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## Biodiesel synthesis using $K_2CO_3/Al-O-Si$ aerogel catalysts

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**Abstract:** In this study, catalysts for fatty acid methyl esters (FAME or biodiesel) synthesis with  $K_2CO_3$  as the active component on an alumina/silica support were synthesized using the sol–gel method, which was followed by drying the “dense” wet gels with supercritical carbon dioxide to obtain the aerogels. The prepared catalysts were characterized by XRD analysis, FTIR spectroscopy and  $N_2$  physisorption at 77 K, and tested in the methanolysis of sunflower oil. The effects of reaction variables, such as reaction time, temperature and methanol to oil molar ratio, on the yield of FAME were investigated. The aerogel catalysts with  $K_2CO_3$  as the active component on an alumina/silica support exhibited good activity in the methanolysis of sunflower oil. The leaching of potassium when the catalyst was in contact with pure methanol under the working conditions of methanolysis was also tested in this study, indicating that it occurred only at higher temperatures, while at lower ones, it was negligible.

**Keywords:** biodiesel; aerogel; alumina/silica;  $K_2CO_3$ .

### INTRODUCTION

Biodiesel, consisting of FAME, produced by the alcoholysis of vegetable oils or animal fats, is an excellent substitute for conventional diesel fuels. It is non-toxic, biodegradable and made from renewable sources. Increasing biodiesel consumption requires optimized production processes allowing high production capacities, simplified operations, high yields, and the absence of special chemical requirements and wastes. The development of solid catalysts has recently gained much attention because a successful heterogeneous catalyst alleviate most of the economic and environmental drawbacks of a homogeneous process, such as neu-

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tralization of alkali catalysts after reaction and creation of large amount of wastewater produced during washing and separation of the final products.

To date, only one industrial application, developed by the French Institute of Petroleum (IFP), employs heterogeneous based catalysts for the methanolysis of vegetable oils to produce biodiesel.<sup>1</sup> The IFP has announced the construction of further similar industrial plants in Europe based on the use of a heterogeneous catalyst consisting of a mixed oxide of zinc and aluminum with a spinel structure.

On the laboratory scale, many different heterogeneous catalysts have been developed to catalyze the alcoholysis of vegetable oils. Alumina loaded with alkali metal salts or different potassium compounds were demonstrated to be efficient solid-base catalysts.<sup>2</sup> Alumina exhibited no activity, but when loaded with KI, KF, KNO<sub>3</sub>, K<sub>2</sub>CO<sub>3</sub> or KOH and activated at high temperatures, the supported catalyst showed catalytic activities.<sup>3–9</sup> A good activity of K<sub>2</sub>CO<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> xerogel catalyst was previously reported, but undesired leaching of the active components was also observed.<sup>9</sup> Xie and Li<sup>7</sup> reported lower activity of K<sub>2</sub>CO<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> due to its lower basicity compared to other potassium compounds on alumina. Namely, a catalyst with 35 wt. % KI loading on Al<sub>2</sub>O<sub>3</sub> (calcined at 500 °C for 3 h) had the highest basicity and the best catalytic activity. Other catalysts that showed efficiency as heterogeneous catalysts for the alcoholysis of vegetable oil are commercial hydrotalcite,<sup>10</sup> zeolites and modified zeolites<sup>11,12</sup> and Na/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub><sup>13</sup> but they are either quite expensive or complicated to prepare, which has limited their industrial application. At temperature above 250 °C, a high conversion of soybean oil (90 %) was obtained after 20 hours of reaction using WO<sub>3</sub>/ZrO<sub>2</sub>, TiO<sub>2</sub>/ZrO<sub>2</sub> or Al<sub>2</sub>O<sub>3</sub>/ZrO<sub>2</sub> as catalysts.<sup>14,15</sup> The catalytic ability of CaO and MgO was found to be quite weak at lower temperatures, but increasing the reaction temperature had a favorable influence on the methyl ester yield.<sup>16–21</sup> Veljković *et al.*<sup>22</sup> determined 550 °C to be the optimal CaO calcination temperature and studied the kinetics of CaO catalyzed methanolysis. In order to improve the catalytic activity of CaO, it was promoted with Li salts<sup>23,24</sup> or lanthanum,<sup>25</sup> which both increased the basic strength and led to an enhancement of the catalyst activity.

