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Continuous biodiesel production under subcritical condition of methanol – Design of pilot plant and packed bed reactor with $MnCO_3$/Na-silicate catalyst

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Abstract

The continuous biodiesel production from soybean oil was carried out under the subcritical condition of methanol with $MnCO_3$/Na-silicate as a heterogeneous catalyst. The transesterification rate was first investigated in a set of experiments performed in a batch autoclave at 448 K using methanol-to-oil molar ratio of 18:1 and various catalyst loadings (5, 10 and 20 wt% based on the oil mass). The results from these experiments, as well as the experimental data and the appropriate kinetic model recently reported in the literature were used for designing a packed bed tubular reactor (PBTR), a main unit of the pilot plant with the capacity of 100 liters of biodiesel per day. The pilot plant was constructed and tested under various operating conditions. The first 11 h of the pilot-plant operation was realized in the tubular reactor packed with inert glass beads (i.e. without the catalyst) in order to analyze the effect of the non-catalyzed subcritical biodiesel (fatty acid methyl esters, FAME) production. Then, glass beads were replaced with a mix of $MnCO_3$/Na-silicate catalyst particles and glass beads, and the catalytic biodiesel production was continuously run under the subcritical methanol condition for 85 h. Two mass balance tests during the continuous pilot plant operation were performed.

Keywords: Biodiesel; Subcritical methanolysis; Kinetic modeling; $MnCO_3$/Na-silicate catalyst; Pilot-plant design.

1. Introduction

In the past several years, many researchers have made efforts to synthesize efficient heterogeneous catalysts for biodiesel production in order to substitute the conventional technology based on homogeneous catalysis, which is currently applied in many industrial facilities. Numerous investigations have been undertaken in order to estimate the potential catalytic activity of both naturally originated and synthesized materials. Among the heterogeneous catalysts, the CaO-based catalysts are frequently studied [1][2][3][4][5] due to their high activity and possibility to be obtained from inexpensive natural and waste materials [6]. The other low-cost materials, like $MnCO_3$, Na-silicate and $MnCO_3$/Na-silicate, also show, after thermal activation, a high catalytic activity for biodiesel production [7][8][9][10]. Some of them, like Na-silicate, can be used even for transesterification of waste vegetable oils with a high amount of water owing to the hydolysis of the activated Na-silicate into OH^- and $Si–O–H^+$, thus avoiding soap formation. Another advantage is the simple regeneration of the used Na-silicate catalyst with NaOH [7]. Other materials, like ion-exchange resins [11][12] and hydrotalcite [13], have also been tested in order to obtain long-lifetime catalysts that can be used for continuous processes.

Heterogeneously-catalyzed methanolysis reactions are slower than homogeneously-catalyzed ones due to the mass transfer limitations in the three-phase system mainly at the beginning of the transesterification process [14][15][16] The nature of heterogeneously catalyzed oil methanolysis reactions has been explained by different reaction mechanisms [17][18][19][20][21][22]. However, the resulting kinetic models based on these mechanisms are rather complex since a large number of parameters need to be determined. The recently reported studies described the suitable, relatively simple kinetic models of the vegetable oil methanolysis requiring no complicated computations [2][14]. The model proposed by Lukić et al. [14] is based on the pseudo-first order kinetics that involves the triacylglycerols (TAGs) mass transfer and chemical reaction controlled regimes. The model proposed by Miladinović et al. [2] includes a changing reaction mechanism with respect to TAGs and the first order reaction with respect to fatty acid methyl esters (FAMEs). The applicability of both models was confirmed for the sunflower oil methanolysis catalyzed by the CaO-based catalysts ($CaO{\cdot}ZnO$, pure CaO and

74 quicklime) under various reaction conditions [23][24]. They were applied and verified under
75 continuous conditions at small scale, too [13][23].

76 The continuous methanolysis has been investigated at both atmospheric pressure and
77 moderate temperature [11][21][25][26][27][28] and high pressure and temperature [29][30][31]
78 [32][33]. However, the most of the reported studies were conducted in laboratory scale devices
79 for a short period of time [34]. Kouzu et al. reported the pilot scale transesterification of the
80 waste cooking oil in the higher volume reactor (150 L), but it was performed in a stirred tank
81 reactor with powdery CaO catalyst since it was concluded that the CaO-catalyzed
82 transesterification is difficult to perform with the fixed bed reactor, due to the mass transfer
83 limitations as well as plausible crushing of catalysts particles [35]. Catalysts used in powder
84 form in the packed bed reactors caused blocking of the flow of the reactants throughout the
85 catalyst bed by particle agglomeration [28] and high pressure drop inside small column at the
86 end of the experiment due to the very dense packed bed formed [8]. Also, separation of the solid
87 catalyst in powder form from the products of transesterification is difficult, thus, important issue
88 for packed bed reactors, which are commonly used for continuous heterogeneously catalyzed
89 processes at the industrial scale, is the use of coarse catalyst particles, with good mechanical
90 strength that would not collapse during the process.

91 The recent investigations of the heterogeneously catalyzed oil transesterification with
92 subcritical methanol have been aimed at improving the process efficiency, i.e. at reducing the
93 temperature, pressure and methanol-to-oil molar ratio applied under supercritical non-catalyzed
94 vegetable oil methanolysis. Furthermore, the problem of a huge amount of waste water generated
95 during the homogeneous transesterification and biodiesel purification, could be easily avoided by
96 conducting the transesterification with subcritical methanol and an appropriate solid catalyst
97 [36].

98 Common reaction conditions for various heterogeneous catalysts at higher temperature
99 and pressure are >150 ^{o}C and >30 bar [37][38][39][40] and the methanol-to-oil molar ratio
100 higher than 15:1 (methanol is in subcritical or supercritical condition) [41][42]. High temperature
101 synthesis have recently been applied with $MnCO_3$, $MnCO_3$/Na-silicate [8][9] and $MnCO_3$/ZnO
102 [43] catalysts in the form of powder or granules (coarse particles). Furthermore, it is worth

mentioning that methanol-to-oil molar ratio and reaction temperature applied in the biodiesel production with $MnCO_3$ or $MnCO_3$/Na-silicate catalyst were lower than those suggested by Yin et al. [44] for the subcritical sodium silicate-catalyzed soybean oil methanolysis. The $MnCO_3$/Na-silicate catalyst prepared in the form of granulated particles have an acceptable activity, excellent selectivity towards FAME formation from TAGs, and acceptable lifetime at high temperature [9].

This article reports designing and testing of a pilot plant applied for the biodiesel production by the soybean oil transesterification catalyzed by $MnCO_3$/Na-silicate with the capacity of 100 liters of biodiesel per day. Results of the recently reported study [9] supplemented with information from several additional experiments realized in batch autoclave with different amount of $MnCO_3$/Na-silicate (5–20 wt% based on oil) at 448 K and 18:1 methanol to oil molar ratio, were the basis for design of packed bed tubular reactor (PBTR) as main equipment of corresponding pilot plant. PBTR was filled with $MnCO_3$/Na-silicate as catalyst mixed with inert glass beads and such reactor was applied for continuous transesterification at subcritical condition of methanol. Test of continuous operation was used to prove designed capacity and operational characteristics of pilot plant unit during 100 hours of operation. Investigation was started using PBTR filled only with glass beads for 11 h, and then, the catalyzed transesterification of soybean oil with $MnCO_3$/Na-silicate as catalyst was realized during 85 h of continuous operation. Two complete mass balances were determined for detailed examination of the content of produced biodiesel while sample of used catalyst after 85 h of continuous process was withdrawn from reactor and its characteristics were analyzed using XRD, TG/DSC and FTIR.

