TAG0}} = k_{app}(1 - x_{TAG}) \tag{7}$$

or by the model designated here as the MM model:[26]

$$\frac{dx_{TAG}}{dt} = \frac{(-r_{TAG})_{MM}}{c_{TAG0}} = k_{app}\frac{(1 - x_{TAG})(c_{R0} + 3c_{TAG0}x_{TAG})}{K + c_{TAG0}(1 - x_{TAG})} \tag{8}$$

and by IL model,[25] which defines the rate of TAG conversion by the equation:

$$\frac{dx_{TAG}}{dt} = k_{app,IL}(1 - x_{TAG}) \tag{9}$$

where:

$$k_{app,IL} = \frac{k_{app}k_{mt}}{k_{app} + k_{mt}} = \frac{k_{app}k_{mt0}\left[1 + \alpha(x_{TAG})^{\beta}\right]}{k_{app} + k_{mt0}\left[1 + \alpha(x_{TAG})^{\beta}\right]} \tag{9a}$$

In all three models, the apparent reaction rate constant (k_{app}) was defined either by k_{LT} or k_{HT} depending on the temperature of transesterification:

$$k_{LT} = 7.918\exp(-2465/T) \text{ min}^{-1} \tag{10}$$
$$k_{HT} = 635527\exp(-7272/T) \text{ min}^{-1} \tag{11}$$

The first three columns of Table I define the temperature, the heating time to the pre-set temperature and the total time of transesterification which represents the sum of time used for the heating and the duration of process under isothermal condition (60 min). It is necessary to point out that, for the process in the batch reactor, the heating of the reaction mixture from the room temperature to the pre--set temperature of the isothermal transesterification T, could be defined by the derived reaction rate constants, k_{LT} or k_{HT}. This heating period is different and obviously a shorter time was required to attain, for example, 333 K (10 min) compared to the heating up to other higher temperatures, for example, 54 min to 448 K.

The best agreement between the calculated and the experimentally determined TAG conversion was obtained with the IL kinetic model which includes the influence of the mass transfer rate using the corresponding parameters

adopted from Wan *et al.*[8] ($\alpha = 55$; $\beta = 3.5$ and $k_{mto} = 0.085$ min^{-1}). The values of MM model parameters were also taken from data obtained for transesterification with MnCO$_3$ catalyst[8] ($c_{Ro} = 1.05$ mol L^{-1}; $K = 1.72$ mol L^{-1}; $c_{TAGo} = 0.6$ mol L^{-1}) and are within the range of values used when CaO was used as catalyst.[26] The actual rate of the mass transfer of TAG to catalyst surface and active sites, defined by IL model,[8,25] showed that a higher rate of transesterification process was caused by the formation of DAG and MAG which substantially affected the apparent reaction rate constant at lower temperature or reduces the resistance of the TAG mass transfer toward the catalyst surface.

TABLE I. Comparison of the first-order, IL and MM model with respect to TAG conversion degrees

T / K	Time, min		Exp. data	Kinetic models, x_{TAG} $(x_{TAGo})^b$, %		
	Heating up to T / °C	Total[a]	x_{TAG} $(x_{TAGo})^b$ %	First order model	IL model[25]	MM model[26]
333	10	70	24.6 (2.5)	27.6 (3.2)	26.4 (3.1)	15.6 (1.5)
388	32	92	68.2 (13.6)	64.6 (19.1)	62.4 (17.6)	51.9 (10.0)
398	36	96	75.2 (16.4)	71.0 (23.6)	69.0 (21.6)	60.9 (12.8)
408	39	99	74.2 (19.1)	76.7 (27.8)	74.8 (25.4)	69.6 (15.7)
418	43	103	83.8 (22.3)	81.9 (33.1)	80.2 (30.2)	77.8 (19.5)
428	46	106	90.0 (25.3)	90.6 (41.6)	89.4 (37.8)	90.8 (25.9)
438	50	110	94.6 (37.4)	94.7 (45.2)	94.0 (41.4)	96.5 (29.8)
448	54	114	98.5 (54.6)	98.4 (54.1)	98.2 (50.0)	99.5 (31.0)
453	55	115	99.6 (60.6)	99.3 (58.3)	99.1 (54.1)	99.9 (43.9)
MRPD				±2.32	±1.05	±2.75

[a]Reaction time was 60 min after reaching isothermal condition (*T*); [b]TAG conversion degree at *t* = 0, when the pre-set temperature was reached

Reaction time

Fig. 3 shows the change of TAG conversion with time during the transesterification of soybean oil performed at 448 K, with 5 mass% of granular MnCO$_3$//Na silicate catalyst and methanol-to-oil mole ratio of 18:1. Within the period of 1.5 h of transesterification, the conversion of TAG was increased from 80 to 99 % while FAME yield was changed from 64 to 90 %. After additional 1 h, the TAG conversion was still complete but the increase of FAME yield was not observed. These results indicated that the highest FAME yield could be obtained even after 1.5 h of transesterification at 448 K. The moment when 448 K was attained defines the beginning of the isothermal biodiesel synthesis (*t* = 0) in the batch autoclave. The heating of the reaction mixture from the ambient temperature to 448 K takes 54 min, thus during that period the non-isothermal process occurred with LT and HT period of transesterification. The initial TAG conversion and the FAME yield determined for *t* = 0 are much higher, compared to the non-catalyzed subcritical methanolysis[37] and slightly higher than the methanol-

ysis with MnCO$_3$ as a catalyst.[8] Knowing that Na silicate is a good catalyst at lower temperature, this may be attributed to the fact that Na at outer surface and also a part from the interior of catalyst particle, could be leached into methanol, and therefore acts as homogeneous catalyst.[20]