Different techniques have been used for the preparation of catalysts. Sol–gel chemistry was usually applied having many advantages over other methods of catalyst synthesis. It allows control of homogeneity on the nanoscale and results in high surface areas and pore volumes. After dissolution of the reactants in an appropriate solvent and subsequent gelation of the sol, the formed wet gel can be dried using different methods. An available drying method is the extraction of the solvent using the supercritical drying process (SCD), which was performed in this study. Namely, supercritical drying preserves the original gel structure by eliminating capillary pressure while, at the same time, the solvent and sol–gel reaction byproducts present in the gel pores are extracted at a temperature and pres-

sure higher than the critical temperature and pressure of the solvent, thereby producing a material known as an aerogel.<sup>26</sup> Supercritical drying can also be realized using another supercritical extracting fluid with moderate values of the critical parameters (commonly carbon dioxide). Due to their unique morphological and physicochemical properties, aerogels are being widely studied for potential applications in heterogeneous catalysis.<sup>27</sup>

In this study, a new type of heterogeneous catalyst with  $K_2CO_3$  as the active component on an alumina/silica support was synthesized using the sol-gel method, which was followed by drying the wet gel with supercritical carbon dioxide. The characteristics of the obtained aerogels and their activity in the methanolysis reaction were studied. The activity of the prepared aerogel catalysts was tested in the methanolysis of sunflower oil and the efficiency of process at different temperatures (80–200 °C) and molar ratios of methanol to oil (6:1–30:1) was also analyzed. Eventual leaching of  $K_2CO_3$  from the catalyst would reduce the activity of the catalyst and decrease its activity in the second repeated process of methanolysis. For this reason, the leaching of potassium on contact of the catalyst with pure methanol under working conditions of methanolysis was also tested in this study.

## EXPERIMENTAL

### *Catalyst preparation*

The catalysts were synthesized by a one-step sol-gel procedure. Aluminum tri-*sec*-butoxide, tetraethoxy orthosilane (TEOS), 1-butanol, anhydrous potassium carbonate (all Fluka) were used as reagents. Aluminum tri-*sec*-butoxide (29.1 g, 0.120 mol) was mixed with 1-butanol (200 cm<sup>3</sup>) and then TEOS (8.32 g, 0.0400 mol) was added. The mixture was stirred vigorously and heated to 70 °C for 5 min until a clear solution was obtained. The solution was cooled to room temperature and then hydrolyzed with water (37.5 cm<sup>3</sup>, 2.08 mol) containing dissolved potassium carbonate (2.86 g; 0.0210 mol). The solution was stirred for 15 min and left to stand overnight (gelation). Water and a certain amount of 1-butanol (excess) were then removed by heating the gel to 150 °C, and a “dense” wet gel was obtained. The above procedure describes the wet gel synthesis of samples with ratio Al/Si = 3/1 and an amount of  $K_2CO_3$  which was calculated to be 45 wt. % based on the support.

Aerogels were obtained by drying the “dense” wet gels with supercritical carbon dioxide in a previously described 300 cm<sup>3</sup> tubular extractor, Autoclave Engineers SCE Screening System.<sup>28</sup> During the supercritical drying, the extractor was filled with liquid CO<sub>2</sub> at the beginning of drying process, then the pressure was increased above the critical value for CO<sub>2</sub> and finally the temperature was raised to the desired value. After reaching the working conditions of pressure and temperature, the flow of CO<sub>2</sub> was maintained and kept constant at about 100 g CO<sub>2</sub>/h. This procedure was necessary to avoid the presence of two CO<sub>2</sub> phases of in the extractor. The duration of the SCD depended on the employed drying conditions. The parameters of sol-gel synthesis and gel drying are presented in Table I, together with the experimental conditions used for calcination of the prepared catalysts (four samples defined as AG1–AG4).

TABLE I. The experimental conditions for the SCD process performed at 100 bar

Condition	AG1	AG2	AG3	AG4
Drying temperature, °C	40	40	200	200
Duration of SCD, h	9	9	5	5
Total consumption of CO <sub>2</sub> , kg	0.9	0.9	0.5	0.5
Temperature of calcinations, °C ( <i>t</i> = 12h)	600	300	600	300

#### Catalyst characterization

The XRD measurements were performed on a Philips PW1710 powder X-ray diffractometer using Cu K $\alpha$  radiation, over the  $2\theta$  range 4–90 ° in the scan mode (step size 0.02°, counting 0.5 s per step).

