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HIGH TEMPERATURE TRANSESTERIFICATION OF SOYBEAN OIL WITH METHANOL USING MANGANESE CARBONATE AS CATALYST

Abstract

The manganese carbonate catalyst, prepared by precipitation method, was used in transesterification of soybean oil under subcritical condition of methanol. Catalyst samples were characterized by X-ray diffraction (XRD), Fourier transform infrared (FT-IR) spectroscopy, scanning electron microscopy (SEM) with energy dispersive spectroscopy (EDS). The triacylglycerol (TAG) conversion and fatty acid methyl esters (FAME) yield were determined using high performance liquid chromatography (HPLC). The transesterification was realized for 1 h using various working conditions: 0-3 wt.% of catalyst (based on the mass of oil), the mole ratio of methanol to oil from 13:1 to 27:1 and temperature ranging from 393 to 473 K. A maximum TAG conversion of 98.1% could be obtained at the optimal reaction conditions: 2 wt.% of catalyst, methanol/oil mole ratio of 21:1, for 1 h in a batch reactor at 453 K. Kinetic analysis showed that the model based on mass transfer and chemical reaction at the catalyst surface confirmed the experimental data. Using that kinetic expression, the effect of continuous transesterification was proposed and verified by a 360-h long realized experiment in a laboratory packed-bed reactor (PBR). Slow deactivation of the catalyst was caused by leaching of Mn in both biodiesel and glycerol phases and by blocking the active sites of the catalyst with organic compounds.

Keywords: biodiesel, continuous process, heterogeneous catalyst, kinetics, manganese carbonate, subcritical condition.

Over the last few decades, great attention has been paid to the development of an active, stable and inexpensive solid catalyst, which will successfully replace the homogeneous catalyst, today most commonly used in commercial biodiesel production processes. A large number of solid catalysts such as single, supported or mixed metal oxides, Al-Mg hydrotalcites, zeolites etc. have been thoroughly studied in transesterification of different vegetable oils into a mixture of fatty acid methyl esters (FAME, or biodiesel). However, the search for the solid catalyst that will make the heterogeneously catalyzed process competitive with the homogeneous one is still a challenge.

Manganese in oxide form or in a complex mixture with some other metals has been reported to be a promising catalyst for vegetable oil transesterification [1-10]. In all these studies, high conversions of TAG were obtained with different oils, both edible and low grade feedstock with high fatty acid contents [4--6]. Although low temperature synthesis of biodiesel was applied in a few studies [2,5], it can be noticed that in all these cases, catalysts which contained Ca and Mn, showed activity at lower temperatures [11], while in all other studies high pressure and high temperature were necessary. The $MnCO_3$/ZnO catalyst exhibited high catalytic activity and maintained it after being reused for 17 cycles without any regeneration during the transesterification of soybean oil with methanol [9], while $MnCO_3$ mixed with zinc glycerolate could be reused 13 times [10]. A group of authors rep-

orted that pure $MnCO_3$ was active in transesterification of different oils at 333 K with 80-95% conversion achieved [12,13]. However, it must be pointed out that the authors did not specify the characteristics of the used $MnCO_3$ and they noted only the name of company which produces the technical $MnCO_3$, with purity of 90%, thus leading to the conclusion that the inclusion of some other compound may be responsible for such high activity of $MnCO_3$ under mild reaction conditions. $MnCO_3$ was also tested at high temperature transesterification, showing very good catalytic efficiency, although slightly lower than that of $MnCO_3$//ZnO at the defined conditions [9]. This paper aims to investigate the possibility of improvement of $MnCO_3$ efficiency by optimization of reaction conditions, considering that $MnCO_3$ is naturally abundant, thus relatively cheap and commercially available, and also environmentally friendly, making it promising for commercial application as a low cost catalyst for biodiesel production.

Kinetics of transesterification at high temperature

Various models used to describe the kinetics of heterogeneously catalyzed transesterification, including the most commonly used simple pseudo-first order model [14-16], second-order [17,18] and more complex models based on the Eley-Rideal or Langmuir-Hinshelwood reaction mechanisms, were analyzed [19,20]. The kinetic models proposed by Miladinović *et al.* [21] and Lukić *et al.* [22,23] deserve the greatest attention, predicting correctly the reaction rate of the transesterification process at low temperature (LTT). It was shown that both of them are suitable for describing the kinetics of transesterification over various calcium-based catalysts [24,25]. Furthermore, the recently reported study verified their capability to successfully describe the kinetics of trancesterification at high temperature (HTT) using different catalysts (La/Mn, Ce/Mn, Sr/cinder, Fe-Zn double--metal cyanide complex or La_2O_3/ZrO_2) [26]. In the present study, the kinetic model proposed by Miladinović *et al.* [21] (MM model), the model developed by Lukić *et al.* [22,23] (IL model) and, the most widely used, simple pseudo-first order reaction model were applied to define the kinetics of transesterification of soybean oil using $MnCO_3$ catalyst at high temperature. The model that showed the best agreement with experimental results was further used for a continuous transesterification process simulation.

Continuous transesterification

To better describe the activity and life of the specific catalyst suitable for the transesterification process, different techniques could be applied. The repeated use of the same amount of catalyst for transesterification in a batch process is one of them, but the most important techniques that always give valuable information about catalyst activity, are tests performed in the continuous transesterification process. Many of these reports could be also divided in three different groups according to the temperature used for analyzing continuous transesterification processes: a) at lower temperature (<373 K, the continuous low temperature transesterification; c-LTT) [27,28]; b) at average temperature (373 K < *T* < 423 K; c-MTT) [29] and c) at high temperature (>423 K; c-HTT) [4,30-34]. Characteristic of c-LTT processes is the application of base oxide in which Ca is a common active component, while different active species were tested in c-HTT mainly based on metal oxides [4,31,34] or mixed Zn with Al, La or Fe [32,33]. A tubular reactor was packed with various particle sizes of catalyst and in several cases mixed by inert glass beads. Different type of oils (palm, soybean, coconut, rapeseed, sunflower, rubber seed) or a model mixture of pure triacylglycerols (*e.g.*, triolein) and free fatty acids (*e.g.*, oleic acid) were tested for biodiesel synthesis. The main objective of all experiments of continuous transesterification is to define the change of catalyst activity after varied time of continuous operation. Processes of c-HTT were usually realized in less than 300 h, and only two reports gave the results of catalyst activity during 70 and 150 days, respectively [31,32].

According to the above analysis, the main goal of this study was to define: a) activity of $MnCO_3$ at different working conditions; b) a kinetic model which might be used for presenting conversion of triacylglycerols at optimal working condition in a batch reactor; c) activity of $MnCO_3$ during long term c-HTT and d) conversion of TAG during c-HTT by using determined kinetic models.