The same three kinetic models were used for the TAG conversion modelling at 448 K. The values of the kinetic parameters of both MM and IL model and the apparent reaction rate constant (k_{ap}) were the same as those used in the previous analysis of the TAG conversion degree at different temperatures.
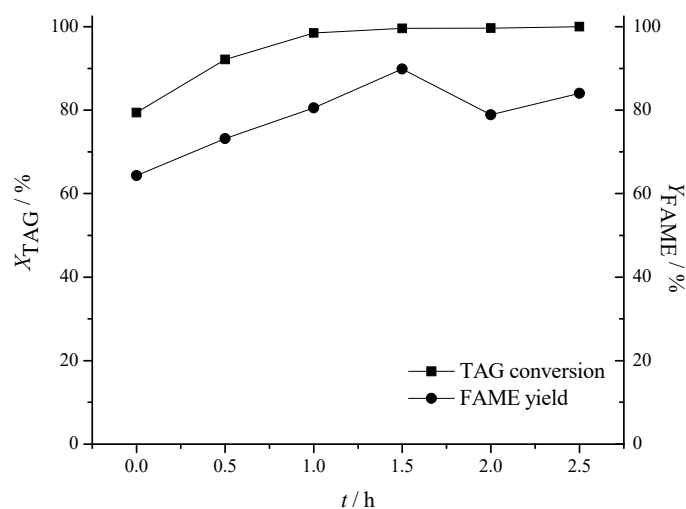

Fig. 3. The effect of reaction time on TAG conversion and FAME yield (448 K; methanol-to-oil mole ratio 18:1; catalyst amount, 5 %).

As can be seen from Table II, the values of the TAG conversion degree at various reaction times, calculated using IL model, gave the best agreement with the experimentally determined values (*MRPD* = ±0.27 %), confirming the conclusion previously made for the transesterification at different temperatures, that

TABLE II. Analysis of the TAG conversion degree versus time at 448 K, the methanol-to-oil mole ratio of 18:1 and the catalyst loading of 5mass% based on mass of oil

Time, min		Exp. data	Kinetic models, x_{TAG} / %		
Heating to 448 K	Total	x_{TAG} / %	First order model	IL model[25]	MM model[26]
54	54	54.6	61.0	56.1	51.0
54	84	92.1	92.9	91.6	95.0
54	114	98.5	98.7	98.4	99.7
54	144	99.6	99.8	99.7	99.98
54	174	99.6	99.96	99.94	99.99
54	204	100	100	100	100
MRPD			±1.08 %	±0.27 %	±0.80 %

the model based on mass transfer and chemical reaction at catalyst surface could be successfully used for representing the rate of transesterification in the presence of $MnCO_3$/Na silicate catalyst. Since all the other model parameters remained unchanged, the results of kinetic analysis also confirmed the necessity to interpret the transesterification using $MnCO_3$/Na silicate as the process at low--temperature ($T < 423$ K), where Na silicate mainly catalyze the transesterification of TAG and at high temperature (423 K $< T < 458$ K) when the process is catalyzed by the heterogeneous effect of both components ($MnCO_3$ and Na silicate).

Influence of methanol-to-oil mole ratio

A higher methanol-to-oil mole ratio (>3:1) is required to obtain the desired conversion and to shift equilibrium conversion toward FAME formation either from TAG, DAG or MAG (Eq. (1)). As shown in Fig. 4, the FAME yield was only 70 % when methanol-to-oil mole ratio was 12:1, and it was increased to 93 % for methanol-to-oil mole ratio of 30:1. The same effect of methanol-to-oil mole ratio was obtained with $MnCO_3$ catalyst used in the powder form, but FAME yield was only increased to 80 % for methanol-to-oil ratio of 24:1.[8] These findings indicate that the observed positive effect of $MnCO_3$/Na silicate as a catalyst, compared to $MnCO_3$, is the result of combined effects of both components, *i.e.*, Na silicate and $MnCO_3$.
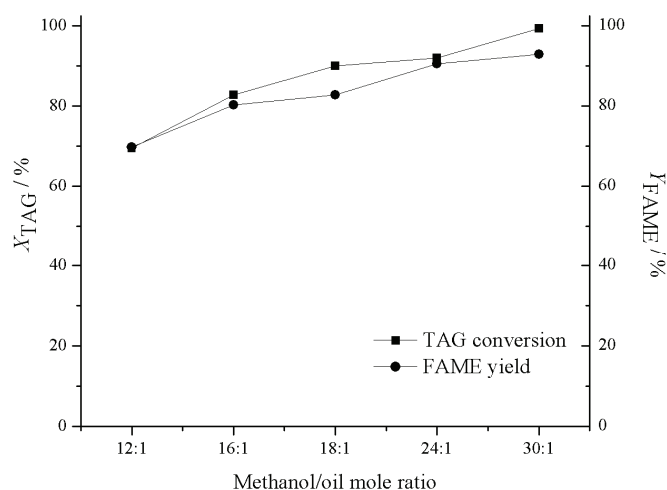

Fig. 4. The effect of methanol-to-oil mole ratio on TAG conversion and FAME yield (reaction time, 1 h; reaction temperature, 428 K; catalyst amount, 5 %).