2. Materials and methods

2.1. Catalyst preparation

The preparation and characterization of the $MnCO_3$/Na-silicate catalyst have recently been reported [9]. The catalyst was activated by drying at 473 K for 2 h, followed by the calcination in an oven at 773 K for 3 h.

130 *2.2. Experimental procedure*

131 *2.3.1. Batch reactor*

132 The soybean oil transesterification was conducted in 300 mL batch autoclave (AE –
133 Autoclave Engineers, USA), with an electrical heater and a Rushton-type mixer (560 rpm) at the
134 methanol to soybean oil ratio of 18:1, 448 K [45] and different $MnCO_3$/Na-silicate catalyst
135 amounts (5, 10 and 20 wt% of the mass of oil). The reaction mixture samples withdrawn from
136 the batch autoclave was analyzed as recently described [9][45]. The standard deviation for all
137 experiments was determined to be ±2.86%.

138 *2.3.2. Pilot plant*

139 A pilot plant with a PBTR, designed on the basis of the kinetic data obtained in the
140 laboratory batch reactors, was constructed and used for biodiesel production from soybean oil.
141 During the test of the pilot-plant capacity and the catalyst activity, the following parameters were
142 monitored: pressure, temperature and the mass flow rates of the reactants (methanol and soybean
143 oil) while the masses of the produced biodiesel and glycerol were measured. Two tests during the
144 continuous soybean oil transesterification were conducted:

145 1) the non-catalyzed reaction in the PBTR only filled with 2 mm glass beads for 11 h (so
146 called ZERO test) and

147 2) the catalyzed reaction in the PBTR filled with a mix of 2 mm glass beads and catalyst
148 particles ($0.99 < d < 1.99$ mm) in the proportion 60:40 by weight for 85 h (so called LONG
149 TERM test, *LT-t*).

150 *2.3.3 Catalyst characterization*

151 The properties of the used catalyst (withdrawn from the PBTR after 85 h of continuous
152 operation) were characterized by X-ray diffraction (XRD) on a Philips PW 1050 X-ray powder
153 diffractometer using Ni-filtered Cu $K\alpha_{1,2}$ ($\lambda = 1.54178$ Å) radiation with a scanning step width of
154 0.05^{o} and a counting time of 3 s per step, thermal analysis (TG/DTA) on a Setaram Instrument
155 between 293 K and 1273 K in air flow (20 K min^{-1}) and Furrier transformed infrared
156 spectroscopy (FTIR) using a BOMEM spectrometer (Hartmann & Braun) in the wave number
157 range of 4000–400 cm^{-1} with 4 cm^{-1} resolution.

3. Results and discussion

3.1. Analysis of soybean oil transesterification in a batch reactor

The soybean oil transesterification in the presence of the $MnCO_3$/Na-silicate catalyst occurs via two simultaneous catalytic processes [9]: one is catalyzed heterogeneously by both active species (Mn and Na) fixed on the surface of solid catalyst particles and homogeneously by Na dissolved in the esters and methanol/glycerol phases. It is important to point out that the batch transesterification reaction takes place during the heating of the reaction mixture from the room temperature to the specified reaction temperature (non-isothermal regime), and while keeping the reaction temperature constant (isothermal regime). The apparent reaction rates are simply defined by the reaction rate constants, k_{LT} and k_{HT}, depending on the reaction temperature and determined for the process performed with 5 wt% of the catalyst (based on the oil) [9]:

For the isothermal operation at $T < 423$ K

$$k = k_{LT} = 7.918\exp(-2465/T), \text{min}^{-1} \quad (1a)$$

For heating above 423 K and the isothermal transesterification at $T > 423$ K

$$k = k_{HT} = 6.355\times10^{5}\exp(-7272/T), \text{min}^{-1} \quad (1b)$$

$$k = k_{LT} = 7.918\exp(-2465/T), \text{min}^{-1} \quad \text{for } T < 423 \text{ K} \quad (1a)$$

$$k = k_{HT} = 6.355\times10^{5}\exp(-7272/T), \text{min}^{-1} \quad \text{for } T > 423 \text{ K} \quad (1b)$$

The rate of TAG conversion was defined by the following kinetic equation [9]:

$$\frac{dx_{TG}}{dt} = k_{app}(1 - x_{TG}) \quad (2)$$

where k_{app}, according to the IL kinetic model, is defined as follows:

$$k_{app} = \frac{k \cdot k_{mt}}{k + k_{mt}} = \frac{k_{app}\cdot k_{mt0}\cdot\left[1+\alpha(x_{TAG})^{\beta}\right]}{k_{app} + k_{mt0}\cdot\left[1+\alpha(x_{TAG})^{\beta}\right]} \quad (3)$$

The best agreement between the calculated and experimentally determined TAG conversion degrees was obtained using the values of the reaction rate constant k (i.e. k_{LT} or k_{HT}), the initial value of the mass transfer coefficient k_{mt0} = 0.085 min^{-1}, and the values of the parameters α = 55 and β = 3.5 [9].

3.2. Analysis of the transesterification in the batch reactor performed with different amounts of catalyst

In the present study, several experiments were conducted in the AE batch reactor using 5%, 10% and 20% of $MnCO_3$/Na-silicate catalyst based on mass of oil (particle size 0.99–1.99 mm) at 448 K to verify the proposed IL kinetic model at higher catalyst amounts [9]. Besides, unlike previously reported results [9] the isothermal temperature of 448 K in this study was reached in the batch autoclave for 113 min. The difference in the heating time needed to reach the isothermal transesterification temperature in the batch autoclave could give additional information about the flexibility of the proposed IL kinetic model used to predict TAG conversion at 448 K.

The experiments with 5% of catalyst (based on oil) showed that the TAG conversion of 62.6% was obtained during heating period of 113 min (54.6% for 54 min [9]), while TAG conversion of 81.3% and 98.2% were obtained with 10% and 20% of catalyst, respectively for the same time of non-isothermal heating. Further 1 h of isothermal transesterification at 448 K with 5% and 10% of catalyst gave almost the complete TAG conversion (>99%). According to these data the following recalculations of the reaction apparent rate constant k (i.e. k_{LT} and k_{HT}) and mass transfer coefficient k_{mt0}, which depended on the total catalytic surface area [8], were used to determine the reaction rate constant k_{app} applicable for both non-isothermal (heating to 448 K) and isothermal regime:

$$k_{(w)} = k_{(5)} \frac{c_{cat(w)}}{c_{cat(5)}} \tag{4a}$$

and

$$k_{mt0(w)} = k_{mt0(5)} \frac{c_{cat(w)}}{c_{cat(5)}} \tag{4b}$$

thus leading to:

$$k_{app(w)} = k_{app(5)} \frac{c_{cat(w)}}{c_{cat(5)}} \quad (4c)$$

where $c_{cat(w)}$ is the catalyst amount used for the transesterification of soybean oil (valid for $2 < w < 8$ wt% based on the mass of oil).

Furthermore, recently reported results showed only a slight increase of TAG conversion (to 95%) during heating to 428 K and 1 h of isothermal transesterification at 428 K with increasing the catalyst amount from 8 to 13% [9], which implied that the apparent reaction rate constant ($k_{app(w)}$) depended almost linearly on the catalyst concentration only in the range of catalyst amount between 2% and 8%, as shown by Eq. (4).

The relation between $k_{app(w)}$ and catalyst concentration might deviate from the linear dependence (valid for $5 < w < 8$, Table 1), when larger catalyst concentrations are used. Namely, the apparent reaction rate constant $k_{app(w)}$, as a "lumped parameter", includes the resistance of TAG mass transfer to the surface of catalyst particles and the resistance of chemical reaction between TAGs and methoxide ions at the catalyst surface. These resistances have different and specific relation to temperature and catalyst concentration. The mass transfer coefficient is related to square root of temperature ($T^{0.5}$) while the chemical reaction rate constant is an exponential function of temperature according to the Arrhenius equation. Also, the resistance of chemical reaction can be correlated directly to the catalyst concentration (i.e. to the available catalyst surface area) while the resistance of mass transfer depends on the hydrodynamic conditions in the reactor (mixing, viscosity). Therefore, the relation between $k_{app(w)}$ and catalyst concentration may be non-linear, as shown in some recently reported investigations [8].