EXPERIMENTAL

Materials

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. The reagents K_2CO_3 (99%), methanol (99.5%), $MnCl_2$ (99%) and HNO_3 (68%), are of analytical grade, and were purchased from Aopu Chemical Company (Wuhan, China).

Catalyst preparation

The catalyst was prepared according to the pre-cipitation method. K_2CO_3 was used as a precipitant to deposit the aqueous solution of $MnCl_2$. For a typical catalyst preparation, 100 mL 1.25 M $MnCl_2$ was slowly added into 600 mL 0.25 M K_2CO_3 aqueous solution under vigorous stirring at 333 K. The mixture was then aged at room temperature for 2 h. The solid product was recovered by filtration, followed by thorough washing with deionized water and drying in an oven at 323 K overnight. The dried solid was cal-cinated in a muffle furnace at 573 K for 0.5 h, and was stored in a desiccator.

Catalyst characterization

XRD was performed on a D/MAX-RB powder X-ray diffractometer (Rigaku Corporation, Japan) at room temperature. CuKα radiation (λ = 0.15418 nm), with a step size of 0.02° in the 2θ range from 5 to 65°, was used in all samples. The data was processed with the X'Pert HighScore Plus software. The peaks were identified using the Powder Diffraction File (PDF) database created by the International Centre for Diffraction Data (ICDD).

FTIR spectra were recorded on a Nicolet FT-IR 5700 spectrometer (Thermo Electron Corporation, USA）over the wave number range of 4000-500 cm^{-1}, with 2 cm^{-1} resolution. The KBr pellet technique was applied in order to prepare samples. All measure-ments were conducted at room temperature.

Sample morphology and elemental chemical analysis at chosen points of the samples were char-acterized at room temperature by a Quanta 200 SEM system equipped with EDS detector (FEI Company, Netherlands). The accelerating voltage was 20 kV.

Batch experiment of transesterification reaction

For catalytic tests a 500 mL stainless steel auto-clave containing a stirrer, an internal cooling pipe, a temperature sensor and an external heating jacket was used (PCF0.5-10 JianBang Chemical Machinery Co. Limited, China). The maximum working pressure and temperature of the autoclave are 10 MPa and 573 K, respectively. The following procedure of the transesterification process in a batch reactor was applied: soybean oil with 0.12 wt.% of water and 0.2 mgKOH/g acid values [35], methanol, and catalyst were placed into the autoclave and then heated to the pre-set temperature and stirred at a constant speed of 200 rpm. The reaction time was counted when the temperature in autoclave reached the pre-set value at the controller. The reaction pressure (1.8-3.2 MPa) in the reactor was measured by a pressure sensor. After

the expected reaction time, the transesterification of soybean oil was stopped by the tap water flowing through the internal cooling pipe. Then, the autoclave was opened and the product was analyzed to deter-mine TAG conversion and FAME yield.

Continuous process of biodiesel synthesis

Methanol and oil in mole ratio 21:1 were stirred in a container and 0.2 cm^3 min^{-1} of the mixture was pumped to a packed-bed reactor (PBR; inside dia-meter of 0.78 cm and a length of 30 cm) using an HPLC pump. The reactor and inlet line (1.6 mm tube) were placed in the oven at 453 K.

The fixed-bed reactor was packed with prepared $MnCO_3$ catalyst (m_{cat} = 14.6 g). The mass flow rate of the reaction mixture into reactor was m_{rm} = 0.17 g min^{-1}. The mass of the catalyst and its bulk density was used to calculate the volume of the reactor occupied by the catalyst. The void fraction in the reac-tor was determined on the basis of the mass of meth-anol (and its density) used to fill the PBR. The resi-dence time of the reaction mixture in the reactor and the weight hourly space velocity ($WHSV = m_{rm}/m_{cat}$) were 0.92 h and 1.43 h^{-1}, respectively.

The reaction mixture, taken from the batch reactor or collected at the outlet of PBR, was separ-ated into ester and glycerol phases. A sample of the ester phase was analyzed by HPLC to determine the content of triacylglycerols (TAG), diacylglycerols (DAG), monoacylglycerols (MAG) and fatty acid methyl esters (FAME). The results of HPLC analysis were used for TAG conversion and FAME yield cal-culation, respectively.

The content of Mn in the samples of glycerol and ester phases was also determined using atomic abs-orption spectrophotometer (AAS).

Analysis of the ester phase

Collected samples were diluted with isopropa-nol-hexane and filtered through a membrane (0.45 μm pore) and the concentrations of TAG, DAG, MAG and FAME were determined by HPLC analysis using Agil-ent 1100 series with a C18 column (40 °C, particle size 5 μm, 200 mm×4.6 mm I.D.) with UV/Visible detection at 205 nm. A linear gradient from 100% methanol to 50% methanol + 50% isopropanol-hex-ane (5:5 volume ratio) in 25 min was employed.

Calculation of TAG conversion and FAME yield

The ester phase contains products of trancester-ification (FAME, MAG and DAG) and TAG and it was analyzed to determine the peak areas (A_i, i = TAG or FAME) of the HPLC chromatogram. Calculation of

TAG conversion and FAME yield was done using the following equations:

$$X_{TAG} = 100 \frac{A_{TAG,0} - A_{TAG}}{A_{TAG,0}} \qquad (1)$$

$$FAME = 100 \frac{A_{FAME,f} - A_{FAME}}{A_{FAME,f}}$$

where $A_{TAG,0}$ is the peak area of TAG in the soybean oil sample, and $A_{FAME,f}$ is the peak area of FAME in the sample of the ester phase containing only FAME (TAG was completely converted into FAME; MAG and DAG were not detected).

RESULTS AND DISCUSSION

Analysis of transesterification realized at different working conditions

Influence of the catalyst amount used for transesterification

TAG conversion and FAME yield were increased when a higher amount of MnCO$_3$ catalyst was used at 453 K and methanol to oil mole ratio of 21:1, as shown in Figure 1a. It was detected that without the presence of a catalyst, the TAG conversion and FAME yield were 72.3 and 55% after 60 min, measuring time from the moment when the reaction mixture in the batch reactor reached 453 K. Knowing that 55 min was necessary for heating to 453 K (non-isothermal process), it means that the total reaction time in the batch reactor was 115 min. TAG conversion and FAME yields obtained in this study are higher than those reported by other authors that analyzed non-catalytic biodiesel synthesis at subcritical condition of methanol [36].

