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1                   **Continuous biodiesel production under subcritical condition of**  
2                   **methanol – Design of pilot plant and packed bed reactor with MnCO<sub>3</sub>/Na-**  
3                   **silicate catalyst**

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24 **Abstract**

25       The continuous biodiesel production from soybean oil was carried out under the  
26 subcritical condition of methanol with  $\text{MnCO}_3/\text{Na-silicate}$  as a heterogeneous catalyst. The  
27 transesterification rate was first investigated in a set of experiments performed in a batch  
28 autoclave at 448 K using methanol-to-oil molar ratio of 18:1 and various catalyst loadings (5, 10  
29 and 20 wt% based on the oil mass). The results from these experiments, as well as the  
30 experimental data and the appropriate kinetic model recently reported in the literature were used  
31 for designing a packed bed tubular reactor (PBTR), a main unit of the pilot plant with the  
32 capacity of 100 liters of biodiesel per day. The pilot plant was constructed and tested under  
33 various operating conditions. The first 11 h of the pilot-plant operation was realized in the  
34 tubular reactor packed with inert glass beads (i.e. without the catalyst) in order to analyze the  
35 effect of the non-catalyzed subcritical biodiesel (fatty acid methyl esters, FAME) production.  
36 Then, glass beads were replaced with a mix of  $\text{MnCO}_3/\text{Na-silicate}$  catalyst particles and glass  
37 beads, and the catalytic biodiesel production was continuously run under the subcritical methanol  
38 condition for 85 h. Two mass balance tests during the continuous pilot plant operation were  
39 performed.

40

41       **Keywords:** Biodiesel; Subcritical methanolysis; Kinetic modeling;  $\text{MnCO}_3/\text{Na-silicate}$   
42 catalyst; Pilot-plant design.

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## 45 1. Introduction

46 In the past several years, many researchers have made efforts to synthesize efficient  
47 heterogeneous catalysts for biodiesel production in order to substitute the conventional  
48 technology based on homogeneous catalysis, which is currently applied in many industrial  
49 facilities. Numerous investigations have been undertaken in order to estimate the potential  
50 catalytic activity of both naturally originated and synthesized materials. Among the  
51 heterogeneous catalysts, the CaO-based catalysts are frequently studied [1][2][3][4][5] due to  
52 their high activity and possibility to be obtained from inexpensive natural and waste materials  
53 [6]. The other low-cost materials, like  $\text{MnCO}_3$ , Na-silicate and  $\text{MnCO}_3/\text{Na-silicate}$ , also show,  
54 after thermal activation, a high catalytic activity for biodiesel production [7][8][9][10]. Some of  
55 them, like Na-silicate, can be used even for transesterification of waste vegetable oils with a high  
56 amount of water owing to the hydrolysis of the activated Na-silicate into  $\text{OH}^-$  and  $\text{Si-O-H}^+$ , thus  
57 avoiding soap formation. Another advantage is the simple regeneration of the used Na-silicate  
58 catalyst with NaOH [7]. Other materials, like ion-exchange resins [11][12] and hydrotalcite [13],  
59 have also been tested in order to obtain long-lifetime catalysts that can be used for continuous  
60 processes.

61 Heterogeneously-catalyzed methanolysis reactions are slower than homogeneously-  
62 catalyzed ones due to the mass transfer limitations in the three-phase system mainly at the  
63 beginning of the transesterification process [14][15][16]. The nature of heterogeneously catalyzed  
64 oil methanolysis reactions has been explained by different reaction mechanisms  
65 [17][18][19][20][21][22]. However, the resulting kinetic models based on these mechanisms are  
66 rather complex since a large number of parameters need to be determined. The recently reported  
67 studies described the suitable, relatively simple kinetic models of the vegetable oil methanolysis  
68 requiring no complicated computations [2][14]. The model proposed by Lukić et al. [14] is based  
69 on the pseudo-first order kinetics that involves the triacylglycerols (TAGs) mass transfer and  
70 chemical reaction controlled regimes. The model proposed by Miladinović et al. [2] includes a  
71 changing reaction mechanism with respect to TAGs and the first order reaction with respect to  
72 fatty acid methyl esters (FAMES). The applicability of both models was confirmed for the  
73 sunflower oil methanolysis catalyzed by the CaO-based catalysts ( $\text{CaO}\cdot\text{ZnO}$ , 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  $>150\text{ }^{\circ}\text{C}$  and  $>30\text{ bar}$  [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  $\text{MnCO}_3$ ,  $\text{MnCO}_3/\text{Na-silicate}$  [8][9] and  $\text{MnCO}_3/\text{ZnO}$   
102 [43] catalysts in the form of powder or granules (coarse particles). Furthermore, it is worth

103 mentioning that methanol-to-oil molar ratio and reaction temperature applied in the biodiesel  
104 production with  $\text{MnCO}_3$  or  $\text{MnCO}_3/\text{Na-silicate}$  catalyst were lower than those suggested by Yin  
105 et al. [44] for the subcritical sodium silicate-catalyzed soybean oil methanolysis. The  
106  $\text{MnCO}_3/\text{Na-silicate}$  catalyst prepared in the form of granulated particles have an acceptable  
107 activity, excellent selectivity towards FAME formation from TAGs, and acceptable lifetime at  
108 high temperature [9].