While the linear correlation between $k_{app(w)}$ and catalyst concentration was assumed for the catalyst concentration between 2 and 8%, a different correlation was proposed for the catalyst concentration higher than 8% (i.e. 10% and 20% in this study) according to relation:

$$k_{app(w)} = \varphi k_{app(5)} \quad (5a)$$

$$\varphi = 1.6\left[2 - \exp\left(\frac{8-w}{8}\right)\right] \quad (5b)$$

which means that the maximal increase of the apparent reaction rate constant might be 2 times related to the value determined or 3.2 times higher than the value valid when 8% or 5% of catalyst is used, respectively. Thus, for the experiments conducted in the batch autoclave (300 mL, 560 rpm), the corresponding values of k_{app} and two other kinetic model parameters (α = 55 and β = 3.5, accepted from the previous work [9]) were used for calculation and comparison with the experimentally determined TAG conversions (Table 1).

Table 1. Experimental results of the soybean oil transesterification during non-isothermal heating from 288 K to448 K and subsequent isothermal heating at 448 K for 1 h.

M_{cat}, based on the mass of oil (wt%)	Operation regime	Time (min)	Temperature (K)	$x_{TAG,\ exp}$ (%)	$x_{TAG,\ calculated}$ (%)	
					After 113 min	At the end of isothermal operation
5	Heating	113	288→448	62.6	66.9	–
	Isothermal operation	60	448	98.3	–	98.8
10	Heating	113	288→448	81.3	88.7	–
	Isothermal operation	60	448	97.2	–	99.9
20	Heating	113	288→448	98.2	95.9	–
	Isothermal operation	60	448	99.9	–	100

An excellent agreement between the calculated and experimentally determined TAG conversions at the end of non-isothermal heating (113 min) and the end of the overall process was observed as confirmed by small mean relative percentage deviations (4.4% and 1.6%, respectively). These results proved the proposed and used correlation between the apparent reaction rate constant and the applied catalyst amount and validated the kinetic parameters involved in the IL kinetic model.

3.3. Design of packed bed tubular reactor

Since the methanolysis reaction was performed in the batch stirred reactor with perfect mixing, the design equation coming out from the mole balance of TAG is the same for the PBTR with ideal plug flow. In order to calculate the residence time of the reaction mixture in the pilot PBTR operating under adiabatic condition, the following differential equations of mole and energy balances were applied:

$$\frac{dx_{TAG}}{d\tau} = k_{app}(1 - x_{TAG}) \tag{6}$$

$$\frac{dT}{dx_{TAG}} = -\frac{F_{TAG,0}\Delta H_r}{m_0 c_p} \tag{7}$$

Using Eqs. (5a) and (5b) and assuming that the catalyst-to-oil mass ratio in the reactor would be much higher than 20%, the following equation, that connects reaction rate constant with temperature, was used to calculate the k_{app} values:

$$k = 3.2 \cdot k_{HT(w=5\%)} = 2.034 \times 10^6 \exp\left(-\frac{7272}{T}\right), \text{ min}^{-1} \tag{8}$$

Simultaneous solution of Eqs. (6) and (7) for the initial condition:

$x_{TAG} = 0$ for $\tau = 0$ and $T(0) = T_{in} = 443$ K

gave the TAG conversion degree, x_{TAG}, and the temperature at the outlet of the reactor, T_{ex}, for the residence time of $\tau = 50$ min. The values of the specific heat, c_p, and the heat of reaction, ($-\Delta H_r$), were taken from the literature [46].

For the initial activity of catalyst (100%), almost complete TAG conversion ($x_{TAG} = 1$ or 100%) could be obtained at the outlet of the reactor after 50 min of residence time. If the catalyst activity in the PBTR dropped to 50% of its initial value, then the TAG conversion degree at the reactor outlet would be 98%. Further decrease of the average catalyst activity in the PBTR, e.g. to 10% of its initial activity would result in 55% TAG conversion degree, as shown in Fig. 1.

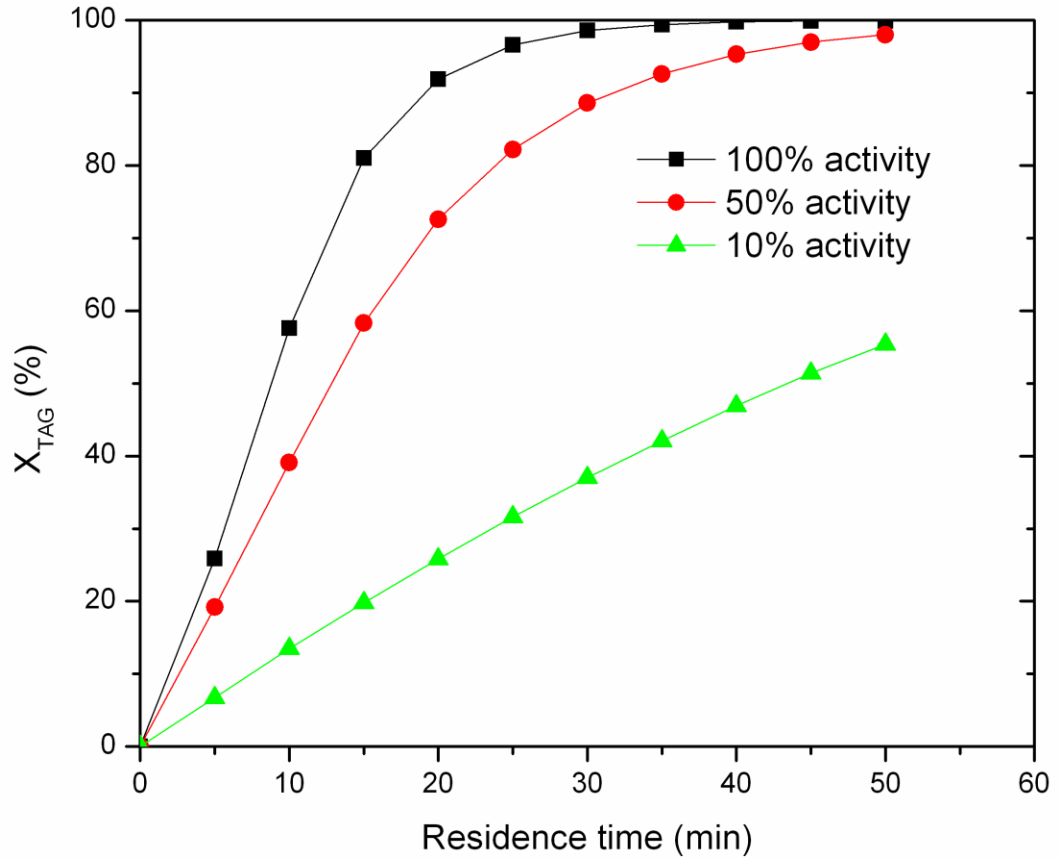


Fig. 1. Conversion degree versus residence time of the reaction mixture for different average catalyst activities in the PBTR.