TAG conversion of 97.8% and FAME yield of 80.2% were obtained after 115 min (55 min of non--isothermal + 60 min of isothermal process) with 2 wt.% of catalyst. They did not increase when a larger amount of catalyst (3 wt.%) was used. On the basis of these results, the influence of other parameters of the transesterification process was analyzed using 2 wt.% of catalyst.
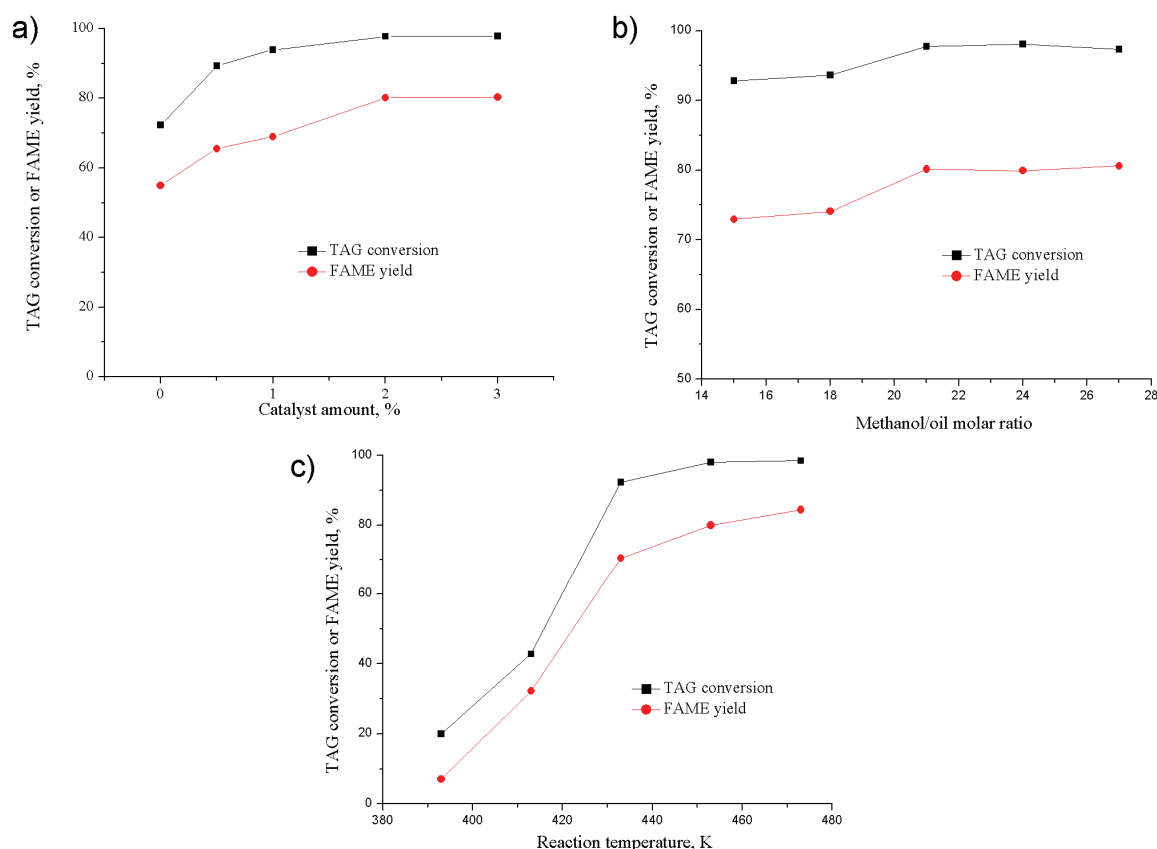

Figure 1. Influence of: a) catalyst amount (reaction conditions: molae ratio of methanol to soybean oil, 21:1; reaction temperature, 453 K; reaction time, 115 min (55 min heating to 453 K and 60 min of isothermal operation); b) mole ratio of methanol to soybean oil (reaction condition: 453 K; 2% of catalyst and reaction time, 115 min (55 min heating to 453 K and 60 min of isothermal operation); c) temperature (reaction conditions: catalyst amount, 2%; mole ratio of methanol to oil, 21:1; reaction time, 60 min of transesterification at isothermal temperature and various time necessary for heating to isothermal temperature) on TAG conversion of soybean oil and FAME yield.

Influence of methanol to oil mole ratio

The transesterification reaction consists of three reversible reactions where TAG is transformed into FAME, glycerol and the intermediate products (DAG and MAG). The mole ratio of methanol to oil is an important parameter that mainly affects the possible equilibrium conditions of reversible reactions between DAG and methanol and MAG and methanol, followed by formation of FAME:

TAG + MeOH ⇆ DAG + FAME

DAG + MeOH ⇆ MAG + FAME
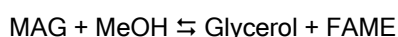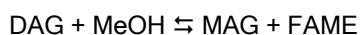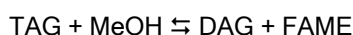
MAG + MeOH ⇆ Glycerol + FAME

Figure 1b represents the effect of methanol to oil mole ratio, showing TAG conversion and FAME yield increase to 98.1 and 80% with the increase of this parameter to 21:1. However, further increase of methanol to oil mole ratio to 27:1 used for transesterification at 453 K and 2 wt.% of $MnCO_3$ catalyst exhibited only a small effect on TAG conversion and FAME yield. Therefore, knowing that the total cost of biodiesel production also depends on the excess of alcohol used and its recovery, the methanol to oil mole ratio of 21:1 was considered to be optimal for transesterification of soybean oil with methanol.

Influence of reaction temperature

Temperature is a very important parameter which strongly defines and increases the rate of either non-catalyzed [36,37] or catalyzed transesterification of TAG. For the temperature and pressure close to, or slightly above, the critical temperature and pressure of methanol, and for the conditions of a large excess of supercritical methanol (mole ratio of methanol and oil >42:1), the reaction mixture (oil and methanol) could be in one phase [37]. In such "supercritical condition" for methanol the rate of transesterification is very fast [38]. However, such extreme conditions of transesterification, necessary to obtain the reaction mixture of oil and methanol in one phase, could be avoided by transesterification of oil with methanol in the presence of a solid catalyst under subcritical condition of methanol, as shown and realized in this study.

The influence of reaction temperature between 393 and 473 K (pressure from 0.5 to 1.5 MPa) on TAG conversion and FAME yield were analyzed using 2 wt.% of catalyst and mole ratio of methanol to oil 21:1. Experimental data are shown in Figure 1c. TAG conversion increased from 20 to 98% and FAME yield from 7.1 to 80%.

It is evident that for transesterification realized at higher temperature (> 453 K), TAG conversion is complete and the same as that determined at 453 K,

while only a small increase in FAME yield could be expected. For that reason, the above analysis and optimization of other working parameters were performed at 453 K, which is defined as the optimal temperature for soybean oil transesterification in the presence of $MnCO_3$ catalyst.