The nitrogen adsorption–desorption isotherms were determined using a Sorptomatic 1990 Thermo Electron instrument at –196 °C. All samples were degassed at 120 °C for 12 h under reduced pressure (< 1 torr) prior to the sorption measurements. Various models and appropriate software – ADP, Thermo Electron, version 5.1, were used to analyze the obtained isotherms. The specific surface area of samples ( $S_{\text{BET}}$ ) was calculated according to the Brunauer, Emmett, Teller (BET) method from the linear part of the nitrogen adsorption isotherms.<sup>29</sup> The total pore volume ( $V_{\text{tot}}$ ) was taken at  $p/p_0 = 0.998$ . The mesopores volume and pore size distribution was calculated according to the Barrett, Joyner and Halenda method from the desorption branch of the isotherm.<sup>30</sup> The micropores were analyzed using the Dubinin–Radushkevich method.<sup>31</sup>

The Fourier-transform infrared (FTIR) spectra were recorded in the transmission mode using a BOMEM (Hartmann & Braun) spectrometer. All measurements were conducted at room temperature in the wave number range 400–4000 cm<sup>-1</sup>, with a 2 cm<sup>-1</sup> resolution.

#### Methanolysis reaction

Synthesized catalysts were tested in the methanolysis of sunflower oil. Commercial edible sunflower oil (Sunce, Sombor, Serbia) was used for the experimental studies. The experiments were performed in a 300 cm<sup>3</sup> batch autoclave (Autoclave Engineers, Country), equipped with an electrical heater and a mixer. Prior to the reaction, the catalyst samples (fraction <500  $\mu\text{m}$ ) were activated by heating in an oven at 120 °C for 2 h. The preliminary tests of the activity of the prepared aerogel catalysts (AG1–AG4; 2 wt. % catalyst based on the oil) were realized at 200 °C and 37 bar using an agitation speed of 400 rpm and a molar ratio of sunflower oil to methanol of 1:30. The pressure in the autoclave was resulted from the vapor pressure methanol at the working conditions. The time when the reaction temperature was achieved was taken as zero reaction time. Reaction samples were withdrawn periodically, without stopping of the reaction, and after filtration and separation of the residual methanol using a rotational evaporator, the samples were analyzed by gas chromatography (Varian 3400; FID detector, a fused silica capillary column 5 m $\times$ 0.53 mm, film thickness 0.5  $\mu\text{m}$  and an on-column injector). Quantitative analysis of FAME was realized using correction factors for FAME, tri-, di- and monoglycerides and glycerol. The calculated correction factors were used for calculating the mass percentage of FAME. The catalyst sample AG2 was used to study the influence of different working conditions (temperature, ratio of methanol to oil) on the synthesis of FAME.

The leaching of potassium from the catalyst was tested by contacting catalyst AG2 with methanol for 2 h at 120 °C, and then the methanol solution after filtering to remove solids was used in the reaction with vegetable oil.

## RESULTS AND DISCUSSION

*Catalyst characterization*

X-Ray diffraction analysis was conducted to investigate the structure and crystallinity of the catalysts. The XRD patterns of the aerogels presented no sharp diffraction peaks. A similar effect was observed and recently reported in literature.<sup>9</sup> This fact indicated that the synthesized catalysts were amorphous, regardless of the preparation procedure. The XRD pattern for aerogel AG2 is presented in Fig. 1.

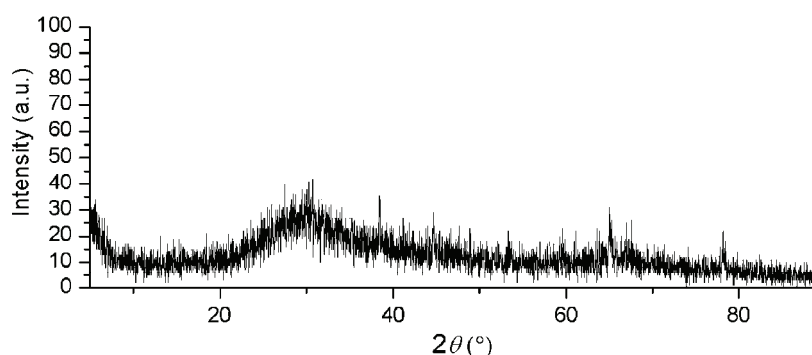


Fig. 1. XRD Pattern for aerogel AG2.