The design of the PBTR having capacity of 100 L/day was based on the following assumptions:

- The process efficiency of 90% was adopted, resulting the biodiesel production capacity of 4.17 kg/h (0.07 kg/min).
- For the complete conversion of soybean oil (>99%), the inlet soybean oil (TAG) mass flow rate ($m_{o,TAG}$) should be 4.17 kg/h.
- Taking into account the molar masses of soybean oil (890 g/mol) and methanol (32 g/mol) and their molar ratio of 1:18, the inlet concentration of TAGs, represented by triolein as a key compound (c_{TAGo}) would be 0.60 mol/L, while the molar and mass flow rates of the reaction mixture (M_o and m_o) into the PBTR would be 89 mol/h and 6870 g/h, respectively; the inlet TAG molar flow rate of (F_{TAGo}) was 4.68 mol/h.

- The catalyst bed would be prepared by mixing $MnCO_3$/Na-silicate catalyst particles (bulk density of 1.2 g/mL) and inert glass beads (2 mm; 2.5 g/mL) with the mass ratio of 40:60.
- The porosity of the catalyst bed was assumed to be 50%.
- The proposed residence time of the reaction mixture in the PBTR would be 50 min.
- The reaction mixture would be heated in a preheater to 448 K to the reaction temperature in the PBTR.
- The inlet mass flow rates of the soybean oil and methanol would be 6870 g/h or 8.6 L/h, corresponding to the methanol-to-oil molar ratio of 18: 1.
- The density of the reaction mixture at 448 K and 25 bar was assumed to be about 800 kg/L.
- A simple calculation gave the volume of the reaction mixture which occupied the void space of the bed of 7.16 L and the volume of the empty reactor of 14.33 L. Thus, the reactor could be packed with 8.33 L of $MnCO_3$/Na-silicate catalyst (or 10 kg; density 1.2 kg/L) and 6 L of inert glass beads (spheres) (15 kg; density of 2.5 kg/L).
- The amount of oil in the reactor would be 3.90 kg, so the catalyst concentration (based on the mass of oil) in the reactor would be 10/3.90 = 2.56 kg/kg or 256%.

The final design of the PBTR was based on the following:

a. Volume of the tubular reactor would be 14 L.
b. Mass of 10.2 kg of catalyst particles (cylindrical granules with the average diameter between 0.9 and 1.99 mm) and mass of 15.3 kg of glass beads (2 mm), respectively should be used for preparing the packed bed.
c. The biodiesel production capacity would be 4.05 kg/h or 97 kg/day, i.e. slightly above 100 L/day (density of biodiesel: 0.9 kg/L).

3.4. Assessment of catalyst deactivation during long-term continuous operation

The catalyst activity in the successive batches was evaluated in the batch autoclave with the same amount of catalyst (10 wt% based on the oil weight) at 458 K and with the 30:1 methanol-to-oil molar ratio [9]. It was found that the catalyst might be reused 8–9 times without substantial decrease of the TAG conversion degree (from 100% to 97.4%) but with the change of FAME yield from 99%, to 92.6% and 88.3% after 8^{th} and 9^{th} catalyst reuse, respectively [9].

309 Therefore, 10 kg of the catalyst placed in the PBTR could be used for processing 800 kg of
310 soybean oil. In other words, the catalyst might be used for 8-day continuous operation of the
311 PBTR when TAG conversion degree would be slightly decreased to 97.4%. However, the
312 catalyst activity after 8 days of continuous operation would be only 35% of the initial activity.

313 **4. Pilot plant design**

314 The main steps of the proposed continuous biodiesel production are the mixing of oil and
315 methanol and preheating their mixture to the reaction temperature, the transesterification of
316 soybean oil in the PBTR, the separation of the excess of methanol, the separation of biodiesel
317 and glycerol and the purification of biodiesel and glycerol. In order to reduce the overall
318 investment and operational costs of the pilot plant operation, only the capacity of the pilot plant
319 was tested while the downstream glycerol and biodiesel purification was not considered at the
320 present stage of the pilot plant construction. Hence, the main process scheme included:

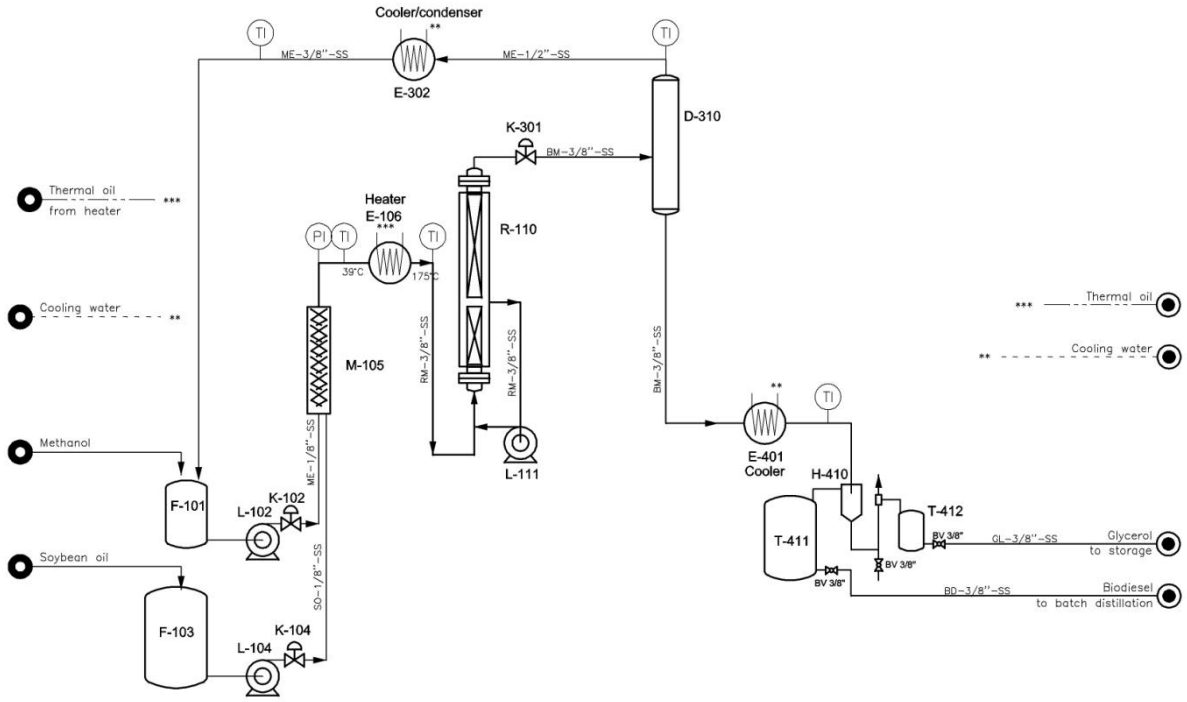
321 • pumping, mixing and preheating of methanol and oil;

322 • flowing of the soybean oil/methanol mixture into the PBTR;

323 • flash separation of the excess of methanol from the reaction mixture; and

324 • separation of biodiesel (upper) and glycerol (lower) layer.

325 The process flow sheet with the main streams and units is shown in Fig. 2a while the
326 photo of the pilot plant is presented in Fig. 2b. The main equipment units of the pilot plant are
327 specified in Table 2.


Cooler/condenser
E-302
ME-3/8"-SS
ME-1/2"-SS
D-310
K-301
BM-3/8"-SS
Thermal oil
from heater
Heater
E-106
R-110
39°C
175°C
Cooling water
M-105
RM-3/8"-SS
RM-3/8"-SS
Thermal oil
Cooling water
Methanol
ME-1/8"-SS
BM-3/8"-SS
E-401
Cooler
H-410
T-411
T-412
F-101
L-102
K-102
Soybean oil
SO-1/8"-SS
GL-3/8"-SS
Glycerol
to storage
BV 3/8"
BD-3/8"-SS
Biodiesel
to batch distillation
F-103
L-104
K-104
L-111

328

329 (a)

330

(b)

Fig. 2. The pilot plant for FAME synthesis: (a) layout and (b) photo.