The optimal kinetic models (explained in the Appendix), which might be successfully used for representing the rate of HTT in the presence of $MnCO_3$ catalyst, were determined on the basis of TAG conversion at different temperatures [26]. Briefly, using first order kinetics, the apparent reaction rate constant, k_{app}, at different temperatures was calculated. The activation energy (E) and the pre-exponential factor (A) were estimated from the Arrhenius plot of ln k_{app} *versus* $1/T$ (Figure 2).
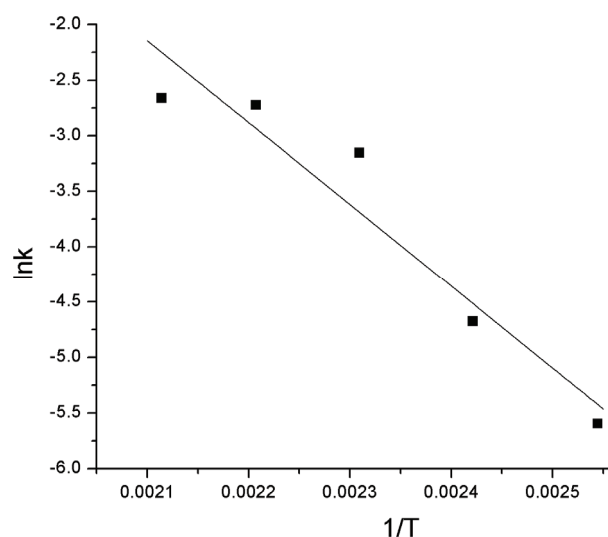

Figure 2. The temperature dependency of the reaction rate constant determined by applying the first-order irreversible reaction as kinetic model.

However, time for heating the reaction mixture in the batch autoclave is required to reach desired isothermal conditions. That time must be taken into account for the analysis of experimental data of TAG conversion *vs.* time during isothermal transesterification. The duration of the non-isothermal period of heating is different for specific isothermal temperature; it is longer for higher isothermal temperature used for transesterification, as shown in Table 1.

The time at which the TAG conversion was determined, thus, represents the sum of the non-isothermal and isothermal periods of transesterification. During that period, the miscibility of oil in methanol, as well as the formation of DAG, MAG and FAME have a large influence on mass transfer of TAG to the active centers of the catalyst. It was important to verify that

Table 1. Modeling of non-isothermal and isothermal HTT performed in a batch autoclave with 2 wt.% of catalyst and mole ratio of methanol to soybean oil 21:1

Reaction temperature, K, and time of non-isothermal and isothermal transesterification	TAG Exp., %	TAG Calcd., %		
		I order	MM model	IL model
393 (34+60 = 94 min)	19.9	23.3	12.9	22.7
413 (41+60 = 101 min)	42.8	48.1	32.8	46.5
433 (48+60 = 108 min)	92.3	77.6	69.8	75.8
453 (55+60 = 115 min)	98.1	95.8	96.9	95.1
473 (62+60 = 122 min)	98.5	99.8	99.9	99.8
MRPD / %		9.73	17.12	8.89

the resistance to mass transfer is much lower compared to the resistance to the chemical reaction on the active center of the catalyst, even at the smallest mixing intensity. For that reason, the calculation of mass transfer resistance for different mixing intensities (500 and 900 rpm) was done and is shown in the appendix. The results of these calculations proved that the mass transfer of TAG to the active centers of the catalyst had a smaller influence on the overall rate of HTT with $MnCO_3$ catalyst.

Information about the influence of mass transfer resistance indicated that the temperature dependency of the reaction rate constant is what determined the apparent reaction rate constant (Figure 2) and could also be applied for more complex IL and MM models (Appendix). Other MM and IL models parameters were tested with the goal to minimize the mean relative percent deviation (*MRPD*) between experimentally determined and calculated TAG conversion (Table 1). The best agreement between calculated and experimentally determined TAG conversions at different temperatures was achieved with IL model (*MRPD* 8.9%). The prediction of TAG conversion was also acceptable assuming the first order reaction model (*MRPD* 9.7%), while the largest deviation was obtained with MM model (17.1%). A similar conclusion was reported in literature by other researchers analyzing various catalysts which contain Mn (Ce/Mn and La/Mn) [26]. The simulation of TAG conversion at different temperatures for La/Mn catalyzed transesterification of soybean oil was best with the IL kinetic model, while the first order reaction and IL model gave similar results when the Ce/Mn catalyst was used [26].

Kinetics of the transesterification process

The effect of reaction time at 453 K and 21:1 mole ratio of methanol to oil was investigated as well. After 55 min of heating, the temperature in the batch reactor reached 453 K (Table 1). Then the isothermal transesterification started and that moment is defined

as *t* = 0, when the first sample was also withdrawn from the reactor and TAG conversion and FAME yield were determined. Next samples were analyzed after 30, 40, 50, 60 and 70 min counted from *t* = 0 and the results are shown in Figure 3.

Near equilibrium TAG conversion was observed to be 98.1% with a FAME yield of 80.0% after 60 min of isothermal process at 453 K. After that time, there was no obvious impact on the transesterification efficiency at 453 K. According to these results, the optimal reaction time of 60 min during isothermal operation at 453 K was selected to be the most appropriate.

In summary, the optimal reaction conditions for batch process of biodiesel production using 2 wt.% of $MnCO_3$ could be defined as: mole ratio of methanol and oil 21:1, and reaction time of 60 min after 453 K was reached in the batch reactor.

The TAG conversion at various reaction times was calculated using corresponding parameters shown in Table 2 (the first order order, MM and IL models).

The values of *MRPD* between experimental and calculated TAG conversion were 2.34, 1.68 and 1.62% for I order, MM and IL model, respectively. The more complex MM and IL models gave slightly better simulations of isothermal operations, which is also consistent with previously reported results [26]. The MM kinetic model is based on the changing reaction mechanism, *i.e.*, the reaction rate from zero to the first order, while the IL model takes into account mass transfer of TAG from the oil phase to active sites of the catalyst and the chemical reaction between methanol and TAG. The physical meaning of IL model parameters appears to be more realistic. Taking into account results of simulation of TAG conversion in the batch autoclave at different temperatures (Table 1) and at isothermal conditions (Figure 3), the IL model was chosen for the prediction of TAG conversion during c-HTT process.
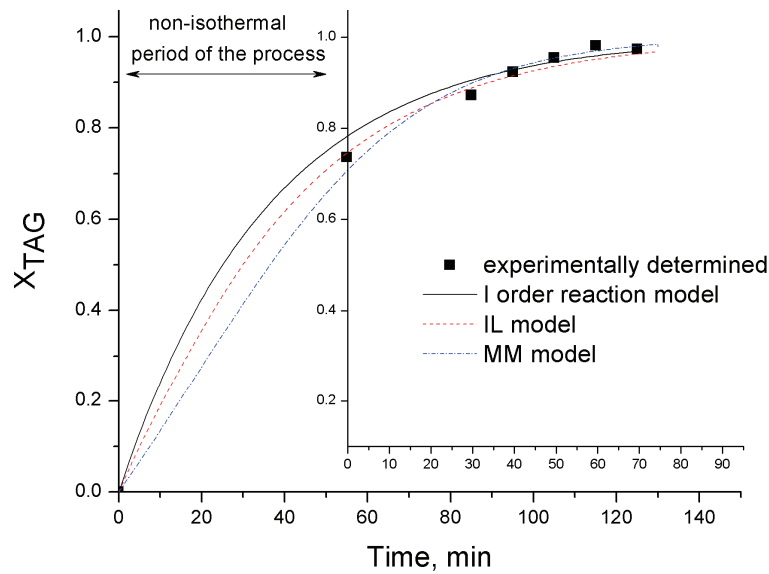
Figure 3. Comparison of experimentally determined and calculated TAG conversion applying various kinetic models. Reaction conditions: 2 wt.% of catalyst, 453 K, mole ratio of methanol and oil 21:1.