The measured BET surface area, the volumes of the mesopores and micropores, the overall pore volume,  $D_{max}$ , the pore diameter where the maximum of the derivative cumulative volume curve is reached, and  $D$ , the average pore diameter, are given in Table II, and the pore size distribution in Fig. 2.

TABLE II. Textural properties of the catalysts

Catalyst	$S_{BET} / m^2 g^{-1}$	$V_{tot} / cm^3 g^{-1}$	$V_{meso} / cm^3 g^{-1}$	$V_{mic} / cm^3 g^{-1}$	$D_{max} / nm$	$D / nm$
AG1	114	0.225	0.182	0.039	3.808	4.925
AG2	107	0.144	0.137	0.036	3.764	3.838
AG3	122	0.206	0.202	0.042	3.734	4.979
AG4	113	0.175	0.172	0.035	3.786	4.427

The results of the BET analyses indicated that the synthesized catalysts were mesoporous, while the  $D_{max}$  values were similar around 3.8 nm and the  $D$  values were between 3.8 and 4.9 nm. The aerogel AG2 had a value of  $D_{max}$  very similar to that of  $D$ , which means that the sizes of all pores were equally distributed around  $D_{max}$ . A very slight shift of the pore sizes to larger pore diameters was observed for the other 3 catalysts. When calcination of the prepared catalysts was realized at higher temperature (AG1 and AG3), a slightly larger surface area and pore volume was observed than for aerogels AG2 and AG4. The BET analysis

indicated that the different SCD conditions had only a moderate influence on the porous structure of the prepared aerogels.

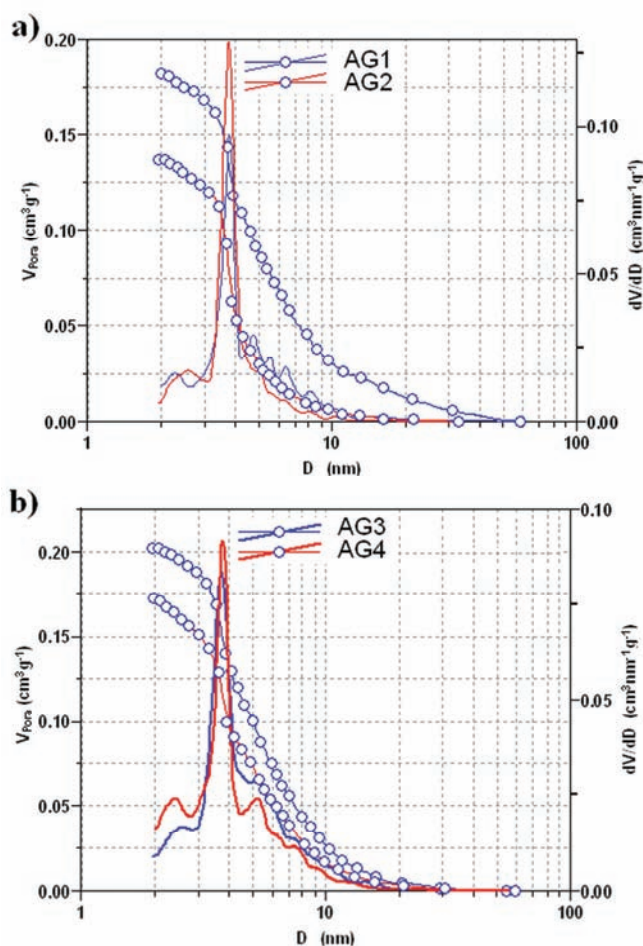


Fig. 2. Pore size distribution of the catalysts a) AG1 and AG2; b) AG3 and AG4.