Table 2. The main units of pilot plant.

Unit	Used as	Dimensions	Volume
F-101	Storage tank for oil	∅600 × 1200 mm	0.4 m^3
F-103	Storage tank for methanol	∅450 × 1000 mm	0.176 m^3
M-105	Static mixer	DN15	–
E-106	Preheater	380 V, 10 kW	–
R-110	Reactor	∅133 × 5 mm H = 1400 mm	0.019 m^3
D-310	Flash evaporator	∅159 × 4 mm H = 500 mm	0.01 m^3
E-302	Condenser for methanol	A = 0.004 m^2	–
E-401	Cooler of FAME–glycerol mixture	A = 0.008 m^2	–
T-411	Separator	∅159 × 4 mm H = 300 mm	0.006 m^3
F-104	Storage tank for FAME	∅600 × 1200 mm	0.33 m^3
F-105	Storage tank for glycerol	∅377 × 500 mm	0.06 m^3

The proposed operation conditions for the biodiesel production in the pilot plant facility were the methanol to soybean oil molar ratio of 18:1, the reaction temperature of 448 K and the maximal working pressure of 30 bar. The minimal TAG conversion degree achieved in the

PBTR after 8th day of the use the $MnCO_3$/Na-silicate catalyst was assumed to be 97.4%. After 8 days of continuous operation, the catalyst must be replaced by a packed-bed of fresh catalyst.

4.1. Analysis of operating parameters

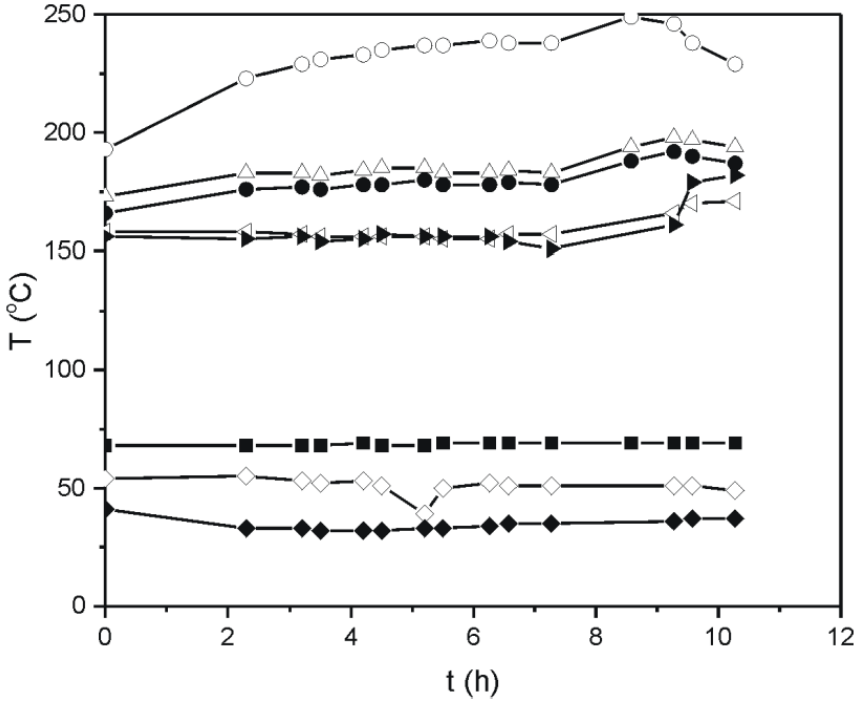
The main objectives of testing the pilot plant were to investigate the soybean oil methanolysis catalyzed by $MnCO_3$/Na-silicate for the biodiesel production under the conditions established in the laboratory batch reactor and to prove the designed capacity of the pilot plant.

4.1.1. Pilot plant testing

First, the pilot plant was tested on the leakage and the pressure by flowing the tap room temperature water (so-called cold test) and then soybean oil preheated in the preheater to 175 °C (448 K) at the flow rate of 6.3 L/h (maximum capacity of the pump). The pilot plant comprised the system for monitoring (measuring and manual control) temperature of the heater, the reactor (inside the packed bed, in the jacket and the reactor outlet), the flash evaporator, the condenser and the cooler as well as the system for measuring the pressure at the inlet and outlet of the reactor.

4.1.2. Non-catalyzed FAME synthesis in pilot plant (ZERO test)

After passing through the static mixer (M-105) and the preheater (E-106), methanol and soybean oil were pumped into the PBTR (R-110). The residence time of the reaction mixture in the preheater and the connecting pipeline between the preheater and the PBTR enabled only a minimal effect of the non-catalyzed transesterification [36]. The variation of temperature, which was controlled at several points of the pilot plant, during 11 h of the non-catalyzed FAME synthesis is shown in Fig. 3.



358

359 **Fig. 3.** Variations of temperature at the measuring points during the non-catalyzed synthesis of
360 FAMEs (thermal oil at the heater inlet – ○; the reactants' mixture at the heater outlet – ●; the
361 reactor – △; the reactor jacket – ◁; the reactor outlet – ▶; the evaporator – ■; the condenser –
362 ◇; and, the cooler – ◆).

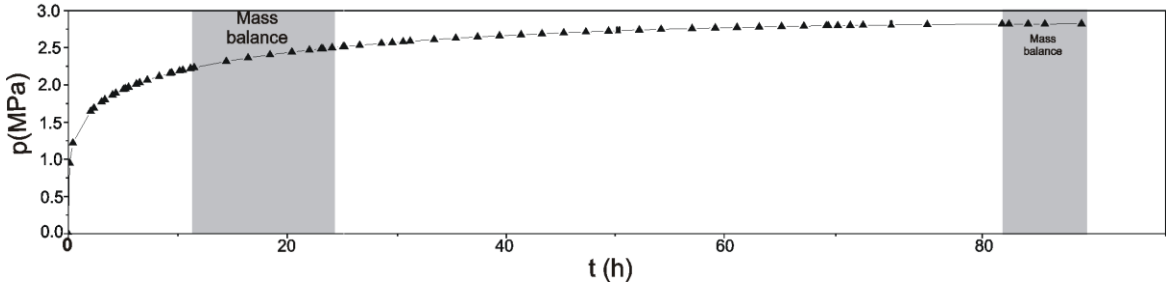
363 The temperature of the reactants leaving the preheater was slightly higher than the
364 desired reaction temperature of 175 °C as well as the temperature inside the reactor. However,
365 the measured temperature of the reaction mixture at the reactor outlet was about 155 °C at the
366 beginning of the non-catalyzed (so-called ZERO test). This was attributed to the temperature
367 sensor position which was mounted on the outside surface of the reactor wall. The detected
368 temperature at the top of the flash evaporator was lower than the desired one (>80 ^{o}C), which
369 was explained also by the position of the temperature sensor which was placed on the outside
370 surface of the evaporator. The temperatures in the condenser and the cooler were relatively
371 stable.