109 This article reports designing and testing of a pilot plant applied for the biodiesel  
110 production by the soybean oil transesterification catalyzed by  $\text{MnCO}_3/\text{Na-silicate}$  with the  
111 capacity of 100 liters of biodiesel per day. Results of the recently reported study [9]  
112 supplemented with information from several additional experiments realized in batch autoclave  
113 with different amount of  $\text{MnCO}_3/\text{Na-silicate}$  (5–20 wt% based on oil) at 448 K and 18:1  
114 methanol to oil molar ratio, were the basis for design of packed bed tubular reactor (PBTR) as  
115 main equipment of corresponding pilot plant. PBTR was filled with  $\text{MnCO}_3/\text{Na-silicate}$  as  
116 catalyst mixed with inert glass beads and such reactor was applied for continuous  
117 transesterification at subcritical condition of methanol. Test of continuous operation was used to  
118 prove designed capacity and operational characteristics of pilot plant unit during 100 hours of  
119 operation. Investigation was started using PBTR filled only with glass beads for 11 h, and then,  
120 the catalyzed transesterification of soybean oil with  $\text{MnCO}_3/\text{Na-silicate}$  as catalyst was realized  
121 during 85 h of continuous operation. Two complete mass balances were determined for detailed  
122 examination of the content of produced biodiesel while sample of used catalyst after 85 h of  
123 continuous process was withdrawn from reactor and its characteristics were analyzed using  
124 XRD, TG/DSC and FTIR.

## 125 **2. Materials and methods**

### 126 *2.1. Catalyst preparation*

127 The preparation and characterization of the  $\text{MnCO}_3/\text{Na-silicate}$  catalyst have recently  
128 been reported [9]. The catalyst was activated by drying at 473 K for 2 h, followed by the  
129 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  $\text{MnCO}_3/\text{Na-silicate}$  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  $\pm 2.86\%$ .

### 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  $\text{Cu K}\alpha_{1,2}$  ( $\lambda = 1.54178 \text{ \AA}$ ) radiation with a scanning step width of  
154  $0.05^\circ$  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 ( $20 \text{ K min}^{-1}$ ) and Fourier transformed infrared  
156 spectroscopy (FTIR) using a BOMEM spectrometer (Hartmann & Braun) in the wave number  
157 range of  $4000\text{--}400 \text{ cm}^{-1}$  with  $4 \text{ cm}^{-1}$  resolution.

### 158 3. Results and discussion

#### 159 3.1. Analysis of soybean oil transesterification in a batch reactor

160 The soybean oil transesterification in the presence of the  $\text{MnCO}_3/\text{Na}$ -silicate catalyst  
161 occurs via two simultaneous catalytic processes [9]: one is catalyzed heterogeneously by both  
162 active species (Mn and Na) fixed on the surface of solid catalyst particles and homogeneously by  
163 Na dissolved in the esters and methanol/glycerol phases. It is important to point out that the  
164 batch transesterification reaction takes place during the heating of the reaction mixture from the  
165 room temperature to the specified reaction temperature (non-isothermal regime), and while  
166 keeping the reaction temperature constant (isothermal regime). The apparent reaction rates are  
167 simply defined by the reaction rate constants,  $k_{\text{LT}}$  and  $k_{\text{HT}}$ , depending on the reaction temperature  
168 and determined for the process performed with 5 wt% of the catalyst (based on the oil) [9]:

169 For the isothermal operation at  $T < 423$  K

$$170 \quad k = k_{\text{LT}} = 7.918 \exp(-2465 / T), \text{ min}^{-1} \quad (1a)$$

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

$$172 \quad k = k_{\text{HT}} = 6.355 \times 10^5 \exp(-7272 / T), \text{ min}^{-1} \quad (1b)$$

$$173 \quad k = k_{\text{LT}} = 7.918 \exp(-2465 / T), \text{ min}^{-1} \quad \text{for } T < 423 \text{ K} \quad (1a)$$

$$174 \quad k = k_{\text{HT}} = 6.355 \times 10^5 \exp(-7272 / T), \text{ min}^{-1} \quad \text{for } T > 423 \text{ K} \quad (1b)$$

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

$$176 \quad \frac{dx_{\text{TAG}}}{dt} = k_{\text{app}}(1 - x_{\text{TAG}}) \quad (2)$$

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

$$178 \quad k_{\text{app}} = \frac{k \cdot k_{\text{mt}}}{k + k_{\text{mt}}} = \frac{k_{\text{app}} \cdot k_{\text{mt}0} \cdot [1 + \alpha(x_{\text{TAG}})^\beta]}{k_{\text{app}} + k_{\text{mt}0} \cdot [1 + \alpha(x_{\text{TAG}})^\beta]} \quad (3)$$



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

### 183 3.2. Analysis of the transesterification in the batch reactor performed with different amounts of 184 catalyst

185 In the present study, several experiments were conducted in the AE batch reactor using  
186 5%, 10% and 20% of  $\text{MnCO}_3/\text{Na-silicate}$  catalyst based on mass of oil (particle size 0.99–1.99  
187 mm) at 448 K to verify the proposed IL kinetic model at higher catalyst amounts [9]. Besides,  
188 unlike previously reported results [9] the isothermal temperature of 448 K in this study was  
189 reached in the batch autoclave for 113 min. The difference in the heating time needed to reach  
190 the isothermal transesterification temperature in the batch autoclave could give additional  
191 information about the flexibility of the proposed IL kinetic model used to predict TAG  
192 conversion at 448 K.

193 The experiments with 5% of catalyst (based on oil) showed that the TAG conversion of  
194 62.6% was obtained during heating period of 113 min (54.6% for 54 min [9]), while TAG  
195 conversion of 81.3% and 98.2% were obtained with 10% and 20% of catalyst, respectively for  
196 the same time of non-isothermal heating. Further 1 h of isothermal transesterification at 448 K  
197 with 5% and 10% of catalyst gave almost the complete TAG conversion (>99%). According to  
198 these data the following recalculations of the reaction apparent rate constant  $k$  (i.e.  $k_{LT}$  and  $k_{HT}$ )  
199 and mass transfer coefficient  $k_{mt0}$ , which depended on the total catalytic surface area [8], were  
200 used to determine the reaction rate constant  $k_{app}$  applicable for both non-isothermal (heating to  
201 448 K) and isothermal regime:

$$202 \quad k_{(w)} = k_{(5)} \frac{C_{cat(w)}}{C_{cat(5)}} \quad (4a)$$

203 and

$$204 \quad k_{mt0(w)} = k_{mt0(5)} \frac{C_{cat(w)}}{C_{cat(5)}} \quad (4b)$$

205 thus leading to:

$$206 \quad k_{app(w)} = k_{app(5)} \frac{c_{cat(w)}}{c_{cat(5)}} \quad (4c)$$

207 where  $c_{cat(w)}$  is the catalyst amount used for the transesterification of soybean oil (valid for  $2 < w$   
208  $< 8$  wt% based on the mass of oil).