As can be seen from Fig. 2 and Table II, the major part of the catalyst volume was occupied by pores with an average diameter of 3.8–4.9 nm, which is common for samples of aerogels. According to Fernandez *et al.*,<sup>34</sup> the critical diameter of the triglyceride molecule, defined as the diameter of the smallest cylinder through which the molecule can pass without distortion, is around 2 nm; Lopez Granados *et al.*<sup>19</sup> reported that methyl oleate has a diameter around 2.5 nm, and the diameter of triglycerides is certainly at least two times larger. A number of studies showed that restricted diffusion, which transpires when the dimensions of the reactant molecule and the pore are comparable, occurs in silica–

–alumina catalysts with pore diameters less than 5 nm.<sup>35</sup> For a narrow pore catalyst (mean pore diameter  $\approx$  4 nm), a 50 % decrease in catalytic activity relative to the activity of a catalyst with medium ( $d \approx$  6 nm) and wide pore ( $d \approx$  8 nm) size could be expected.<sup>36</sup> The problem of the access of the voluminous triglycerides molecules to the active sites within the pores of a catalyst were calculated for a xerogel catalyst taking into account the mean pore size diameter (3.8 nm) and the dimensions of the triglycerides molecule and the results indicated that internal diffusion resistance obviously exists.<sup>9</sup> Taking into account that space occupation by triglyceride could be represented by 5 nm in diameter,<sup>19</sup> which is larger than the pore diameter, molecules of triglycerides obviously cannot easily diffuse through the pores of the major part of the catalyst and that efficient contact between reactant and active site is mainly possible only on the external surface of the catalyst.

FTIR Spectra of the catalyst samples are shown in Fig. 3. The characteristic bands are: a band at about  $1000\text{ cm}^{-1}$ , attributed to the Si–O stretching vibration; a band at around  $460\text{ cm}^{-1}$ , attributed to Si–O bending;<sup>37,38</sup> bands in the range  $500\text{--}700\text{ cm}^{-1}$ , attributed to octahedral Al–O, and  $700\text{--}900\text{ cm}^{-1}$ , attributed to tetrahedral Al–O.<sup>39</sup> The shift of the absorption band of Si–O stretching from  $1000\text{ cm}^{-1}$  to lower wavenumbers indicates the presence of Al–O–Si bonds in the investigated samples and the intensity of the shifting indicates the level of mixing of Al and Si in the alumina/silica network.<sup>38</sup> The band at about  $3430\text{ cm}^{-1}$  is associated with stretching vibrations due to OH groups of water molecules adsorbed onto the surface of the catalyst but, according to Xie and Li<sup>7</sup>, this band could be partly assigned to the stretching vibrations of Al–O–K groups. Another band associated with the presence of water is located at  $1635\text{ cm}^{-1}$ .<sup>40</sup> Supported  $K_2CO_3$  and bulk  $K_2CO_3$  give slightly different absorption bands.<sup>41</sup> Bands at

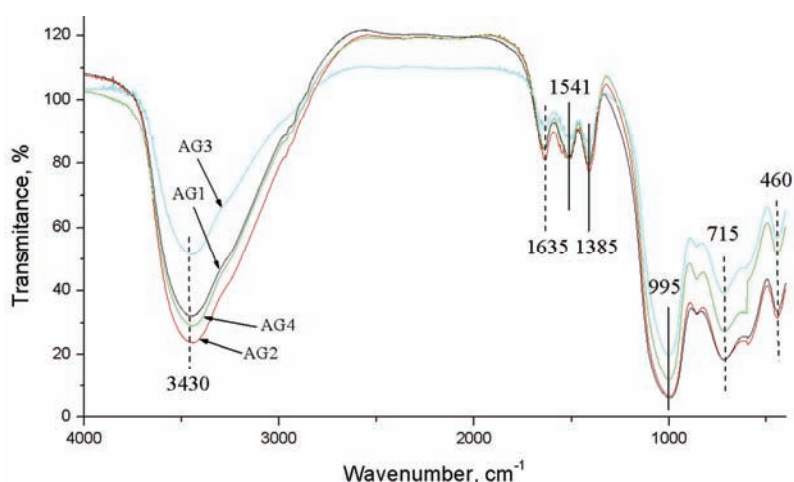


Fig. 3. FTIR Spectra of prepared catalysts.