According to the IL model, the rate of TAG conversion could be proposed by equation:

$$(-r_{TAG}) = k_{app}(1 - X_{TAG}) \tag{3}$$

where:

$$k_{app} = \frac{k k_{mt}}{k + k_{mt}} \tag{3a}$$

$$k_{mt} = k_{mt,0}(1 + \alpha X_{TAG}^{\beta}) \tag{3b}$$

Simulation of the continuous process

Assuming the plug flow of the reaction mixture in PBR, the mass balance of TAG is defined by equation:

$$(-r_{TAG})dm_{cat} = m_{TAG,0}dX_{TAG} \tag{4}$$

where $(-r_{TAG})$ is the rate of TAG conversion defined by Eq. (3), $m_{TAG,0} = 5.61$ g h^{-1} is the mass flow rate of soybean oil at inlet of PBR defined knowing the mass flow rate of the reaction mixture into the reactor (10.2 g h^{-1}) and oil (TAG) mass fraction (55%), and m_{cat} is the mass of the catalyst.

Using Eq. (4), the mass balance for calculation of the TAG conversion at reactor exit is:

$$\frac{dX_{TAG}}{dm_{cat}} = \frac{1.66 k_{mt,0}(1 - 55 X_{TAG}^{3.5})}{5.61 \left[1.66 + k_{mt,0}(1 - 55 X_{TAG}^{3.5}) \right]}(1 - X_{TAG}) \tag{4a}$$

The initial value of the mass transfer coefficient ($k_{mt,0}$) in a packed-bed reactor was calculated (30 h^{-1}) on the basis of physical characteristics of the reaction mixture and hydrodynamic conditions in the reactor, as shown in the appendix. Using that value of $k_{mt,o}$ in Eq. (4a), $X_{TAG} = 98.6\%$ was calculated at the reactor exit, *i.e.*, for $m_{cat} = 14.6$ g.

Stability of the catalyst

The experiment of continuous transesterification of soybean oil was realized during 17 days. Analysis of TAG and FAME contents in the samples of ester phases collected at the exit from PBR (Figure 4a) was performed every day.

As might be seen from the presented calculation of TAG conversion on the basis of the derived and accepted IL model, the activity of the catalyst would not change after 370 h of continuous operation. A high catalytic activity, which enabled the average TAG conversion of 99.3%, was sustained during the 17 days of continuous transesterification. It is only a 0.7% difference between the calculated by Eq. (4a) and the experimentally determined TAG conversion.

Table 2. Determined parameters for IL and MM kinetic models used for simulation of the transesterification process; k = Aexp(-E/T)

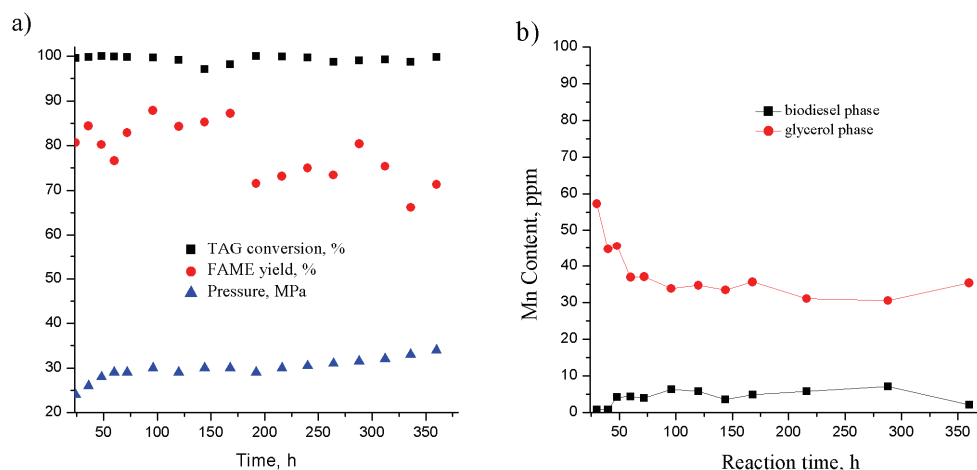| MM model				IL model				
k / min^{-1}		C_{R0} / mol dm^{-3}	K / mol dm^{-3}	k / min^{-1}		$k_{mt,0}$ / min^{-1}	α	β
A / min^{-1}	E / K			A / min^{-1}	E / K			
86682	6776	1.05	1.72	86682	6776	0.085	55	3.5

Figure 4. a) TAG conversion of soybean oil, FAME yield and pressure in PBR at 453 K during c-HTT; b) Mn content in biodiesel phase and glycerol phase collected during c-HTT at 453 K.

The pressure in the PBR was gradually increased from the 3rd to the 17th day of c-HTT (29-34 MPa). The first day of c-HTT was necessary for reaching steady state operation and for approaching good liquid-solid contact in the reactor [31].

FAME yield started to decrease after one week of c-HTT. Taking into account determined values of FAME yield, for the whole period of c-HTT, the simple linear relationship between FAME yield and time was proposed:

$$FAME\,(\%) = 85.1 - 0.0376t \qquad (5)$$

where *t* is time of c-HTT in h.

That calculation indicated, that although TAG conversion was almost complete (>99%), and constant during 17 days of the activity test performed in PBR, the distribution of final products between FAME, MAG and DAG was changed indicating that selectivity toward FAME formation was decreased by 3.76% after each 100 h of continuous use of $MnCO_3$ catalyst. This may be caused by transformation of the catalyst structure in contact with methanol and formed glycerol at high temperature and pressure and by blocking the active sites of the catalyst with different organic compounds (DAG, MAG and glycerol).

The leaching of manganese during continuous transesterification reaction in biodiesel and glycerol phases is shown in Figure 4b. Detected content of Mn in biodiesel and glycerol phases was higher only after the first day of unsteady-state continuous operation. The highest Mn content in the glycerol phase (737 ppm) was almost two times higher than that in the biodiesel phase (393 ppm). After the first day of c-HTT, when steady state of process was attained, the content of Mn in both phases began to decrease (<5 ppm in biodiesel and <40 ppm in glycerol phase).