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

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

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

$$229 \quad k_{app(w)} = \varphi k_{app(5)} \quad (5a)$$

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

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

237 **Table 1.** Experimental results of the soybean oil transesterification during non-isothermal  
 238 heating from 288 K to 448 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

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

245 3.3. Design of packed bed tubular reactor

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

251 
$$\frac{dx_{TAG}}{d\tau} = k_{app}(1 - x_{TAG}) \quad (6)$$

252 
$$\frac{dT}{dx_{TAG}} = -\frac{F_{TAG,0}\Delta H_r}{m_0 c_p} \quad (7)$$

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

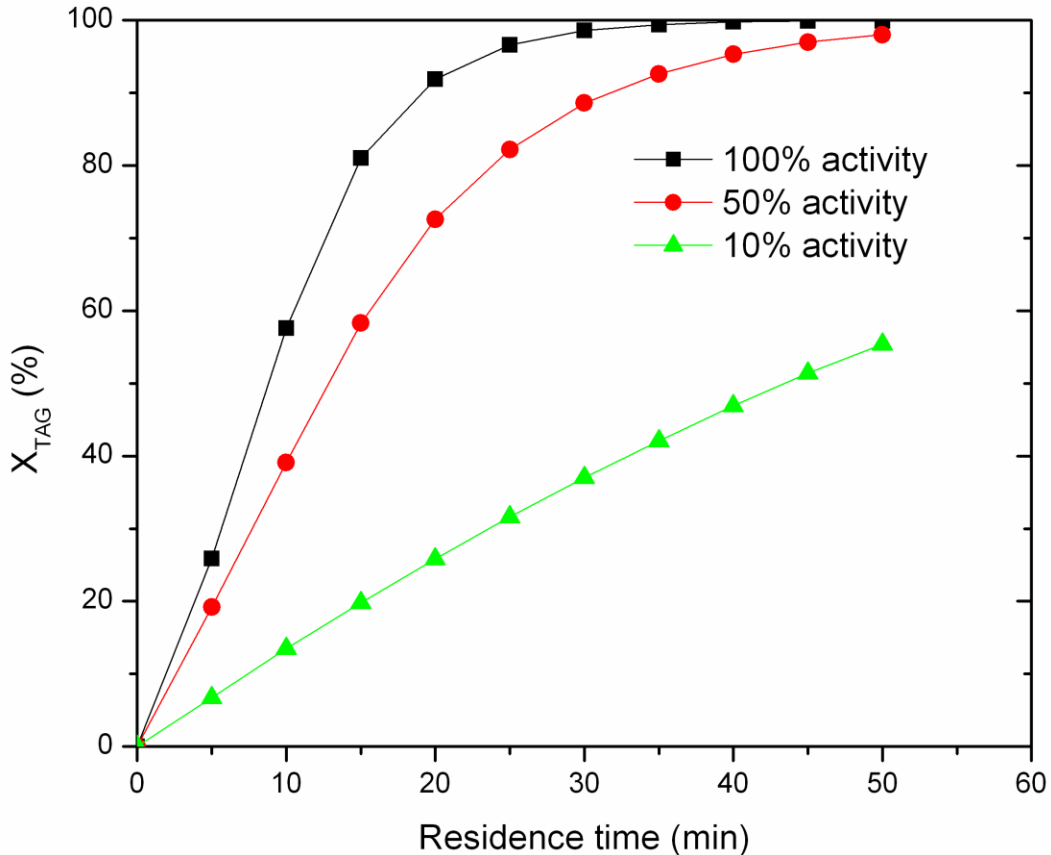
256 
$$k = 3.2 \cdot k_{HT(w=5\%)} = 2.034 \times 10^6 \exp\left(-\frac{7272}{T}\right), \text{ min}^{-1} \quad (8)$$

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

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

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

262 For the initial activity of catalyst (100%), almost complete TAG conversion ( $x_{TAG} = 1$  or  
263 100%) could be obtained at the outlet of the reactor after 50 min of residence time. If the catalyst  
264 activity in the PBTR dropped to 50% of its initial value, then the TAG conversion degree at the  
265 reactor outlet would be 98%. Further decrease of the average catalyst activity in the PBTR, e.g.  
266 to 10% of its initial activity would result in 55% TAG conversion degree, as shown in Fig. 1.



267  
 268 **Fig. 1.** Conversion degree versus residence time of the reaction mixture for different  
 269 average catalyst activities in the PBTR.

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

- 272 • The process efficiency of 90% was adopted, resulting the biodiesel production capacity of  
 273 4.17 kg/h (0.07 kg/min).
- 274 • For the complete conversion of soybean oil (>99%), the inlet soybean oil (TAG) mass flow  
 275 rate ( $m_{o,TAG}$ ) should be 4.17 kg/h.
- 276 • Taking into account the molar masses of soybean oil (890 g/mol) and methanol (32 g/mol)  
 277 and their molar ratio of 1:18, the inlet concentration of TAGs, represented by triolein as a key  
 278 compound ( $c_{TAGo}$ ) would be 0.60 mol/L, while the molar and mass flow rates of the reaction  
 279 mixture ( $M_o$  and  $m_o$ ) into the PBTR would be 89 mol/h and 6870 g/h, respectively; the inlet  
 280 TAG molar flow rate of ( $F_{TAGo}$ ) was 4.68 mol/h.