Influence of catalyst amount

The TAG conversion evidently increased from 54.5 to 95.3 % when the catalyst amount increased from 0 to 7.5 % (Fig. 5). A highest FAME yield was

obtained when the catalyst amount was 10 %, while further increase did not affect the selectivity of process to FAME.
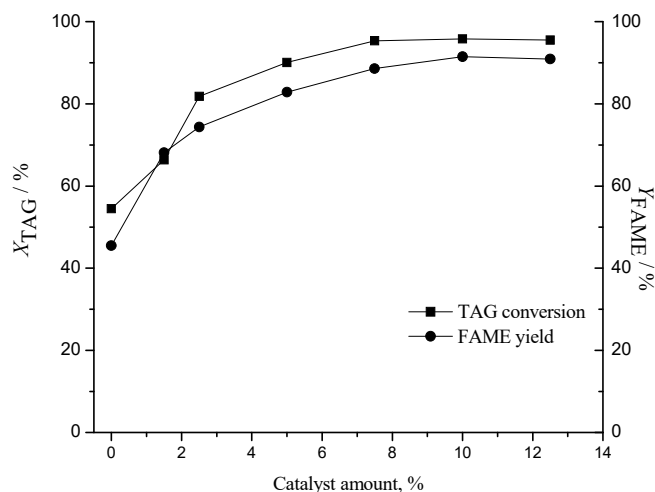

Fig. 5. The effect of catalyst amount on TAG conversion and FAME yield (reaction time, 1 h; reaction temperature, 428 K; mole ratio of methanol to oil, 18:1).

Contrary to the results obtained with $MnCO_3$ as a catalyst for biodiesel synthesis,[8] where the use of catalyst amount over 2 % did not increase the FAME yield or TAG conversion, this study showed that $MnCO_3$/Na silicate particles used in larger amount had a positive effect on FAME yield, but only to some value (10 %). Although the presence and catalytic effect of Na ion in the $MnCO_3$//Na silicate enables higher FAME yield achievement, the active surface area of $MnCO_3$/Na silicate granules is smaller compared to that of $MnCO_3$ in the powdered form and it must be compensated using a larger amount of catalyst.

Reusability of MnCO₃/Na silicate catalyst

The reuse of the catalyst in consecutive runs is of great importance for reducing the cost of biodiesel production on industrial scale. The process of soybean oil transesterification carried out at temperature of 458 K, with 10 mass% of catalyst, 30:1 methanol-to-oil mole ratio and 1 h reaction time, was repeated 9 times. After 8 cycles determined TAG conversion was 97.6 % and FAME yield was 92.6 % as shown in Fig. 6, while after the 9th run FAME yield dropped to 88 % although a high TAG conversion was still attained. This result implies that the prepared $MnCO_3$/Na silicate catalyst could be used eight times with very high TAG conversion (the average value 99.1 % for 8 repeated tests) and FAME yield (the average yield of 97.5 %). Therefore, the application of $MnCO_3$/Na silicate resulted in a higher yield of FAME compared to pure $MnCO_3$ or some other catalyst containing Mn as precursor.[8,38]

Catalyst characterization

Basic strength. The basic strength of Na-silicate in powdered form and MnCO$_3$/Na silicate could be denoted as $9.8 < H\_ < 15$, whereas, the basic strength of MnCO$_3$ powder was $H\_ < 9.8$. Evidently, the basic strength of the catalyst particles ($9.8 < H\_ < 15$) is mainly due to the presence of Na silicate. The basic strength of catalyst 9-times used for transesterification of soybean oil dropped to $H\_ < 9.8$. This finding implies that a certain amount of Na in contact with the reaction mixture during transesterification was dissolved into biodiesel and glycerol.[20]
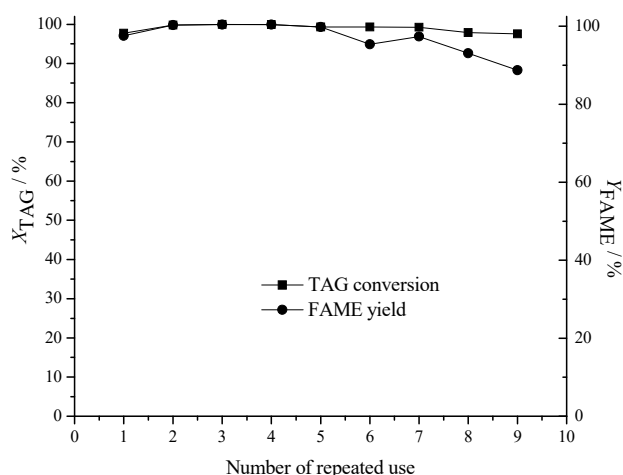

Fig. 6. The effect of repeated use of the catalyst on TAG conversion and FAME yield (458 K; reaction time, 1 h; methanol-to-oil mole ratio 30:1; catalyst amount, 10 %).