1541 and 1385  $\text{cm}^{-1}$  were observed for all catalyst samples and are attributed to carbonate species,<sup>41,42</sup> whereby the band at 1385  $\text{cm}^{-1}$  indicates the presence of bulk  $\text{K}_2\text{CO}_3$ ,<sup>41</sup> the part of the catalyst which is the main reason for its activity.<sup>9</sup>

#### *Influence of various parameters on the yield of FAME*

Yield of FAME achieved in the methanolysis reaction is shown in Fig. 4. As can be seen, all the prepared aerogel catalysts with  $\text{K}_2\text{CO}_3$  as the active component showed very good catalytic activity, with yields of FAME over 90 % after 15 min in the batch process for all catalysts except for AG1, which expressed a slightly lower activity. All four aerogels had very similar textural and structural characteristics and the only difference observed for AG1 which could be the explanation for the lower activity is its smaller fraction of mesopores in the total pore volume.

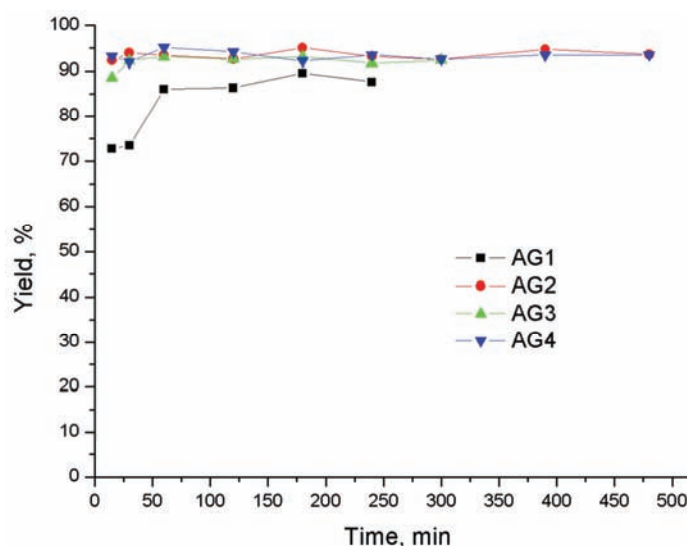


Fig. 4. Effect of reaction time on the yield of FAME synthesized at 200 °C and under 37 bar, using a molar ratio of methanol:oil = 30:1 and 2 wt. % of catalyst based on oil.

The influence of the reaction temperature on the yield of FAME in the methanolysis performed using catalyst AG2 is shown in Fig. 5. The rate of the methanolysis reaction of the vegetable oil was strongly influenced by the reaction temperature and the yield of FAME increased with increasing temperature. At the lower temperature (80 °C), several hours were necessary to achieve the desired high yield of FAME. However, in the batch process at 120 °C, approximately 92 % conversion of the triglycerides giving the desired yield of FAME could be achieved after 15 min of methanolysis.



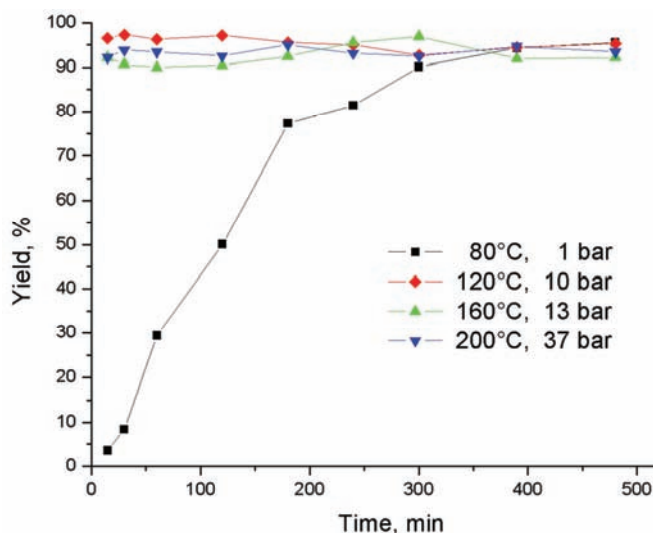


Fig. 5. Influence of reaction temperature on the yield of FAME, using a methanol to oil molar ratio of 30:1 and 2 wt. % of catalyst sample AG2 (based on oil).

The molar ratio of methanol to vegetable oil is also a very important parameter which affects the conversion of triglycerides to methyl esters. The influence of the molar ratio was examined in the methanolysis of sunflower oil with aerogel AG2 at 120 °C using 2 wt. % of catalyst based on oil and the obtained results are shown in Fig. 6.