- 281 • The catalyst bed would be prepared by mixing  $\text{MnCO}_3/\text{Na-silicate}$  catalyst particles (bulk  
282 density of 1.2 g/mL) and inert glass beads (2 mm; 2.5 g/mL) with the mass ratio of 40:60.  
283 • The porosity of the catalyst bed was assumed to be 50%.  
284 • The proposed residence time of the reaction mixture in the PBTR would be 50 min.  
285 • The reaction mixture would be heated in a preheater to 448 K to the reaction temperature in  
286 the PBTR.  
287 • The inlet mass flow rates of the soybean oil and methanol would be 6870 g/h or 8.6 L/h,  
288 corresponding to the methanol-to-oil molar ratio of 18: 1.  
289 • The density of the reaction mixture at 448 K and 25 bar was assumed to be about 800 kg/L.  
290 • A simple calculation gave the volume of the reaction mixture which occupied the void space  
291 of the bed of 7.16 L and the volume of the empty reactor of 14.33 L. Thus, the reactor could  
292 be packed with 8.33 L of  $\text{MnCO}_3/\text{Na-silicate}$  catalyst (or 10 kg; density 1.2 kg/L) and 6 L of  
293 inert glass beads (spheres) (15 kg; density of 2.5 kg/L).  
294 • The amount of oil in the reactor would be 3.90 kg, so the catalyst concentration (based on the  
295 mass of oil) in the reactor would be  $10/3.90 = 2.56$  kg/kg or 256%.

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

- 297 a. Volume of the tubular reactor would be 14 L.  
298 b. Mass of 10.2 kg of catalyst particles (cylindrical granules with the average diameter between  
299 0.9 and 1.99 mm) and mass of 15.3 kg of glass beads (2 mm), respectively should be used for  
300 preparing the packed bed.  
301 c. The biodiesel production capacity would be 4.05 kg/h or 97 kg/day, i.e. slightly above 100  
302 L/day (density of biodiesel: 0.9 kg/L).

### 303 3.4. Assessment of catalyst deactivation during long-term continuous operation

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

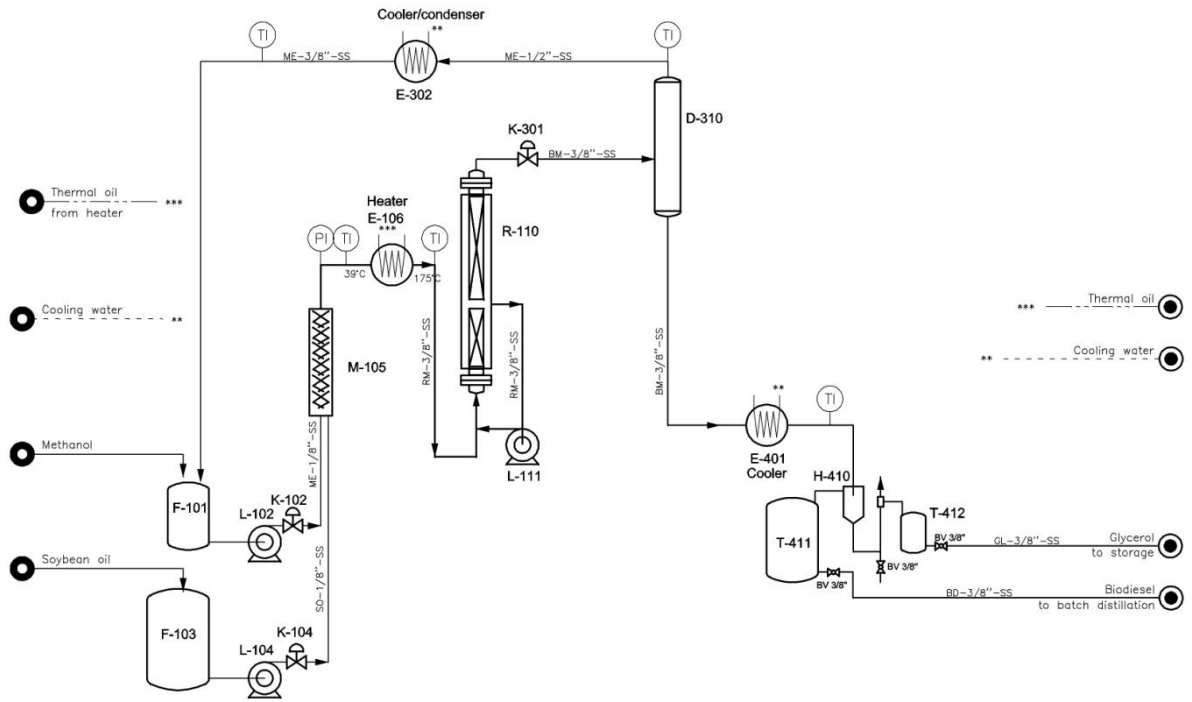
309 Therefore, 10 kg of the catalyst placed in the PBTR could be used for processing 800 kg of  
310 soybean oil. In other words, the catalyst might be used for 8-day continuous operation of the  
311 PBTR when TAG conversion degree would be slightly decreased to 97.4%. However, the  
312 catalyst activity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



328

329

(a)



330



331

(b)

332

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

333

**Table 2.** The main units of pilot plant.

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

334

The proposed operation conditions for the biodiesel production in the pilot plant facility

335

were the methanol to soybean oil molar ratio of 18:1, the reaction temperature of 448 K and the

336

maximal working pressure of 30 bar. The minimal TAG conversion degree achieved in the

337 PBTR after 8<sup>th</sup> day of the use the MnCO<sub>3</sub>/Na-silicate catalyst was assumed to be 97.4%. After 8  
338 days of continuous operation, the catalyst must be replaced by a packed-bed of fresh catalyst.