Thermal analysis

TG–DSC curves of the Na-silicate, MnCO$_3$, as-prepared MnCO$_3$/Na silicate particles, and the catalyst after being reused for 9 cycles are shown in Fig. 7. The continuous weight loss, as shown in Fig. 7a, was observed during the heating of the Na silicate sample from 400 to 700 K, which corresponds to the removal of water. The phase decomposition of MnCO$_3$ was detected at 705.5 K according to the DSC peak (Fig. 7b), and this fact implies that MnCO$_3$ is stable below 650 K. The weight loss of MnCO$_3$/Na silicate appeared from 570 to 700 K as shown in Fig. 7c and for the used MnCO$_3$/Na silicate from 640 to 700 K as shown in Fig.7d. These results support the previous findings related to temperature of MnCO$_3$ decomposition.[39]

X-ray diffraction(XRD)

The bulk phase structure of MnCO$_3$/Na-silicate catalyst, before and after its use in soybean oil transesterification, was analyzed by XRD and results are shown
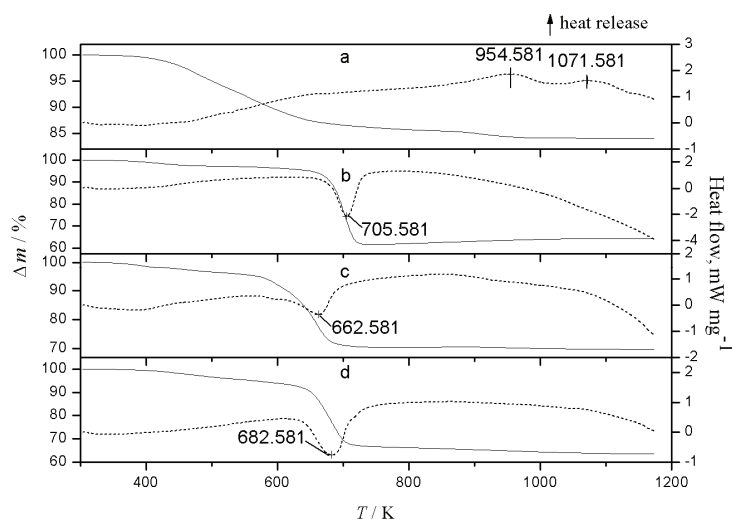
Fig. 7. TG-DSC analysis. a) Na silicate; b) $MnCO_3$; c) as-prepared $MnCO_3$/Na silicate; d) $MnCO_3$/Na silicate being reused for 9 cycles; (—) TG curve; (·····) DSC curve.

in Fig. 8. At the same figure the XRD analysis of Na-silicate and pure $MnCO_3$ are also shown (Fig. 8a and 8b, respectively). No obvious peak of Na silicate was observed in the XRD pattern (Fig.8a) because the temperature at which the sample has been dried (333 K) led only to the formation of amorphous Na silicate, not high enough for crystallization, as shown by TG/DSC analysis. Typical
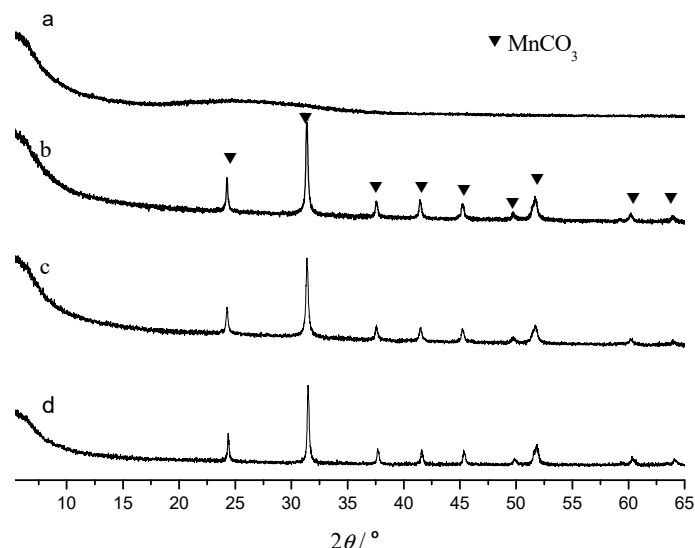

Fig. 8. XRD patterns. a) Na silicate; b) $MnCO_3$; c) as-prepared $MnCO_3$/Na silicate; d) $MnCO_3$/Na silicate being reused for 9 cycles.

diffraction peaks of $MnCO_3$ are presented in Fig. 8b, where almost identical of either as-prepared (Fig. 8c) or used (Fig. 8d) $MnCO_3$/Na silicate catalyst was obtained indicating that the $MnCO_3$ structure did not notably change during the transesterification of soybean oil. While $MnCO_3$ in powder form underwent a slight change in structure after being reused[8], this was not the case when $MnCO_3$//Na silicate was reused several times, showing that Na-silicate positively influenced its stability.