The Mn content in the glycerol phase was obviously higher than that in the biodiesel phase, indicating that the Mn was leached more easily in the glycerol-methanol phase. Other authors also reported that Mn content of 15 ppm was found in the biodiesel phase and much more (525 ppm) in the glycerol phase during the continuous transesterification with MnO as the catalyst [4]. That evidence also indicates that MnO is more soluble in the reaction mixture (FAME, glycerol and methanol), and thus less stable, compared to $MnCO_3$.

Catalyst characterization

X-ray analysis of the fresh $MnCO_3$ catalyst and the sample of catalyst withdrawn from PBR after its use in the continuous process were studied with the goal to determine the change in catalyst structure. As shown in Figure 5a, the fresh $MnCO_3$ catalyst had the typical diffraction peaks at 2θ of 24.3, 31.5, 37.7, 41.6, 45.5 and 52.1°, which were attributed to the crystals of $MnCO_3$. The XRD pattern of the used catalyst obviously changed, some of the peaks which correspond to $MnCO_3$ crystals at 2θ of 45.5 and 52.1° disappeared and several new peaks which are close, but not the same as those corresponding to the main peaks of MnO_2 (JCPDS 65-2821 and 71-0071) appeared. According to XRD and TG/DSC of a fresh sample, it is not possible that $MnCO_3$ crystals could be transformed during c-HTT of soybean oil into MnO_2 or some other manganese oxide structure (MnO, Mn_2O_3 and Mn_3O_4). Namely, decomposition of $MnCO_3$, according to TG/DSC analysis, could be observed at temperatures above 700 K. That fact implies that the sample of used catalyst probably contained adsorbed organic compounds on active sites of the $MnCO_3$ catalyst.
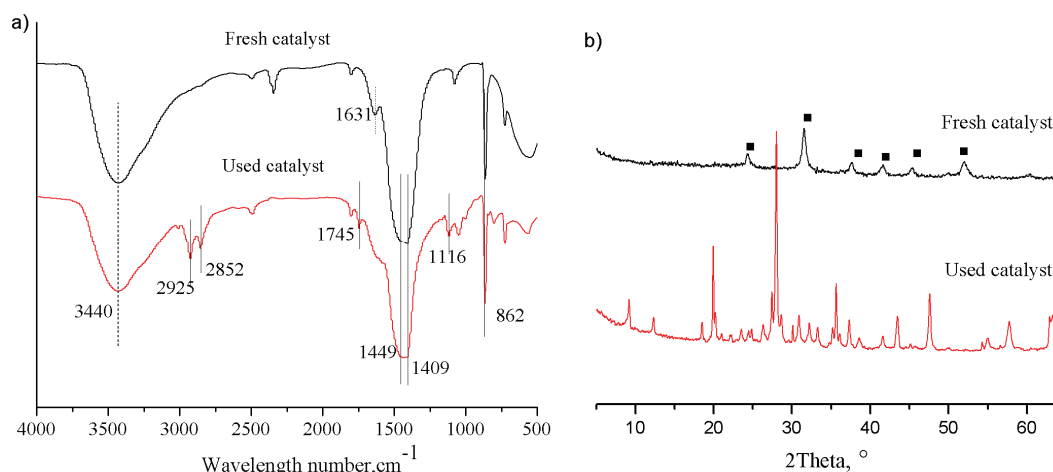
Figure 5. a) X-ray diffraction patterns and b) FTIR spectra of fresh catalyst, and catalyst removed from PBR after 370 h of c-HTT process at 453 K.

FTIR spectroscopy (Figure 5b) was used to investigate the functional groups of the catalysts and to prove the above assumption. A broad band at around 3440 cm^{-1} and a weak band at 1631 cm^{-1} were attributed to O-H bands caused by the water adsorbed from the air onto the surface of the catalyst. The peaks at 1449, 1409 and 862 cm^{-1} are corresponding to the bending vibration of CO_3^{2-} in $MnCO_3$ [3,4,39,40]. FTIR spectrum of the used $MnCO_3$ catalyst implied a similar conclusion as XRD analysis. Some new bending vibration was observed and attributed to C-H bands (at 2925 and 2852 cm^{-1}), C=O bands (at 1745 cm^{-1}) and C-O bands (at 1116 cm^{-1}) [41-43] indicating that different organic compounds present in the reaction mixture were adsorbed onto the catalyst surfaces. Bands at 2925 and 2852 cm^{-1} could be attributed to symmetric and asymmetric stretching vibration of C-H bands from CH_2 groups of alkyl chains of FAME [44], but they might also be related to the presence of methoxide [45,46] or diglyceroxide species [46].

SEM analysis showed the spherical structure of $MnCO_3$ crystal sub-particles, with smooth surface areas and average diameters about 1 μm (Figure 6) [47].

Although the structure of the catalyst used in c-HTT also showed existence of spherical sub-particles, their sizes were unevenly distributed and it might be characterized as a rough surface, different from the fresh catalyst (Figure 6). That observation supports the previous assumption that organic compounds were adsorbed on active sites of $MnCO_3$ catalyst, proposed after examination of the results of XRD and FTIR analysis.

Several typical points on the surface of samples were selected for EDS analysis in order to determine the content of Mn, C, and O. At points A, B and C, marked in Figure 6b (sample of used catalyst), as well as at points A and B shown in Figure 6a (sample of fresh catalyst), the Mn, C and O atomic composition were determined and shown in Table 3. The atomic percentage of Mn is lower, while those corresponding to C and O are higher in used samples, compared to fresh samples of catalyst. These data also indicate that during c-HTT certain amounts of organic compounds were adsorbed on the catalyst surfaces.
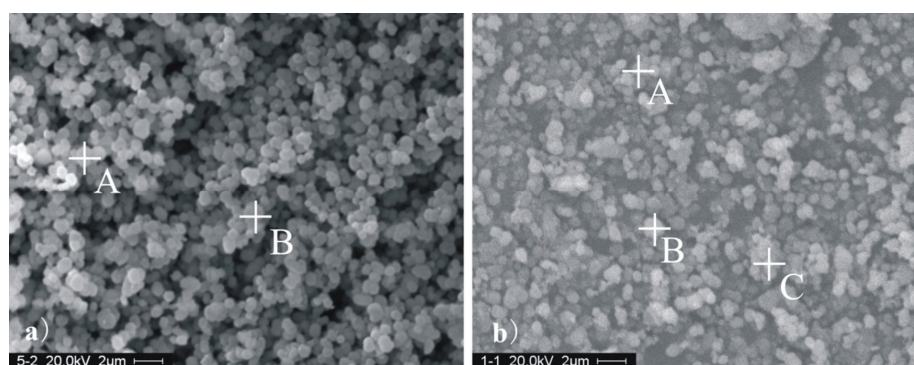

Figure 6. SEM of: a) fresh catalyst and b) catalyst removed from PBR after c-HTT process performed for 370 h at 453 K.