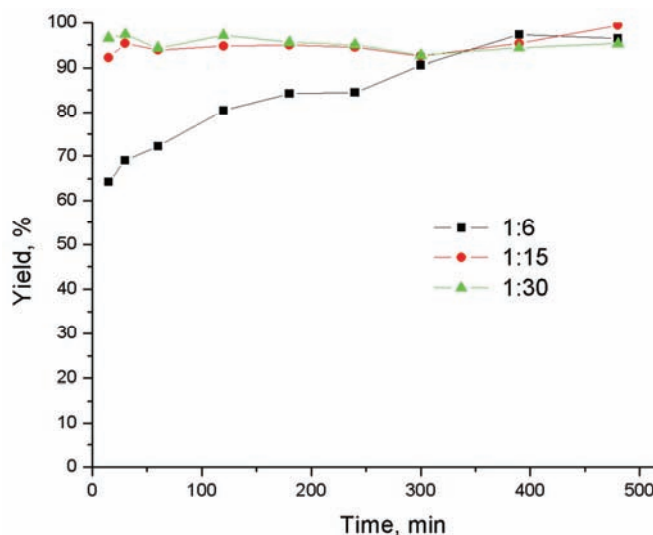


Fig. 6. Influence of the methanol to oil molar ratio on the yield of FAME at 120 °C and with 2 wt. % of catalyst sample AG2 (based on oil).

Stoichiometrically, the methanolysis of vegetable oil requires three moles of methanol for each mole of oil. However, in practice a higher molar ratio is employed in order to shift the reaction equilibrium towards the products side and produce more methyl esters. As shown in Fig. 6, the syntheses realized with larger methanol to oil ratios (15:1 and 30:1) were followed by higher rates of the methanolysis reaction and, thus, the desired high conversions of the triglycerides were observed in shorter times. According to the results of this study, it can be concluded that a molar ratio of methanol to oil of 15:1 was sufficient for a good yield of FAME to be achieved in a relatively short reaction time.

The obtained results were compared to the catalytic activity of a  $K_2CO_3/Al-O-Si$  xerogel (2 wt. % based on oil)<sup>9</sup> used for the methanolysis of sunflower oil at 120 °C with a methanol to oil molar ratio of 15:1. The comparison indicated that the applied drying process gave a catalyst with similar activity.

A kinetic model for the reaction between methanol and triglycerides was determined assuming that a first order irreversible reaction could be used for the prediction the yield of FAME. Simultaneously, solution of the energy and mole balances were realized for a batch, non-isothermal process using Polymath software and the results of the calculation together with the experimentally determined FAME content in the reaction mixture are presented in Fig. 7. The model was described in detail and the parameters defined by Glišić *et al.*<sup>43</sup> As can be seen, this model fits well the experimental data for the performed methanolysis of triglycerides using the studied aerogel catalyst.

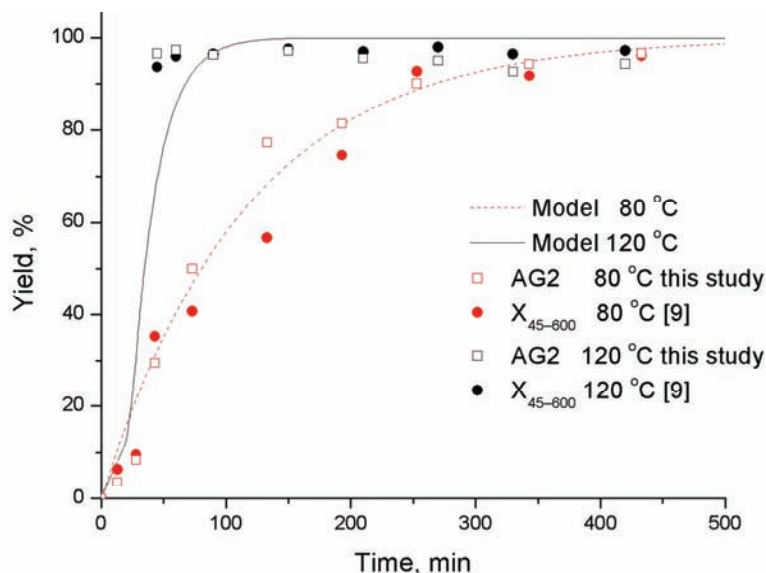


Fig. 7. Comparison of the experimental and simulated data.