372 The contents of FAMEs, TAGs, DAGs and MAGs in the samples of the reaction mixture
373 taken at the outlet of the heater (inlet into the reactor) and the outlet of the reactor during the
374 ZERO test (t = 0, 3, 7, 9 and 11 h) were determined. Only the presence of about 6% of DAGs

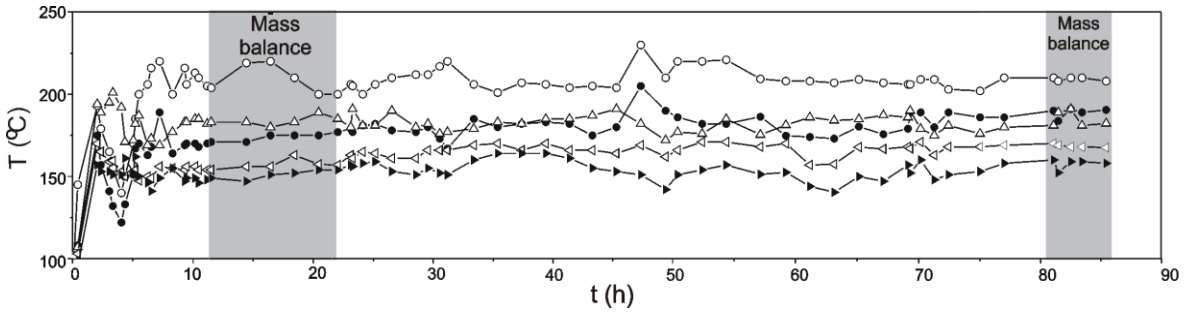
and a negligible concentration of MAGs (0.7%) were detected in the samples at the inlet of the reactor. These data indicate that the reaction started even in a relatively short residence time of the reactants in the heater and the connecting pipeline. The HPLC analysis of the esters phase separated from the samples taken at the outlet of the reactor showed the following average contents: 60% of TAGs, 22.5% of FAME or biodiesel, 11.5% of DAGs and 6% of MAGs during 11 h of non-catalyzed transesterification. Thus, for the applied residence time of oil in the empty tubular reactor, the non-catalyzed conversion of TAGs of about 40% was achieved and that about 50% of TAGs were converted into FAMEs.

4.1.3. Catalyzed synthesis of FAMEs in the PBTR (Long Term test, LT-t)

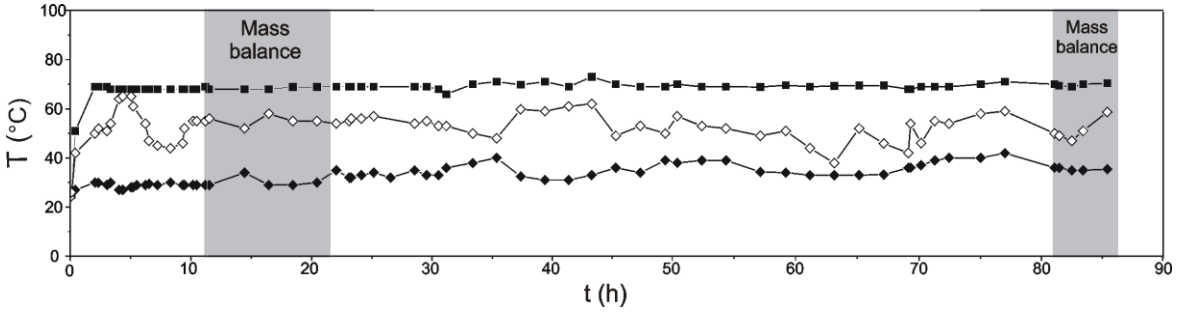
After the non-catalyzed reaction was completed, the reactor was discharged, and filled with catalyst particles and glass beads (mass ratio of 2:3; 10 kg of $MnCO_3$/Na-silicate catalyst and 15 kg of glass beads; 0.51 was experimentally determined porosity of catalyst bed). Methanol and soybean oil were heated to 175 °C and kept at this temperature for 30 min. After that, the mixture of the preheated reactants was fed to the reactor bottom. The temperature of the reaction mixture (mainly soybean oil and methanol) at the outlet of the preheater was close to the temperature inside the reactor and did not exceed 190 ^{o}C, thus preventing the overheating of soybean oil and the unwanted side reactions (e.g. polymerization). This temperature was achieved with the temperature of heating oil in the heater in the range from 180 ^{o}C to 210 ^{o}C (Fig. 4b). The average pressure in the reactor was 2.5 MPa during the *LT-t* and slightly lower during the FIRST mass balance of the *LT-t*, compared to the average pressure during the SECOND mass balance of the *LT-t* (Fig. 4a). The temperature inside the PBTR varied in the range from 175 ^{o}C to 195 ^{o}C (Fig. 4b).



(a)



(b)



(c)

Fig. 4. Variation of pressure and temperature: (**a**) ▲ – pressure at reactor inlet measured at the pump; and temperature measured at different points during the LONG TERM experiment, (**b**) ○ – thermal oil at the heater inlet, ● – the reactants' mixture at the heater outlet, △ – reactor, ◁ – jacket, ▶ – outlet of reactor; (**c**) ■ – evaporator, ◇ – condenser, ◆ – cooler.

Considering the methanol-to-oil molar ratio (18:1 and 25:1) employed in this process during the FIRST and SECOND mass balances, certain difficulties in the separation of the final products could be expected. Therefore, the flash evaporator (D-310, Fig. 2a) was included in the pilot plant facility, where the excess methanol from the outlet reaction mixture was removed by partial vaporization, enhancing the separation between esters and glycerol phases due to their poor mutual solubility. The temperature of 69 °C in the flash evaporator used for removing the excess of methanol from the ester and glycerol mixture was constant (Fig. 4c). After the flash evaporation step, the outlet stream of the main transesterification products, consisting of esters and glycerol phases, pass through the cooler to a gravitational separator.

Generally, the measured temperatures at the outlet of the preheater, the inlet and outlet of the reactor, as well as at the surface of the flash evaporator, were stable, without extreme fluctuation. However, the pilot plant did not have the system for automatic control of temperature in the reactor, so it was regulated manually, thus making difficult to maintain stable both the pressure and the temperature in the reactor at the desired levels, as can be seen in Fig. 4.

Two complete mass balances were realized (highlighted area in Fig. 4) aimed at determining the actual mass flow rates of the reactants and the products and the composition of biodiesel after its separation from glycerol. The masses of different fractions were collected at inlet and outlet of the reactor during the FIRST (between 11^{th} and 21^{th} h of operation) and SECOND (between 81^{th} and 86^{th} h of operation) mass balance and measured on scale; the obtained masses are presented in Table 3 while the composition of esters phase determined by HPLC analysis is shown in Table 4.

Table 3. Mass balances realized during the Long Term test (*LT-t*).

Mass balance experiment	INLET		OUTLET		
	Oil (kg)	Methanol (kg)	Raw ester phase (kg)	Raw glycerol phase (kg)	Recovered methanol (kg)
FIRST	31.91	20.64	32.75	9.55	10.25
SECOND	11.2*	10*	12.56	2.75	5.89

* The value of methanol –to-oil molar ratio during the 2^{nd} mass balance was changed to 25:1.

Table 4. The average composition of the ester phase.

Mass balance	FAME (%)	MAG (%)	DAG (%)	TAG (%)
FIRST	98.56	0.53	0.91	0.00
SECOND	97.49	1.08	1.21	0.22

The samples of crude ester and glycerol phases (1 L each) collected during the mass balance checking were left to stay for 2 days. The phases were separated and the following layers were detected:

- The crude esters sample (vol%): the FAME phase (upper layer) about 93% and the glycerol phase (lower layer) 4% while the evaporated methanol was approximately 3%.

- The crude glycerol sample (vol%): methanol (upper layer) 3.2%, FAME phase (middle layer) 2.5% and lower layer 87.3% as a mixture of glycerol (80.3 %) and methanol (7%).

Based on this observation, it might be concluded that the final products collected during the FIRST mass balance contained 30.8 kg of pure ester phase (30.4 kg of FAMEs and 0.4 kg of DAGs and MAGs), 0.09 kg of methanol and 1.83 kg of glycerol.