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Table 3. EDS analysis of the surface points of fresh catalysts and catalyst removed from PBR after 370 h of c-HTT at 453 K

Test point		Element content, at.%		
		Mn	C	O
a)	A	20.50	34.21	45.29
	B	21.73	31.29	46.97
b)	A	6.60	63.96	29.44
	B	7.87	60.38	31.76
	C	8.02	62.30	29.68

Summarizing the results of catalyst characterization, it might be concluded that the $MnCO_3$ crystal structure is the main constituent of the fresh and used catalysts. The temperature for c-HTT (453 K) of soybean oil is much below the temperature necessary for $MnCO_3$ decomposition (705 K) and, thus, formation of some Mn oxide structures is less probable. It seems that the 370 h-long test of $MnCO_3$ catalyst activity, during the continuous process of soybean oil transesterification, only led to the adsorption of organic compounds (mainly DAG, MAG, FAME and glycerol) on the active sites of the catalyst. Blocking of the active sites of the catalyst led to a continuous increase in pressure drop in the packed bed and change of catalyst selectivity, *i.e.*, decrease of FAME yield.

CONCLUSION

Through this study, it was proven that $MnCO_3$ used as the catalyst in high temperature transesterification of soybean oil with subcritical methanol possessed a high activity and good stability. The achieved triacylglycerol conversion of soybean oil was 98.1% after 60 min at 453 K of the transesterification process in a batch autoclave (2 wt.% of catalyst, 21:1 methanol/oil mole ratio). Activity and selectivity of the $MnCO_3$ catalyst was tested in continuous transesterification and it was shown that it could maintain an almost complete triacylglycerol conversion during 17 days on stream, and that change of catalyst selectivity leads to a linear decrease in FAME yield (3.8%/100 h of continuous operation).

According to experiments performed in a batch autoclave and in a packed-bed tubular reactor (c-HTT), it was shown that the kinetic model which might be effectively used to predict TAG conversion is either the first order irreversible or complex model based on the decrease of mass transfer resistance during the transesterification process. The results of simulations performed using both models are very similar, indicating that the main resistance to the transesterification process is caused by the chemical reaction at the catalyst surface and that only several percent in the overall resistance is caused by the resistance to mass transfer of TAG to the active sites of the catalyst.

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APPENDIX

I. Kinetic models of HTT process

Ia. The pseudo-first order kinetic model:

$$-\frac{\mathrm{d}c_{\mathrm{TAG}}}{\mathrm{d}t} = kc_{\mathrm{TAG}} \text{ and } k = k_{\mathrm{app}} \tag{A.1}$$

where k is the apparent reaction rate constant for the first order irreversible kinetic model and c_{TAG} is TAG concentration, which is related to the TAG conversion degree, X_{TAG}, as follows:

$$c_{\mathrm{TAG}} = c_{\mathrm{TAG,0}}\left(1 - X_{\mathrm{TAG}}\right) \tag{A.2}$$

Eq. (A1) can be transformed into:

$$\frac{\mathrm{d}X_{\mathrm{TAG}}}{\mathrm{d}t} = k(1 - X_{\mathrm{TAG}}) \tag{A.3}$$

Ib. The MM kinetic model [21]

Model proposed by Miladinović *et al*. [21] is based on the changing reaction mechanism and assumes that the reaction rate with respect to TAG is of zero order in the initial reaction period (at high TAG concentrations) and of the first order in the later period of the reaction (at low TAG concentrations). It is expressed as follows:

$$\frac{\mathrm{d}X_{TAG}}{\mathrm{d}t} = k_m \frac{(1-X_{TAG})(c_{R0}+3c_{TAG,0}X_{TAG})}{K + c_{TAG,0}(1-X_{TAG})}$$

where k_m is the apparent reaction rate constant, c_{R0} is the hypothetic initial FAME concentration corresponding to the initial available active catalyst surface, $c_{TAG,0}$ is the initial TAG concentration, and K is the model parameter defining the TAG affinity for the catalyst active sites.

Ic. Model based on analysis of mass transfer (IL model) [22,23]

According to the **IL kinetic model**, developed by Lukić *et al.* [22,23], the rate of transesterification may be presented as an irreversible pseudo-first order reaction with the variable apparent rate constant, k_{app}, which takes into account mass transfer of TAG from oil to the active sites of the catalyst through the overall volumetric mass transfer coefficient, k_{mtTAG}, and the chemical reaction between methanol and TAG defined by pseudo first-order reaction rate constant, k:

$$\frac{\mathrm{d}X_{TAG}}{\mathrm{d}t} = k_{app}(1-X_{TAG}) = \frac{kk_{mtTAG}}{k+k_{mtTAG}}(1-X_{TAG}) = \frac{kk_{mtTAG,0}\left[1+\alpha X_{TAG}^{\beta}\right]}{k+k_{mtTAG,0}\left[1+\alpha X_{TAG}^{\beta}\right]}(1-X_{TAG}) \tag{A.5}$$

where $k_{mtTAG,0}$, the overall volumetric mass transfer coefficient at the beginning of the process, depends on a_0 interfacial area between the oil and methanol, and α and β are fitting parameters. The interfacial area changes with the TAG conversion according to the proposed correlation:

$$\frac{a}{a_0} = 1 + \alpha X_{TAG}^{\beta} \tag{A.6}$$

Since:

$$\frac{k_{mtTAG,0}}{k_{mtTAG}} = \frac{a_0}{a} \tag{A.7}$$

then k_{mtTAG}, which defines the rate of mass transfer, depends on the interfacial area and the proposed correlation assumes that it is also a function of TG conversion:

$$k_{mtTAG} = k_{mtTAG,0}(1+\alpha X_{TAG}^{\beta}) \tag{A.8}$$

II. Physical characteristics of soybean oil and methanol

Table A1. Physical characteristics of soybean oil and methanol at 453 K

Parameter	Soybean oil	Methanol
Density, ρ / kg m^{-3}	800	666
Viscosity, μ / kg m^{-1} s^{-1}	0.00331	0.000142
D, diffusion coefficient of TAG, m^2 s^{-1}	4.3×10^{-10}	2.84×10^{-9}

$$\rho_{mix} = \phi\rho_d + (1-\phi)\rho_c$$

$$\mu_{mix} = \mu_c(1-2.5\phi\frac{\mu_d+0.4\mu_c}{\mu_d+\mu_c})$$

$\varphi = 0.47$

Parameter	T = 453 K
ρ_{mix} / kg m^{-3}	737
μ_{mix} / kg m^{-1} s^{-1}	0.000166

III. Calculation of the mass transfer coefficient for the process performed in a batch autoclave [23]:

a.   The mass transfer coefficient in the continuous phase [23]:

$$k_c = 1.3 \times 10^{-3} \left[\frac{P \mu_c}{V_c \rho_c^2} \right]^{1/4} \left[\frac{\mu_E}{D \rho_c} \right]^{-2/3} \tag{A.9}$$