Fourier transform infrared analysis (FTIR)

FTIR spectroscopy was applied to investigate the functional groups of the $MnCO_3$/Na silicate (as-prepared and used for 9 times in transesterification process of soybean oil), as well as of $MnCO_3$ and Na silicate, and the obtained results are shown in Fig. 9.
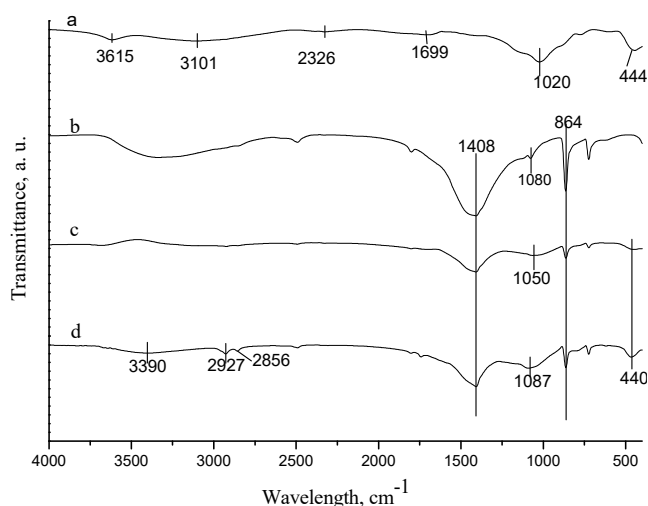

Fig. 9. FTIR spectra of: a) Na silicate dried at 333 K; b) $MnCO_3$; c) as-prepared $MnCO_3$/Na silicate and d) $MnCO_3$/Na silicate catalyst being reused for 9 cycles.

The peaks of Na-silicate (Fig. 9a) at 3615, 3101 and 2326 cm^{-1} correspond to the stretching vibrations of –OH and HOH while the flexural vibration of HOH is at 1699 cm^{-1}. It proves the existence of crystal water in the amorphous Na silicate. The characteristic peak at 1020 cm^{-1} arises from the whirling vibration of Si–O and the peak at around 400 cm^{-1} (Fig. 9a, c and d) is assigned to the Si–O–Si and O–Si–O flexural vibrations in Na silicate.[40,41] The characteristic peaks at 1410 and 864 cm^{-1} (Fig. 9b) are assigned to the CO_3^{2-} vibrations.[42] The broad band at 1408 and 864 cm^{-1} in as-prepared and used $MnCO_3$/Na silicate catalyst (Fig. 9c and d, respectively) are similar to that of the $MnCO_3$, indicating the existence of $MnCO_3$ in the catalyst, and proving that $MnCO_3$ phase did not

change after reuse. The peak at 1050 cm^{-1} in Fig. 9c is identified as the over-lapped peak of the whirling vibration of Si–O and C–O. The peak at 1080 cm^{-1} in the FTIR spectrum of the used catalyst (Fig. 9d), which overlapped the peak at 1050 cm^{-1}, could be the effect of C–O bands in some organic compounds adsorbed on catalyst surface. The O–H bands (at 3390 cm^{-1}) and C–H bands (at 2927 and 2856 cm^{-1}) also prove the existence of some organics adsorbed on the surface of the used catalyst.

N$_2$ adsorption–desorption

The surface area, pore volume and average pore size were determined for as--prepared MnCO$_3$/Na silicate as well as for the 9-times reused sample. This analysis showed that the as-prepared catalyst had the surface area of 3.99 m^2 g^{-1}, the pore volume of 0.015 cm^3 g^{-1} and the average pore size of 15.4 nm with the pore distribution from 1.7 to 233 nm, while the used catalyst exhibited 3 times lower surface area (1.47 m^2 g^{-1}), almost the same pore volume of 0.017 cm^3 g^{-1} and the average pore size of 26.6 nm with the distribution of pores from 5.9 to 429 nm. The decrease of specific area did not have significant influence on TAG conversion, because it was followed by the same value of pore volume while distribution of pores has been shifted toward the larger pore sizes. The high TAG conversion even after 9 repeated uses of catalyst could be explained by the fact that all the pores with higher diameter are still accessible for the large molecules like TAG.[43] The FAME yield decrease is probably caused by the leaching of active metals (Na) from the catalyst surface without the change of silica support.

Scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS)

The images obtained by SEM analysis of as-prepared and 9-times reused MnCO$_3$/Na silicate catalyst are shown in Fig. 10a1 and b1, respectively. A lamellar structure on the surface of as-prepared catalyst, with plenty of channels and micro-pores, indicate the possible active sites for catalysis as shown in Fig.10a2 and a3. Similar and unique globular structure might be also seen on the surface of the used catalyst (Fig. 10b2 and b3). It can be considered as the catalyst surface on which the adsorbed organic compounds, mainly DG and MG, create the "jammed" structure of the catalysts surface.

The SEM–EDS analysis of the atomic percentage of a submicron layer at different points of as-prepared and used catalyst could be used to explain the change of the catalyst during its repeated use in transesterification process. Some of them are indicated as points A, B and C in Fig. 10a3 and 10b3 and the results of EDS analysis for that area are shown in Table III.