#### 339 *4.1. Analysis of operating parameters*

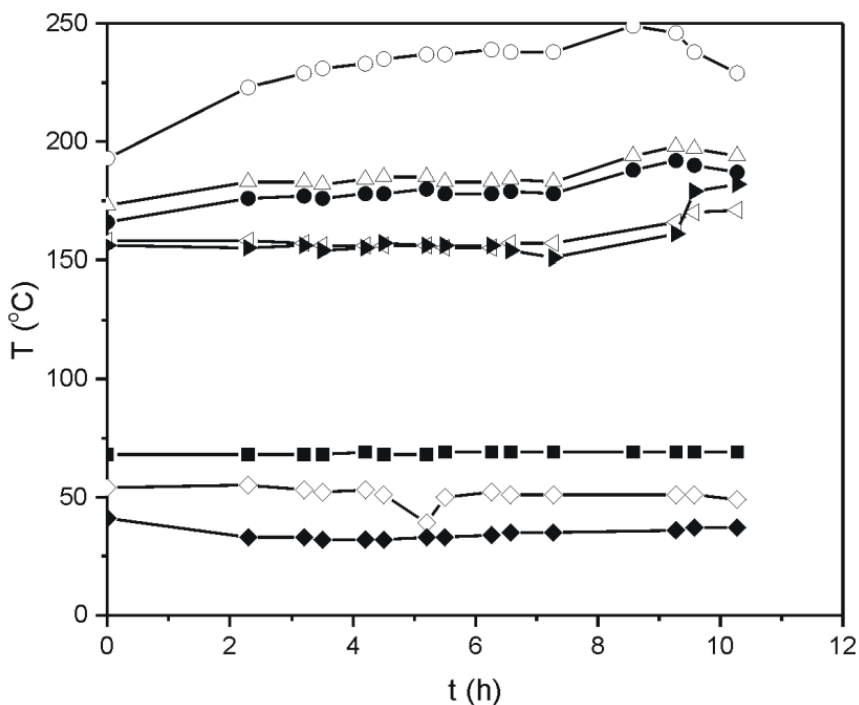
340 The main objectives of testing the pilot plant were to investigate the soybean oil  
341 methanolysis catalyzed by MnCO<sub>3</sub>/Na-silicate for the biodiesel production under the conditions  
342 established in the laboratory batch reactor and to prove the designed capacity of the pilot plant.

##### 343 *4.1.1. Pilot plant testing*

344 First, the pilot plant was tested on the leakage and the pressure by flowing the tap room  
345 temperature water (so-called cold test) and then soybean oil preheated in the preheater to 175 °C  
346 (448 K) at the flow rate of 6.3 L/h (maximum capacity of the pump). The pilot plant comprised  
347 the system for monitoring (measuring and manual control) temperature of the heater, the reactor  
348 (inside the packed bed, in the jacket and the reactor outlet), the flash evaporator, the condenser  
349 and the cooler as well as the system for measuring the pressure at the inlet and outlet of the  
350 reactor.

##### 351 *4.1.2. Non-catalyzed FAME synthesis in pilot plant (ZERO test)*

352 After passing through the static mixer (M-105) and the preheater (E-106), methanol and  
353 soybean oil were pumped into the PBTR (R-110). The residence time of the reaction mixture in  
354 the preheater and the connecting pipeline between the preheater and the PBTR enabled only a  
355 minimal effect of the non-catalyzed transesterification [36]. The variation of temperature, which  
356 was controlled at several points of the pilot plant, during 11 h of the non-catalyzed FAME  
357 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 °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.

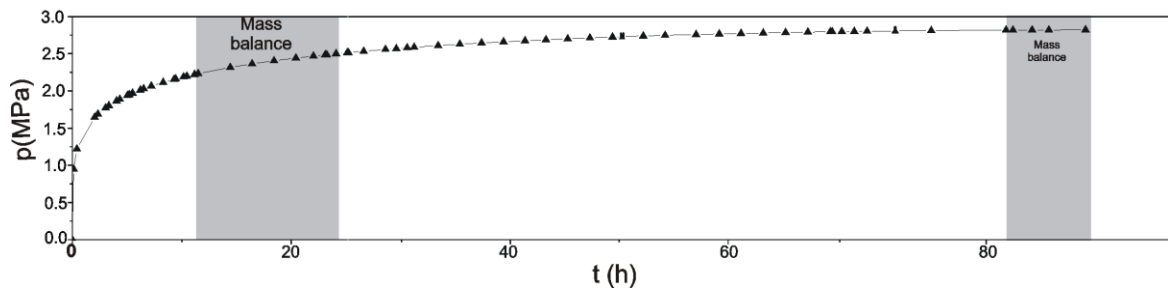
372 The contents of FAMEs, TAGs, DAGs and MAGs in the samples of the reaction mixture  
 373 taken at the outlet of the heater (inlet into the reactor) and the outlet of the reactor during the  
 374 ZERO test ( $t = 0, 3, 7, 9$  and  $11$  h) were determined. Only the presence of about 6% of DAGs

375 and a negligible concentration of MAGs (0.7%) were detected in the samples at the inlet of the  
376 reactor. These data indicate that the reaction started even in a relatively short residence time of  
377 the reactants in the heater and the connecting pipeline. The HPLC analysis of the esters phase  
378 separated from the samples taken at the outlet of the reactor showed the following average  
379 contents: 60% of TAGs, 22.5% of FAME or biodiesel, 11.5% of DAGs and 6% of MAGs during  
380 11 h of non-catalyzed transesterification. Thus, for the applied residence time of oil in the empty  
381 tubular reactor, the non-catalyzed conversion of TAGs of about 40% was achieved and that  
382 about 50% of TAGs were converted into FAMEs.

#### 383 4.1.3. Catalyzed synthesis of FAMEs in the PBTR (Long Term test, *LT-t*)

384 After the non-catalyzed reaction was completed, the reactor was discharged, and filled  
385 with catalyst particles and glass beads (mass ratio of 2:3; 10 kg of  $\text{MnCO}_3/\text{Na-silicate}$  catalyst  
386 and 15 kg of glass beads; 0.51 was experimentally determined porosity of catalyst bed).  
387 Methanol and soybean oil were heated to 175 °C and kept at this temperature for 30 min. After  
388 that, the mixture of the preheated reactants was fed to the reactor bottom. The temperature of the  
389 reaction mixture (mainly soybean oil and methanol) at the outlet of the preheater was close to the  
390 temperature inside the reactor and did not exceed 190 °C, thus preventing the overheating of  
391 soybean oil and the unwanted side reactions (e.g. polymerization). This temperature was  
392 achieved with the temperature of heating oil in the heater in the range from 180 °C to 210 °C  
393 (Fig. 4b). The average pressure in the reactor was 2.5 MPa during the *LT-t* and slightly lower  
394 during the FIRST mass balance of the *LT-t*, compared to the average pressure during the  
395 SECOND mass balance of the *LT-t* (Fig. 4a). The temperature inside the PBTR varied in the  
396 range from 175 °C to 195 °C (Fig. 4b).