This analysis showed that the FAME content was very high in the esters phase analyzed during the *LT-t* (Table 4). In both mass balances FAME content was higher than 96.5%, meeting the requirements of the biodiesel standard specifications (EN 14214). It was worth mentioning that during the *LT-t*, the contents of DAGs and MAGs were very low, but still slightly higher than those defined by standards (0.2% for DAG and 0.8% for MAG). TAGs were not detected in the esters phase of the FIRST mass balance but they started to appear at the end of the SECOND mass balance of *LT-t*, being close to the standard limit (0.2%). Although the conversion of TAGs was still very high (99.8%), the yield of FAME dropped to 97.5%. This result agreed with the observed changes in the esters phase composition during the soybean oil transesterification in the repeated use of the catalyst in the batch transesterification [9].

4.1.4. Catalyst deactivation during Pilot Plant experiment

During 85 h of the *LT-t*, a small fluctuation of the esters phase composition was observed. However, there were no enough data to predict exactly the catalyst deactivation during 85 h of its use. The simple calculation, mentioned above based on data collected in the batch process, indicated that the used amount of $MnCO_3$/Na-silicate catalyst (10 kg) would be active for at least 8–9 days of the continuous process and the data of *LT-t* supported this expectation. At the same time, a gradual increase of the pressure in the PBTR was observed (Fig. 4a). The pressure should be enhanced for keeping the capacity of the pilot plant at the designed value, which was attributed to the blocking of the interparticle space with TAGs and the side products formed at a high temperature as a result of the oil polymerization.

For defining the actual status of the used catalyst in the PBTR after the *LT-t*, the samples were withdrawn from the bottom and the middle part of the PBTR and analyzed by XRD, TG/DTA and FTIR. Figure 5 shows the XRD pattern of the $MnCO_3$/Na-silicate sample (washed and centrifuged with ethanol).

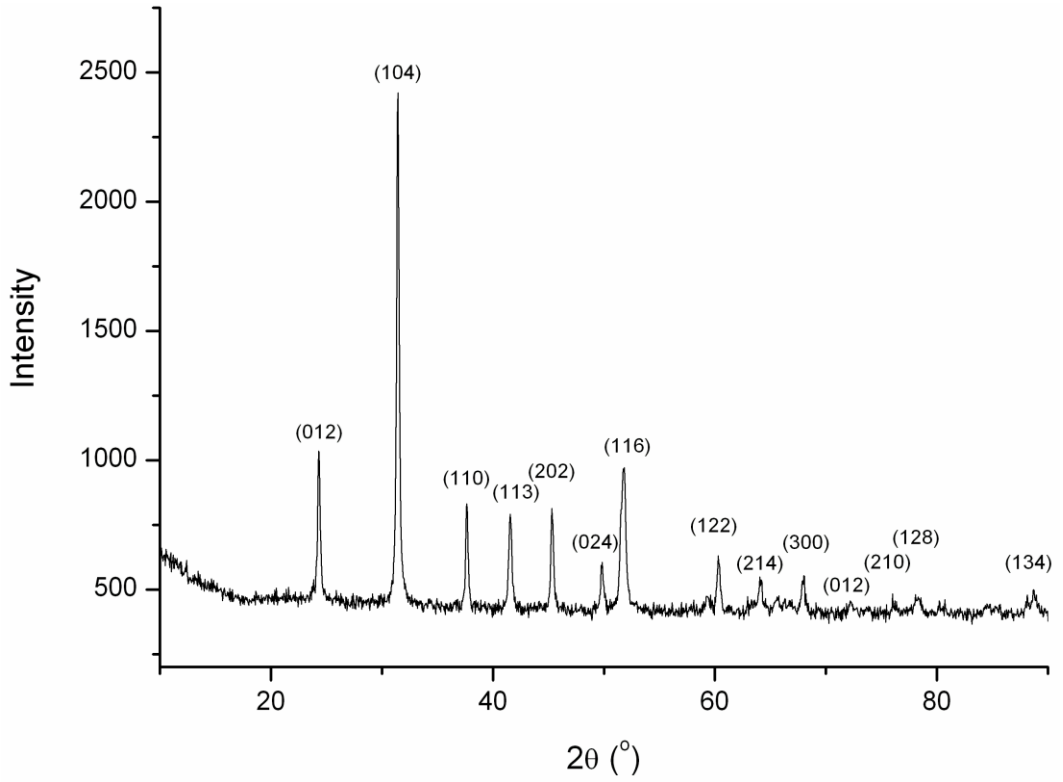
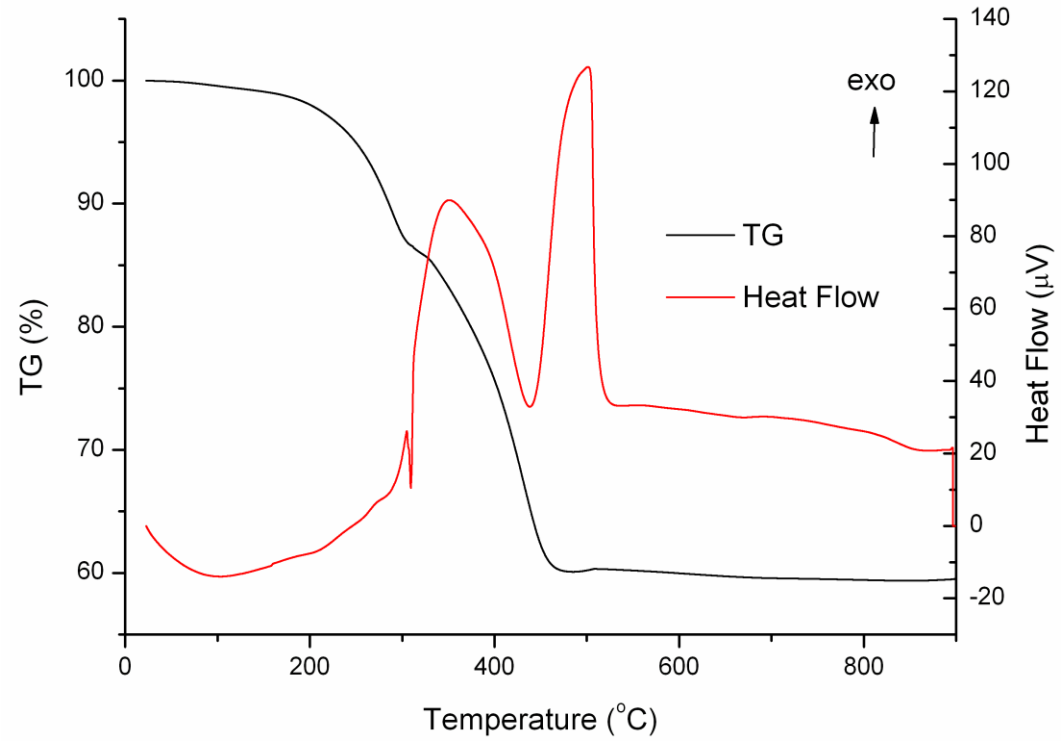


Fig. 5. XRD pattern of the $MnCO_3$/Na-silicate catalyst taken from the middle part of the PBTR after 85 h of the *LT-t* performed at 175 ^oC and 2.5 MPa.

The presence of rhombohedral structure of $MnCO_3$ was consistent with the literature values (JCPDS Card 83-1763). Since the XRD pattern was very similar to the XRD pattern of the fresh catalyst [9] it was concluded that the catalyst did not undergo any noticeable structural changes during the 85 h of the *LT-t*.

Thermal behavior of the as-taken (without washing) $MnCO_3$/Na-silicate is shown in Fig. 6.