Although a large differences of the atomic content of Mn, Na and Si were obtained after the analysis of as-prepared catalyst, an important result of EDS analysis is that the multiple checks of the used catalyst atomic composition did

not indicate the presence of Na. That means that Na atoms were mainly removed from specific part of the catalyst surface by leaching or, as defined in literature, by the ion-exchange in the presence of methanol or glycerol.[19]
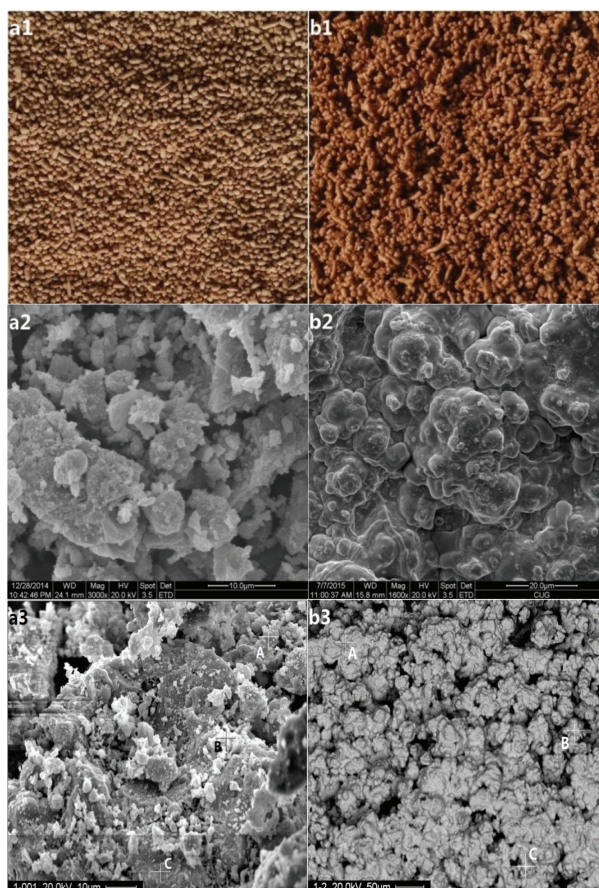

Fig. 10. SEM analysis of as-prepared MnCO$_3$/Na silicate catalyst (a1, a2 and a3) and MnCO$_3$/Na silicate catalyst after being reused 9 times (b1, b2 and b3).

TABLE III. EDS analysis of the surface points of as-prepared and used MnCO$_3$/Na silicate catalyst (the positions of analyzed samples are shown in Fig. 10a3 and b3)

Test point		Content, at.%			
		Mn	Na	C	Si
Fig. 10a3	A	15.00	8.66	52.91	23.43
	B	18.37	10.13	65.39	6.11
	C	29.25	8.67	44.67	17.41
Fig. 10b3	A	13.89	0	82.19	3.92
	B	9.88	0	83.68	6.45
	C	25.40	0	66.55	8.05

Leaching of Na and Mn in biodiesel and glycerol

The amounts of Mn and Na in glycerol and biodiesel phase were analyzed after each of 9 experiments of the repeated use of $MnCO_3$/Na silicate catalyst. The results of AAS analysis are shown in Fig. 11.
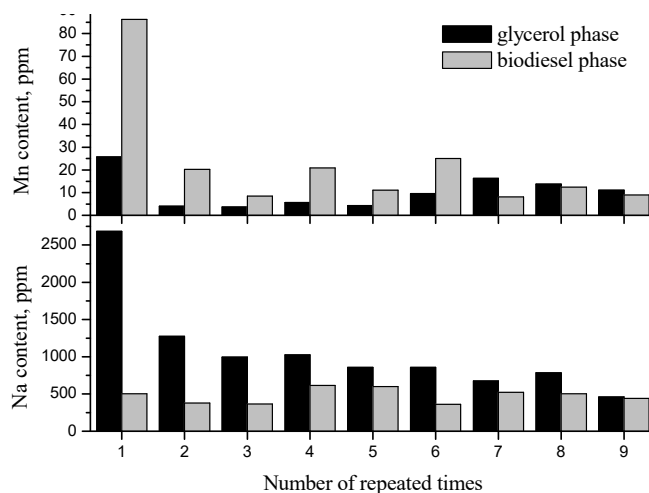

Fig. 11. The effect of repeated use of the catalyst on the amount of dissolved Mn and Na in biodiesel and glycerol phase.

Generally, a larger amount of Na, compared to Mn, was found in both phases; Na amount in glycerol phase was 2680 mg/kg after the first use of catalyst, and almost two times smaller after the second repeated use of catalyst. In other samples of glycerol phase the amount of Na has slightly decreased to 500 mg/kg as found after the 9th repeated use of catalyst (Fig. 11). Amount of Na in esters (biodiesel) phase was almost the same for all of the collected samples (below 500 mg/kg). The large amount of Na dissolved in the products was caused by the ion-exchange after methanol being adsorbed on the surface of catalyst.[19] In contrast to this finding, only a very small amount of Mn was dissolved in both products as shown in Fig. 11. As in the case of Na, a larger amount of Mn was determined after the first use of catalyst; it was about 90 mg/kg in biodiesel phase and about 25 mg/kg in glycerol phase.