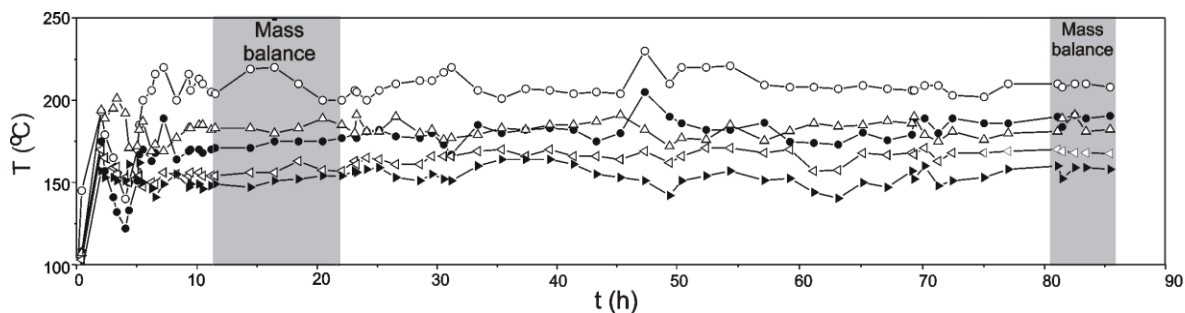
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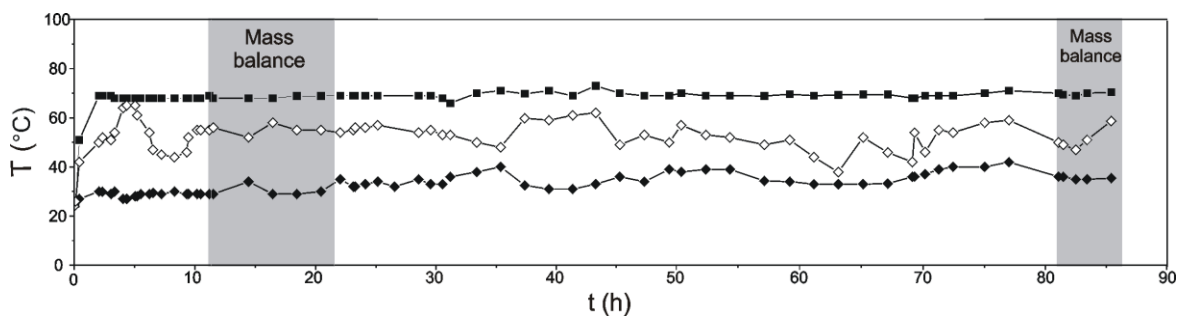
(a)



400

401

(b)



402

403

(c)

404 **Fig. 4.** Variation of pressure and temperature: (a)  $\blacktriangle$  – pressure at reactor inlet measured at the  
 405 pump; and temperature measured at different points during the LONG TERM experiment, (b)  $\circ$   
 406 – thermal oil at the heater inlet,  $\bullet$  – the reactants' mixture at the heater outlet,  $\triangle$  – reactor,  $\triangleleft$  –  
 407 jacket,  $\blacktriangleright$  – outlet of reactor; (c)  $\blacksquare$  – evaporator,  $\diamond$  – condenser,  $\blacklozenge$  – cooler.

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

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

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

429 **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)
<b>FIRST</b>	31.91	20.64	32.75	9.55	10.25
<b>SECOND</b>	11.2*	10*	12.56	2.75	5.89

430 \* The value of methanol –to-oil molar ratio during the 2<sup>nd</sup> mass balance was changed to 25:1.

431 **Table 4.** The average composition of the ester phase.

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

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

- 435 • The crude esters sample (vol%): the FAME phase (upper layer) about 93% and the  
436 glycerol phase (lower layer) 4% while the evaporated methanol was approximately 3%.
- 437 • The crude glycerol sample (vol%): methanol (upper layer) 3.2%, FAME phase (middle  
438 layer) 2.5% and lower layer 87.3% as a mixture of glycerol (80.3 %) and methanol (7%).

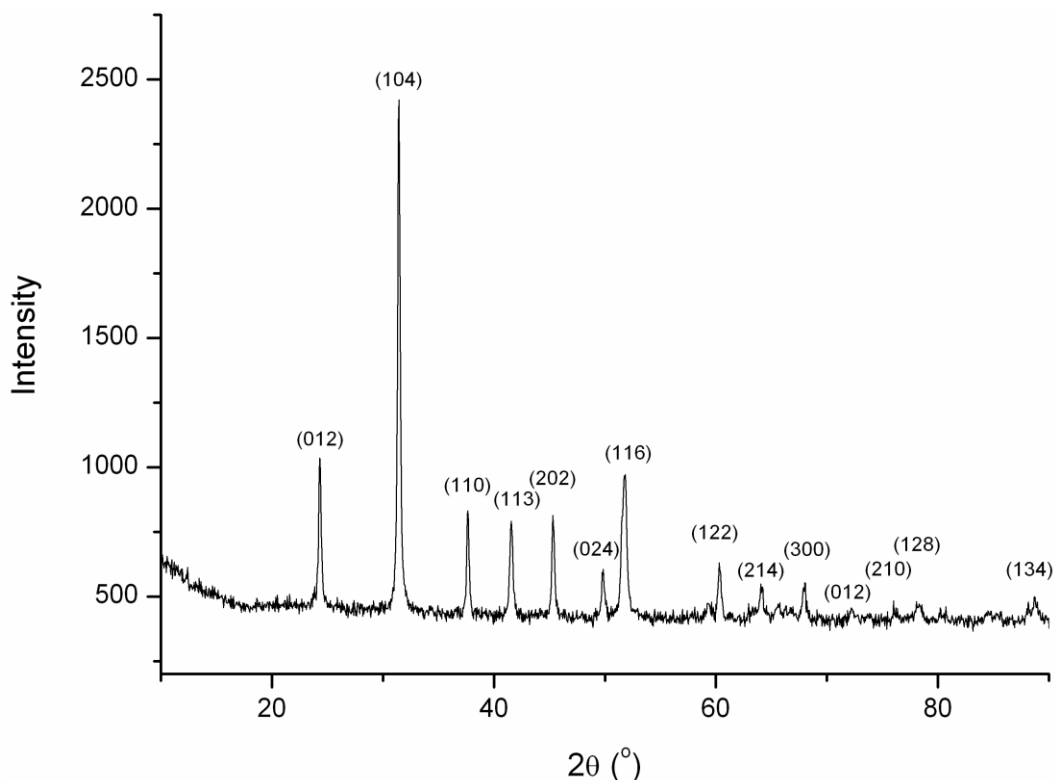
439 Based on this observation, it might be concluded that the final products collected during  
440 the FIRST mass balance contained 30.8 kg of pure ester phase (30.4 kg of FAMEs and 0.4 kg of  
441 DAGs and MAGs), 0.09 kg of methanol and 1.83 kg of glycerol.