The factor P is defined by equation:

$$P = \psi \rho_{mix} n^3 D_i^5 \tag{A.9.1}$$

ψ = 1.5 (the agitator power consumption number); n = 200, 500 and 900 rpm; D_i = 0.04 m; V_c = 2.24×10^{-4} m^3.

      b.   The mass transfer coefficient in the disperse phase [23]:

$$k_d = \frac{2\pi^2 D}{3 d_{32}} \tag{A.10}$$

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.* [48]:

$$d_{32} = 4782 n^{-1.825} \tag{A.10.1}$$

      c.   The mass transfer coefficient near the solid surface [23]:

$$k_s = \frac{D}{d_p} \left[2 + 0.31 \frac{d_p^3 g (\rho_p - \rho_c)}{\mu_c D} \right] \tag{A.11}$$

d_p = 3×10^{-5} m; g = 9.81 m^2 s^{-1}; ρ_p = 3700 kg m^{-3}.

      d.   The overall volumetric mass transfer coefficient:

$$\frac{1}{k_{mtTAG}} = \frac{1}{a} \left[\frac{1}{k_{cTAG}} + \frac{1}{m_{TAG} k_{dTAG}} + \frac{a}{a_s m_{TAG} k_{sTAG}} \right] = \frac{1}{a k_{mtTAG}^s} \tag{A.12}$$

At the beginning of the process:

$$\frac{1}{k_{mtTAG,0}} = \frac{1}{a_0 k_{mtTAG}^s} \tag{A.12.1}$$

$$a_0 = \frac{6\phi}{d_{32}} \; ; \; a_m = 1 \text{ m}^2/\text{g}; \; a_s = \frac{a_m m_{cat}}{V}$$

Used values for the calculation of the mass transfer of TAG to active site of the catalyst: distribution coefficient for TAG in methanol at 180 °C: m_{TAG} = 0.05; φ = 0.47; a_s = 8368 m^{-1}; mole ratio of methanol and oil 21:1; m_{cat} = 2 wt.%; k_s = 0.155 m min^{-1} and $k_{(453 K)}$ = 0.0286 min^{-1}.

Table A2. Calculated values of k_{mt} for various mixing intensity

Calculated parameter	200 rpm	500 rpm	900 rpm
d_{32} / mm	0.302	0.0568	0.0194
a_0 / m^{-1}	9338	49648	145361
k_c / m min^{-1}	2.95x10^{-6}	5.86x10^{-6}	9.1x10^{-6}
k_d / m min^{-1}	3.71x10^{-3}	1.98x10^{-2}	5.78x10^{-2}
$\dfrac{1}{a_0 k_{cTAG}}$	36.3	3.43	0.756
$\dfrac{1}{a_0 m_{TAG} k_{dTAG}}$	0.577	0.02	0.0024
$\dfrac{1}{a_s m_{TAG} k_{sTAG}}$	0.0154	0.0154	0.0154
$k_{mtTAG,0}$ / min^{-1}	0.027	0.289	1.29
k_{mtTAG} / min^{-1}	0.707	7.568	33.781
R_{mt} / min	1.414	0.132	0.030

The overall resistance of transesterification process is R_{totr} = 1/k_{app} = 1/0.0286 = 34.965 min, and thus, the resistance which includes the resistance of chemical reaction for 200 rpm intensity of mixing is R_{cr} = 34.965-1.414 = 33.551 min^{-1}. This calculation showed that the resistance to TAG mass transfer rate contributes with 4% in the total resistance which was governing the rate of transesterification. It will be even smaller for 500 and 900 rpm mixing intensity (less than 0.4 and 0.1%, respectively).

IV. Calculation of the mass transfer coefficient for the process performed in a packed bed reactor

Superficial velocity of the reaction mixture: u = 0.25 m/h = 6.98×10^{-5} m s^{-1}; d_p = 0.03 mm = 3×10^{-5} m

$$Re = \frac{\rho_{mix} u d_p}{\mu_{mix}} = 9.2 \times 10^{-4} \text{ for } d_p = 0.04 \text{ mm}$$

and for d_p = 0.03 mm, Re = 1.23×10^{-3}

$$Sc = \frac{\mu_{mix}}{\rho_{mix} D} = 793$$

$$Sh = 0.99 Re^{1/3} Sc^{1/3} = 0.891 \tag{A.13}$$

$$k_{sTAG} = \frac{Sh D}{d_p} = 8.43 \times 10^{-5} \text{ m s}^{-1} \text{ or } 0.303 \text{ m h}^{-1} \tag{A.14}$$

$$k_{mtTAG} = a_s k_{sTAG} \tag{A.15}$$

$$a_s = a_m \frac{m_{cat}}{V} = 102 \text{ m}^{-1}; \; a_m = 1 \text{ cm}^2 \text{ g}^{-1}$$

$$k_{mtTAG} = 0.0083 \text{ s}^{-1} \text{ or } 30 \text{ h}^{-1} \tag{A.16}$$

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NAUČNI RAD

TRANSESTERIFIKACIJA ULJA SOJE SA METANOLOM NA VISOKOJ TEMPERATURI KORIŠĆENJEM MANGAN-KARBONATA KAO KATALIZATORA

Mangan-karbonat katalizator, pripremljen taložnom metodom, korišćen je u transesterifi-kaciji ulja soje u subkritičnim uslovima metanola. Karakterizacija katalizatora izvršena je metodama rendgenske difrakcije (XRD), infracrvene spektroskopije (FTIR), skenirajuće elektronske mikroskopije (SEM) i energetske disperzione spektroskopije (EDS). Konverzija triacilglicerola (TAG) i prinos metil-estara masnih kiselina (FAME) određeni su korišćenjem tečne hromatografije visokih performansi (HPLC). Transesterifikacija je realizovana u vremenu od 1 h pri različitim reakcionim uslovima: 0-3 mas.% katalizatora (računato u odnosu na masu ulja), pri molarnom odnosu metanola i ulja od 13:1 do 27:1 i temperaturi od 393 do 473 K. Maksimalna konverzija TAG od 98,1% može se ostvariti pri optimalnim reakcionim uslovima: 2 mas.% katalizatora, molskom odnosu metanol/ /ulje od 21:1, 1 h u šaržnom reaktoru na 453 K. Analiza kinetike pokazala je da model zasnovan na prenosu mase i hemijskoj reakciji na površini katalizatora potvrđuje eksperimentalne podatke. Korišćenjem tog kinetičkog izraza predložen je efekat kontinualne transesterifikacije i verifikovan eksperimentom realizovanim u laboratorijskom reaktoru sa pakovanim slojem (PBR) u trajanju od 360 h. Spora deaktivacija katalizatora je posledica izluživanja Mn u obe faze, biodizel i glicerol, kao i blokiranja aktivnih centara katalizatora organskim jedinjenjima.

Ključne reči: biodizel, kontinualni proces, heterogeni katalizator, kinetika, mangan karbonat, subkritični uslovi.