The observed phenomena might be explained by the leaching of Na and Mn which occurs in the later stages of repeated use, followed by the increased resistance of diffusion from the internal surface area of catalyst to the reaction mixture. After the first use of catalyst the active Na and Mn at the surface of catalyst particles, were relatively easily removed and dissolved in the reaction mixture, and then the rate of leaching began to be much slower. The cumulative amount of Na leached in both phases after 9 cycles was calculated to be 57 % based on the

mass of catalyst, indicating that a certain amount of Na remained, probably in the internal part of the catalyst particles. The change of constituents' concentration at catalyst surface (Na/Mn), after the each repeated use of the catalyst, leads to the change of the catalyst selectivity (Fig. 6).

CONCLUSION

The MnCO₃/Na-silicate 0.99–1.99 mm particles (Mn/Na/Si mole ratio of 4.65:1:1.65) were prepared and used for the biodiesel synthesis. The complete conversion of TAG and high FAME yield were obtained at 458 K using the methanol-to-oil mole ratio of 30:1 and 10 % of prepared catalyst. A high conversion of TAG as well as of FAME yield after 8 times of the repeated use of the same amount of catalyst was also proved. The high catalyst selectivity toward FAME synthesis was explained on the basis of the catalyst characterization, and it was found that the leaching of Na into methanol/glycerol phase was the main reason for the observed effect. The best results of calculated TAG conversion were obtained using the kinetic model that includes the mass transfer resistances and the chemical reaction at active sites of the catalyst.

NOMENCLATURE

A	Pre-exponential factor, min^{-1}
c_{TAG}	Concentration of TAG, mol L^{-1}
c_{Ro}	Model parameter, the hypothetic initial FAME concentration corresponding to the initial available amount of TAG close to the active catalyst surface, mol L^{-1}
d	Catalyst particle diameter, mm
DAG	Diacylglycerols amount in the FAME/oil fraction of the reaction mixture, %
FAME	Fatty acid methyl esters amount, %
$H\_$	Basic strength of the samples
k_{LT}	Reaction rate constant up to 423 K, min^{-1}
k_{HT}	Reaction rate constant above 423 K, min^{-1}
k_{app}	Apparent reaction rate constant, min^{-1}
k_{mt}	Overall triglyceride volumetric mass transfer coefficient, min^{-1}
K	Model parameter defining the TAG affinity for the catalyst active sites, mol L^{-1}
MAG	Monoacylglycerols amount in the FAME/oil fraction of the reaction mixture, %
$-r_{TAG}$	Rate of TAG transesterification, mol min^{-1} L^{-1}
t	Time, min
T	Temperature, K
TAG	Triacylglycerols amount in the FAME/oil fraction of the reaction mixture, %
x_{TAG}	TAG conversion
Y_{FAME}	FAME yield, %
α	Fitting parameter in Eq. (9a)
β	Fitting parameter in Eq. (9a)
δ	Mass ratio of Na silicate to MnCO₃

И З В О Д

СИНТЕЗА БИОДИЗЕЛА И АНАЛИЗА КИНЕТИКЕ СА MnCO₃/Na-СИЛИКАТОМ КАО ХЕТЕРОГЕНИМ КАТАЛИЗАТОРОМ

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Катализатор MnCO₃/Na силикат (молски однос Mn/Na/Si од 4,65:1:1,65) у облику чврстих честица величине 0,99–1,99 mm, коришћен је у трансестерификацији сојиног уља у шаржном реактору при различитим условима: 388–468 K, моларни однос метанола и уља 12:1–30:1, 0–12,5 % катализатора у односу на масу уља. Комплетна конверзија триацилглицерола (TAG) и висок принос метил-естара масних киселина (MEMK) постигнути су после 1 сата на 458 K, при молском односу метанола и уља од 30:1 и са 10 % катализатора. Кинетика процеса трансестерификације анализирана је применом три модела: једноставног модела неповратне реакције првог реда, као и сложенијих модела недавно објављених у литератури. Тестирано је поновно коришћење катализатора у процесу трансестерификације и просечне вредности конверзије TAG од 99,0 % и приноса MEMK од 97,5 % добијени су након 8 узастопних циклуса. Примењене су различите технике карактеризације свежег и коришћеног MnCO₃/Na-силикат катализатора. Количина излуженог Na (<500 ppm) и Mn (<20 ppm) у фази биодизела указује на то да хомогено-хетерогени процес утиче на селективност катализатора, пошто излужени Na омогућава комплетну трансформацију TAG у MEMK.