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

#### 452 4.1.4. Catalyst deactivation during Pilot Plant experiment

453 During 85 h of the *LT-t*, a small fluctuation of the esters phase composition was  
454 observed. However, there were no enough data to predict exactly the catalyst deactivation during  
455 85 h of its use. The simple calculation, mentioned above based on data collected in the batch  
456 process, indicated that the used amount of  $\text{MnCO}_3/\text{Na-silicate}$  catalyst (10 kg) would be active  
457 for at least 8–9 days of the continuous process and the data of *LT-t* supported this expectation. At  
458 the same time, a gradual increase of the pressure in the PBTR was observed (Fig. 4a). The  
459 pressure should be enhanced for keeping the capacity of the pilot plant at the designed value,  
460 which was attributed to the blocking of the interparticle space with TAGs and the side products  
461 formed at a high temperature as a result of the oil polymerization.

462 For defining the actual status of the used catalyst in the PBTR after the *LT-t*, the samples  
463 were withdrawn from the bottom and the middle part of the PBTR and analyzed by XRD,  
464 TG/DTA and FTIR. Figure 5 shows the XRD pattern of the  $\text{MnCO}_3/\text{Na-silicate}$  sample (washed  
465 and centrifuged with ethanol).

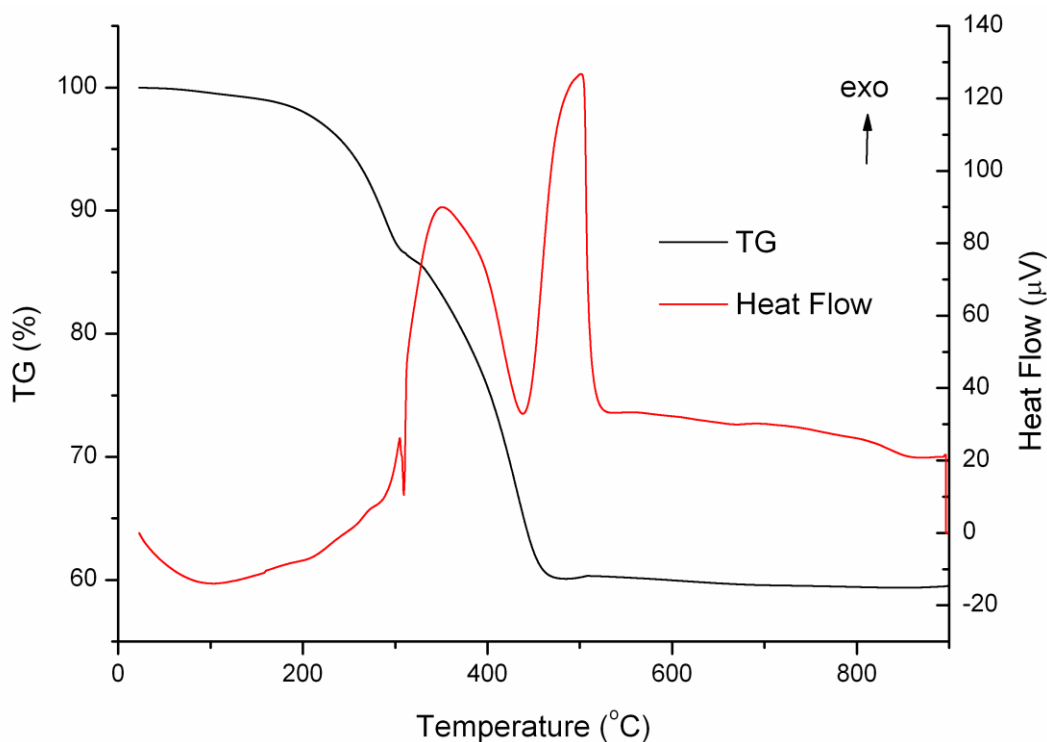


466  
467 **Fig. 5.** XRD pattern of the  $\text{MnCO}_3/\text{Na-silicate}$  catalyst taken from the middle part of the  
468 PBTR after 85 h of the *LT-t* performed at 175 °C and 2.5 MPa.

469 The presence of rhombohedral structure of  $\text{MnCO}_3$  was consistent with the literature  
470 values (JCPDS Card 83-1763). Since the XRD pattern was very similar to the XRD pattern of  
471 the fresh catalyst [9] it was concluded that the catalyst did not undergo any noticeable structural  
472 changes during the 85 h of the *LT-t*.