An additional experiment was performed to check whether leaching of the active phase from aerogel catalyst occurred. The activated catalyst was placed in contact with methanol for 2 h at 120 °C, filtered to remove the solids and then the vegetable oil was placed in contact with the clear methanol solution. The yield of FAME was 43.9 %, after 2 h at 120 °C, indicating that leaching of some amount of active phase had occurred.

The amount of leached potassium carbonate in methanol was measured and the results are shown in Table III. The potassium content at higher temperature is quite high, as expected – 210 mg/l when 120 °C was reached and 390 mg/l after 2 h at 120 °C, confirming that at this temperature the aerogel used in the reaction of triglyceride methanolysis showed activity which could be mainly contributed to the effect of homogeneous–heterogeneous catalyst. However, at temperatures below 100 °C, the leaching of potassium species was negligible with only 7 mg/l. This fact is very important because a high yield could be also achieved at 80 °C but after a longer time of reaction (Fig. 5). Finally, according to these investigations, it can be concluded that at lower temperatures, 100 °C or below, the prepared aerogel catalyst acted as a heterogeneous one.

Table III. Determined amount of K in methanol at different temperatures

Temperature, °C	K amount, mg/l
60	4
100	7
120	210
120 (after 2 h)	390

### CONCLUSIONS

The experiments performed in this study showed that the synthesized aerogel catalysts with potassium carbonate as the active component on an alumina/silica support are very active in the methanolysis of sunflower oil. It was also shown that leaching of some amount of potassium species to the methanol phase during FAME synthesis occurred when the reaction was performed at 120 °C, but when the temperature was below 100 °C, the leaching was negligible and, thus, the catalyst acts as a heterogeneous one under such conditions.

The analysis of different working conditions indicated that the temperature of the reaction and methanol:oil molar ratio mainly affected the reaction rate of methanolysis. Although at 120 °C with a methanol:oil molar ratio of 15:1 a yield of over 92 % was achieved after 15 min, the performed investigation of the catalytic activity of  $K_2CO_3$ /(alumina–silica support) showed that at lower temperatures, a heterogeneously catalyzed methanolysis of triglycerides was possible and that similar conversion of the triglycerides could be achieved but after a longer reaction time.

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## ИЗВОД

СИНТЕЗА БИОДИЗЕЛА КАТАЛИЗОВАНА АЛУМОСИЛИКАТНИМ АЕРОГЕЛОМ СА  $K_2CO_3$ ИВАНА ЛУКИЋ<sup>1</sup>, ЈУГОСЛАВ КРСТИЋ<sup>2</sup>, САНДРА ГЛИШИЋ<sup>1</sup>, ДУШАН ЈОВАНОВИЋ<sup>2</sup> И ДЕЈАН СКАЛА<sup>1</sup><sup>1</sup>Технолошко–металуршки факултет, Карнегијева 4, 11000 Београд и <sup>2</sup>Институт за хемију, технологију и металургију, Центар за катализу и хемијско инжењерство, Нjegoшева 12, 11000 Београд

У овом раду катализатор за синтезу метил естара масних киселина (МЕМК или биодизел) са  $K_2CO_3$  као активном компонентом на алумосиликатном носачу синтетизован је сол–гел методом након чега је добијени гел сушен уз присуство наткритичног угљен диоксида да би се добио аерогел. За карактеризацију синтетизованих катализатора коришћене су методе XRD, FTIR и  $N_2$  физисорпција на 77 К и катализатори су тестирани у реакцији метанолизе сунцокретовог уља. Катализатор је тестиран у реакцији метанолизе сунцокретовог уља и синтези МЕМК. Испитан је утицај различитих параметара као што су време, температура и моларни однос метанол:уље на принос МЕМК. Аерогел катализатор са  $K_2CO_3$  као активном компонентом на алумосиликатном носачу показао је добру каталитичку активност у реакцији метанолизе сунцокретовог уља. Излуживање калијума у контакту са метанолом на радним условима метанолизе такође је тестирано у овом раду, показујући да оно постоји на вишим температурама, док је на нижим занемарљиво.

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