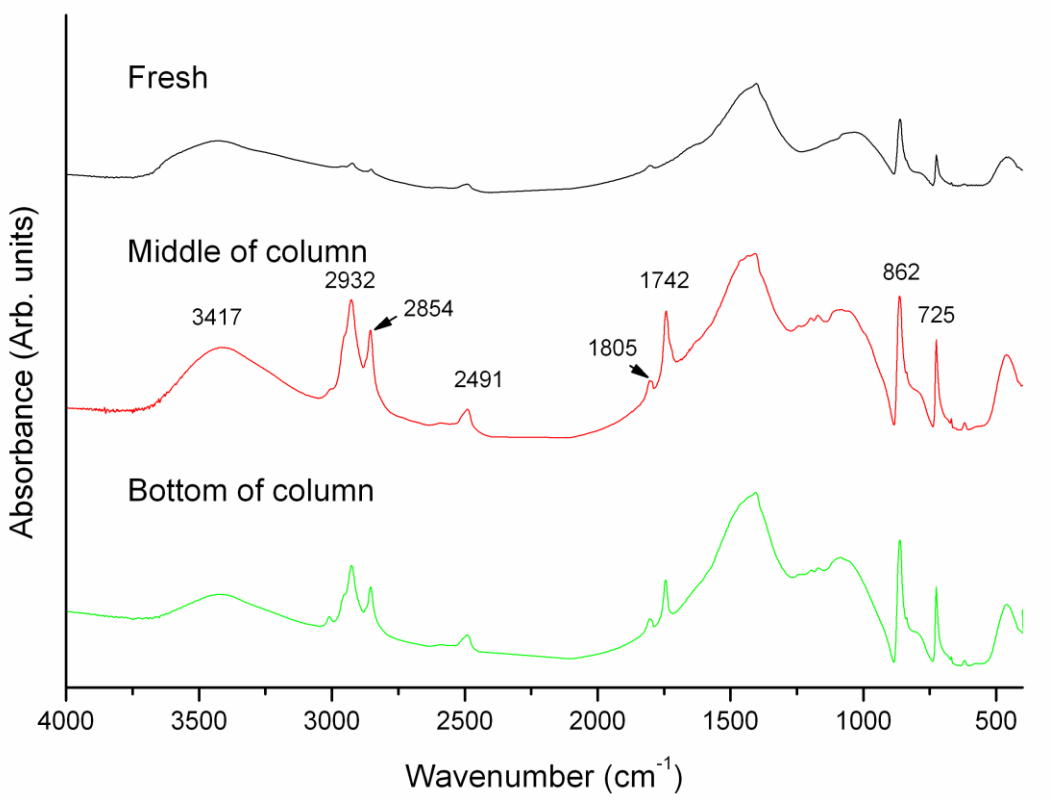
475

476

477 **Fig. 6.** TG/DTA analysis (heating rate: 20 K/min) of the $MnCO_3$/Na-silicate catalyst sample
478 taken from the middle part of the PBTR after 85 h of the *LT-t*.

479 The mass change indicated a weight loss at about 320 °C (16%), which might be
480 attributed to the release of crystalline water and the compounds adsorbed on the catalyst surface
481 (composed of FAMEs, glycerol, and traces of TAGs, DAGs and MAGs). The second mass
482 change was observed in the temperature range from 320 to 500 °C, with an endothermic peak at
483 about 440 °C. It might be attributed to the thermal decomposition of $MnCO_3$ as well to the
484 degradation of the reactants and the products. The total weight loss was about 40%, which was
485 10% higher than that found for the fresh catalyst [9]. Therefore, it was concluded that a part
486 (10%) of oil phase was adsorbed on the catalyst surface.

487 The FTIR spectra of the fresh and used catalysts are shown in Fig. 7 for comparison.



488

489 **Fig. 7.** FTIR spectra of the fresh and used catalyst collected from the bottom and middle part of
490 the PBTR after 85 h of the *LT-t*.

491 The broad band of the spectra with the maximum at about 3400 cm^{-1} might be attributed
492 to the hydrogen (H)-bonded stretching vibration of the O–H group, and could be assigned to the
493 water (moisture) adsorbed from air and/or the reaction mixture on the catalyst surface. The peaks
494 at 2932, 1742 and 725 cm^{-1} might be assigned to C–H, C–O and C–C functional groups,
495 respectively, while the peak at 862 cm^{-1} corresponded to the bending vibration of CO_3^{2-} in
496 $MnCO_3$.

497 It was found that the absorbance values from the wavelength region of 3700–3075 cm^{-1}
498 might be used for estimating the moisture content in the biodiesel samples [47]. The broad peak
499 in this region was more pronounced for the samples taken from the middle and bottom parts of
500 the reactor than that of the fresh sample suggesting the presence of water in the reaction mixture.
501 Furthermore, remarkably higher intensities of the peaks at 2932, 2854 and 1742 cm^{-1} for the

samples of the used catalyst, compared to that for the fresh catalyst, indicate the existence of different compounds from the reaction mixture, which were adsorbed on the catalyst surface.

5. Conclusion

The pilot plant with the capacity of 100 liters of biodiesel per day was successfully designed and tested for biodiesel production from soybean oil catalyzed by $MnCO_3$/Na-silicate. The kinetic model with the parameters determined based on the analysis of the experiments realized in batch autoclave at 175 °C and 25 bar over $MnCO_3$/Na-silicate as a catalyst and taking into account the influence of temperature and catalyst loading on the apparent reaction rate constant, was used for the design of PBTR as a main equipment of corresponding pilot plant.

Test of continuous operation was used to prove designed capacity and operational characteristics of pilot plant unit. Investigation was started using PBTR filled only with glass beads for 11 h, and then, the catalyzed transesterification of soybean oil with $MnCO_3$/Na-silicate as catalyst was realized during 85 h of continuous operation. Two complete mass balances performed for detailed examination of the content of produced biodiesel revealed high TAG conversion (99.8%) and FAME yield over 97.5%, while the sample of used catalyst withdrawn from reactor after 85 h of continuous process did not show any noticeable structural changes. The results of the performed tests in pilot plant showed a good starting point for further experiments planned to be done in order to improve constructed biodiesel production facility and to test other types of catalysts.

Acknowledgements

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673 **Nomenclature**

674	c_{TAG}	concentration of TAG, mol/L
675	$c_{TAG,0}$	initial concentration of TAG, mol/L
676	c_w	catalyst concentration, *% (w, m*ass of catalyst per 100 g of soybean oil)
677	c_p	mass heat capacity of reaction mixture, kJ/kg·K
678	c_{FAME}	concentration of FAME, mol/L
679	d	catalyst particle diameter, mm
680	DAG	diacylglycerols
681	$FAME$	fatty acid methyl esters
682	$F_{TAG,0}$	molar flow rate of TAGs, mol/min
683	$(-\Delta H_r)$	heat effect of TAG transesterification reaction, kJ/mol
684	k_{app}	apparent reaction rate constant of transesterification process, min^{-1}
685	k_{LT}	reaction rate constant valid up to 423 K, min^{-1}
686	k_{HT}	reaction rate constant valid above 423 K, min^{-}
687	$k_{app(w)}$	apparent reaction rate constant as function of catalysts concentration, min^{-1}
688	k_{mt}	mass transfer coefficient during transesterification process, min^{-1}
689	k_{mt0}	mass transfer coefficient at the beginning of transesterification process, min^{-1}
690	m_0	mass flow rate of reaction mixture, kg/h
691	$m_{TAG,0}$	mass flow rate of TAGs into PBTR, kg/h
692	M_0	molar flow rate of reaction mixture, mol/h
693	MAG	monoacylglycerols

$(-r_{TAG})$	rate of triacylglycerols transesterification, mol/(min·L)
t	time, min
T	temperature, K
TAG	triacylglycerols
V	volume of reaction mixture, L
x_{TAG}	degree of TAG conversion

Greek symbols

α	parameter of kinetic model, Eq. (3b)
β	parameter of kinetic model, Eq. (3b
τ	residence time, min