473 Thermal behavior of the as-taken (without washing)  $\text{MnCO}_3/\text{Na-silicate}$  is shown in Fig.  
474 6.





475

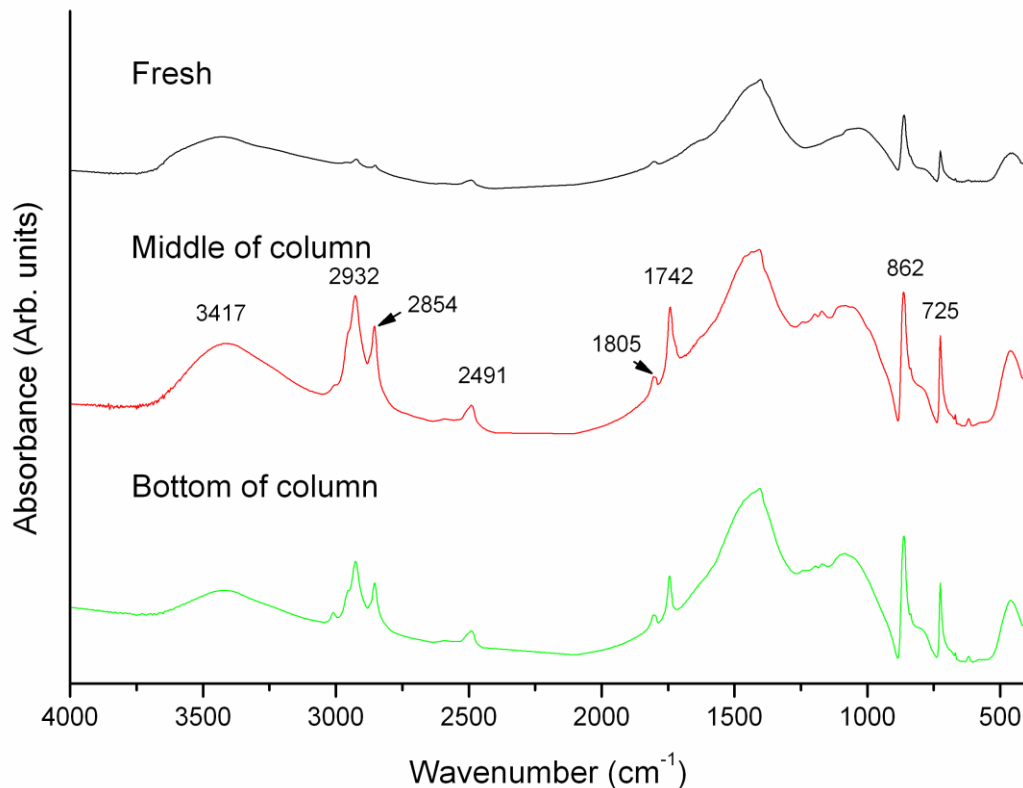
476

477 **Fig. 6.** TG/DTA analysis (heating rate: 20 K/min) of the  $\text{MnCO}_3/\text{Na-silicate}$  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  $\text{MnCO}_3$  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  $3400\text{ cm}^{-1}$  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  $725\text{ cm}^{-1}$  might be assigned to C–H, C–O and C–C functional groups,  
 495 respectively, while the peak at  $862\text{ cm}^{-1}$  corresponded to the bending vibration of  $\text{CO}_3^{2-}$  in  
 496  $\text{MnCO}_3$ .

497 It was found that the absorbance values from the wavelength region of  $3700\text{--}3075\text{ cm}^{-1}$   
 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  $1742\text{ cm}^{-1}$  for the

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

## 504 **5. Conclusion**

505 The pilot plant with the capacity of 100 liters of biodiesel per day was successfully  
506 designed and tested for biodiesel production from soybean oil catalyzed by  $\text{MnCO}_3/\text{Na-silicate}$ .  
507 The kinetic model with the parameters determined based on the analysis of the experiments  
508 realized in batch autoclave at 175 °C and 25 bar over  $\text{MnCO}_3/\text{Na-silicate}$  as a catalyst and taking  
509 into account the influence of temperature and catalyst loading on the apparent reaction rate  
510 constant, was used for the design of PBTR as a main equipment of corresponding pilot plant.

511 Test of continuous operation was used to prove designed capacity and operational  
512 characteristics of pilot plant unit. Investigation was started using PBTR filled only with glass  
513 beads for 11 h, and then, the catalyzed transesterification of soybean oil with  $\text{MnCO}_3/\text{Na-silicate}$   
514 as catalyst was realized during 85 h of continuous operation. Two complete mass balances  
515 performed for detailed examination of the content of produced biodiesel revealed high TAG  
516 conversion (99.8%) and FAME yield over 97.5%, while the sample of used catalyst withdrawn  
517 from reactor after 85 h of continuous process did not show any noticeable structural changes.  
518 The results of the performed tests in pilot plant showed a good starting point for further  
519 experiments planned to be done in order to improve constructed biodiesel production facility and  
520 to test other types of catalysts.

## 521 **Acknowledgements**

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524 Science and Technological Development of the Republic of Serbia.

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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, % ( <i>w</i> , mass 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 <sup>-1</sup>
685	$k_{LT}$	reaction rate constant valid up to 423 K, min <sup>-1</sup>
686	$k_{HT}$	reaction rate constant valid above 423 K, min <sup>-1</sup>
687	$k_{app(w)}$	apparent reaction rate constant as function of catalysts concentration, min <sup>-1</sup>
688	$k_{mt}$	mass transfer coefficient during transesterification process, min <sup>-1</sup>
689	$k_{mt0}$	mass transfer coefficient at the beginning of transesterification process, min <sup>-1</sup>
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

694  $(-r_{TAG})$  rate of triacylglycerols transesterification, mol/(min·L)

695  $t$  time, min

696  $T$  temperature, K

697  $TAG$  triacylglycerols

698  $V$  volume of reaction mixture, L

699  $x_{TAG}$  degree of TAG conversion

700 **Greek symbols**

701  $\alpha$  parameter of kinetic model, Eq. (3b)

702  $\beta$  parameter of kinetic model, Eq. (3b)

703  $\tau$  residence time, min

704