REFERENCES

1. S. L. Yan, S. Mohan, C. DiMaggio, M. Kim, K. Y. S. Ng, S. O. Salley, *Fuel* **89** (2010) 2844
2. W. Jiang, H. F. Lu, T. Qi, S. L. Yan, B. Liang, *Biotechnol. Adv.* **28** (2010) 620
3. X. Yu, Z. Wen, H. Li, S.-T. Tu, J.Yan, *Fuel* **90** (2011) 1868
4. K. Gombotz, R. Parette, G. Austic, D. Kannan, J. V. Matson, *Fuel* **92** (2012) 9
5. M. Zabeti, W. M. A. W. Daud, M. K. Aroua, *Fuel Process Technol.* **90** (2009) 770
6. Y. R. Rao, P. K. Zubaidha, J. N. Reddy, D. D. Kondhare, D. S. Sushma, *Green Sust. Chem.* **2** (2012) 14
7. Y. R. Rao, P. K. Zubaidha, J. N. Reddy, D. D. Kondhare, S. S. Deshmukh, S. P. Saiprakash, *Catal. Sust. Energy* **1** (2013) 22
8. L. Wan, H. Liu, S. Nasreen, I. Lukić, D. Skala, *Chem. Ind. Chem. Eng. Q*, 2017, https://doi.org/10.2298/CICEQ170221013W
9. L. Wan, H. Liu, D. Skala, *Appl.Catal., B* **152–153** (2014) 352
10. X. Zhu, H. Liu, D. Skala, *Chem. Ind. Chem. Eng. Q.* **22** (2016) 431
11. I. Lukić, Ž. Kesić, D. Skala, *Chem. Eng. Technol.* **37** (2014) 1
12. H. P. Zhao, C. S. Ye, Z. T. Fan, *J. Eur. Ceram. Soc.* **34** (2014) 1457
13. S. M. Dobosz, P. Jelinek, K. Major-Gabrys, *China Foundry* **8** (2011) 438
14. Y. S. Zhang, Y. Y. Xue, J. Huang, S. N. Li, L. Xia, C.H. Huang, *J. Wuhan Univ. Technol.* **24** (2009) 5

15. T. Tomita, S. Kawasaki, T. Nagaoka, K. Sato, K. Watari, *J. Ceram. Soc. Jpn.* **116** (2008) 224
16. L. Izdebska-Szanda, A. Balinski, M. Angrecki,A. Palma, *Arch. Metall. Mater.* **59** (2014) 1033
17. A. Rabbii, *Iran Polym. J.* **10** (2001) 229
18. F. Guo, Z. G. Peng, J. Y. Dai, Z. L. Xiu, *Fuel Process. Technol.* **91** (2010) 322
19. F. Guo, N. N. Wei, Z. L. Xiu, Z. Fang, *Fuel* **93** (2012) 468
20. M. A. Portnoff, D. A. Purta, M. A. Nasta, J. Zhang, F. Pourarian, WO2006/002087, 2006
21. Y.-D. Long, F. Guo, Z. Fang, X.-F. Tian, L.-Q. Jiang, F. Zhang, *Bioresour. Technol.* **102** (2011) 6884
22. M. O. Daramola, D. Nkazi, K. Mtshali, *Int. J. Renew. Energ. Res.* **5** (2015) 517
23. Y.-D. Long, Z. Fang, T.-C. Su, Q. Yang, *Appl. Energy* **113** (2014) 1819
24. X. Gui, S. Chen, Z. Yun, *Chin. J. Chem. Eng.* **24** (2016) 499
25. I. Lukić, Ž. Kesić, S. Maksimović, M. Zdujić, H. Liu, J. Krstić, D. Skala, *Fuel* **113** (2013) 367
26. M. R. Miladinović, J. B. Krstić, M. B. Tasić, O. S. Stamenković,V. B. Veljković, *Chem. Eng. Res. Des.* **92** (2014) 1740
27. L. Zhao, Z. Qiu, S. M. Stagg-Williams, *Fuel Process Technol.* **114** (2013) 154
28. D. Kumar, A. Ali, *Energy Fuels* **27** (2013) 3758
29. O. Ilgen, A. N. Akin, *Appl. Catal., B* **126** (2012) 342
30. A. Chantrasa, N. Phlernjai, J. G. Goodwin Jr., *Chem. Eng. J.* **168** (2011) 333
31. V. V. Bokade, G. D. Yadav, *Ind. Eng. Chem. Res.* **48** (2009) 9408
32. Q. Shu, J. Gao, Y. Liao, J. Wang, *Chin. J. Chem. Eng.* **19** (2011) 163
33. M. R. Miladinović, M. B. Tasić, O. S. Stamenković, V. B. Veljković, D. U. Skala, *Chem. Ind. Chem. Eng. Q.* **22** (2016) 137
34. M. B. Tasić, M. R. Miladinović, O. S. Stamenković, V. B. Veljković, D. U. Skala, *Chem. Eng. Technol.* **38** (2015) 1550
35. S. Nasreen, H. Liu, I. Lukic, L. Qurashi, D. Skala, *Chem. Ind. Chem. Eng. Q.* **22** (2016) 419
36. L. Hui, Z. Yanan, CN105536775 A, 2016
37. S. Glisic, A. Orlovic, *J. Supercrit. Fluids* **65** (2012) 61
38. S. Nasreen, H. Liu, L. Ali Qureshi, Z. Sissou, I. Lukic, D. Skala, *Fuel Process. Technol.* **148** (2016) 76
39. L. Biernacki, S. Pokrzywnicki, *J. Therm. Anal. Calorim.* **55** (1999) 227
40. I. K. Battisha, A. El Beyally, S. Abd El Mongy, A. M. Nahrawi, *J. Sol-Gel Sci. Technol.* **41** (2007) 129
41. T. Witoon, N. Tatan, P. Rattanavichian, M. Chareonpanich, *Ceram. Int.* **37** (2011) 2297
42. X. C. Duan, J. B. Lian, J. M. Ma, T. Kim, W. Z. Zheng, *Cryst. Growth Des.* **10** (2010) 4449
43. I. Lukic, J. Krstic, D. Jovanovic, D. Skala, *Bioresour. Technol.* **100** (2009) 4690.