

## Glycerol Acetal Ester as Biofuel Additive

Elena-Emilia Oprescu\*, Dorin Bomboș\*, Steliana Cristea\*,  
Cătălina Călin\*, Emil Stepan\*\*, Ion Bolocan\*

\* Universitatea Petrol-Gaze din Ploiești, bd. București,39, Ploiești  
e-mail: oprescuemilia@gmail.com

\*\* Institutul Național de Cercetare-Dezvoltare pentru Chimie și Petrochimie – ICECHIM,  
Spl. Independenței, nr. 202, București

### Abstract

*This study presents glycerol valorization as biofuel additive. The additive based on glycerol was obtained in two steps: first step: glycerol condensation with n-butanol over solid superacid catalyst  $SO_4^{2-}/SnO_2$  and second step: transesterification of obtained glycerol acetal with methyl propionate. The effect of various reaction parameters on catalytic performance were studied. The influence of glycerol acetal ester on the quality parameters of diesel fuel was tested.*

**Key words:** glycerol, diesel, superacid, bio-additive

### Introduction

Glycerol is produced at a large amount as a byproduct or waste stream from biodiesel production via transesterification reactions. The biodiesel production generates approximately 10% of glycerol by volume [1]. A lot of work has been devoted to the transformation of glycerol by various catalytic processes involving reforming, oxidation, hydrogenolysis, etherification and esterification [2, 3]. Acetalization of glycerol is one of the methods considered to be promising and economically viable for the utilization of glycerol [4]. In this process, glycerol reacts with an aldehyde or a ketone to form an acetal or a ketal, respectively. The addition of cyclic acetals/ketals to standard diesel fuel improves pour point properties [5] and reduces emission [6]. The commercial catalysts used in glycerol acetalization reaction are  $H_2SO_4$ , HF, HCl,  $H_3PO_4$  or p-toluene sulphonic acids [7-9]. However, catalysts mentioned above presents disadvantages in handling, storage and disposal, because of their toxic and corrosive. In this sense, sulfated metal oxides appear to be promising catalysts offering several advantages, since they are stable, regenerable and active over a wide range of temperatures [5, 6, 10].

In this work, the glycerol acetal ester was obtained in two steps: first step: glycerol condensation with n-butanol over solid superacid catalyst  $SO_4^{2-}/SnO_2$  and second step: transesterification of obtained glycerol acetal with methyl propionate. In order to achieve the optimal reaction conditions for the glycerol acetal synthesis, the influence of different amounts of catalyst, mole ratios of reactants and reaction time on the yield of product was investigated. For the transesterification reaction of glycerol acetal/ketal the optimal parameters were established in a previous article [6].

## Experimental Procedure

### Catalyst preparation

The catalyst  $\text{SO}_4^{2-}/\text{SnO}_2$  was prepared using the co-precipitation method [5, 11]. In a typical procedure, stannous chloride (Fluka, AR grade) was dissolved in water under stirring. Aqueous ammonium hydroxide was gradually added into this solution until pH reach 8. The obtained precipitate was filtered, washed with distilled water until free from chloride ions and dried at 110 °C for 12h. The dried hydroxide powder was then equilibrated with 1 N  $\text{H}_2\text{SO}_4$  (5 mL/g) and sonicated under reduced pressure for 10 min. After filtration the solid was dried again and calcined in air at 500 °C for 4 h.

### Catalyst characterization

The XRD measurements were carried out using a Bruker D8 Advance, X-ray diffractometer with  $\text{CuK}\alpha$  radiation ( $\lambda_{\text{Cu}} = 1.5406 \text{ \AA}$ ) operating at a voltage of 40 kV and a current of 40 mA. Data were collected in  $2\theta$  range from 20° to 80°, with a scanning rate of 0.02 deg.min<sup>-1</sup> at room temperature. The FT-IR measurements were performed with a Tensor 27 FT-IR Spectrometer Bruker using KBr technique. Thermogravimetric analysis of the compounds was recorded in a TGA/SDTA 851Mettler Toledo in the temperature range 25-800 °C. The total acidity of the solid samples was measured by thermogravimetric analysis of adsorbed n-butylamine [5].

### Glycerol condensation with n-butyraldehyde

The catalytic experiments were carried out in a 100 mL three-neck round-bottom flask equipped with a mechanical stirrer, thermometer and a Dean-Stark apparatus. In a typical run, the composition of reaction mixture containing in 36.8g glycerol, 0.92 g  $\text{SO}_4^{2-}/\text{SnO}_2$ , 2.88 g n-butanal and 18 g benzene was mechanical stirred at atmospheric pressure and heated to reflux. After the reaction was completed the catalyst was filtrated and the reaction mixture was submitted to distillation at atmospheric pressure to remove solvent and n-butanal excess. Crude glycerol acetal was purified by vacuum distillation. The GC/MS/MS analysis indicated a chromatographic purity over 99% (fig. 1). For simplicity, the four isomers obtained will be referring as one compound.

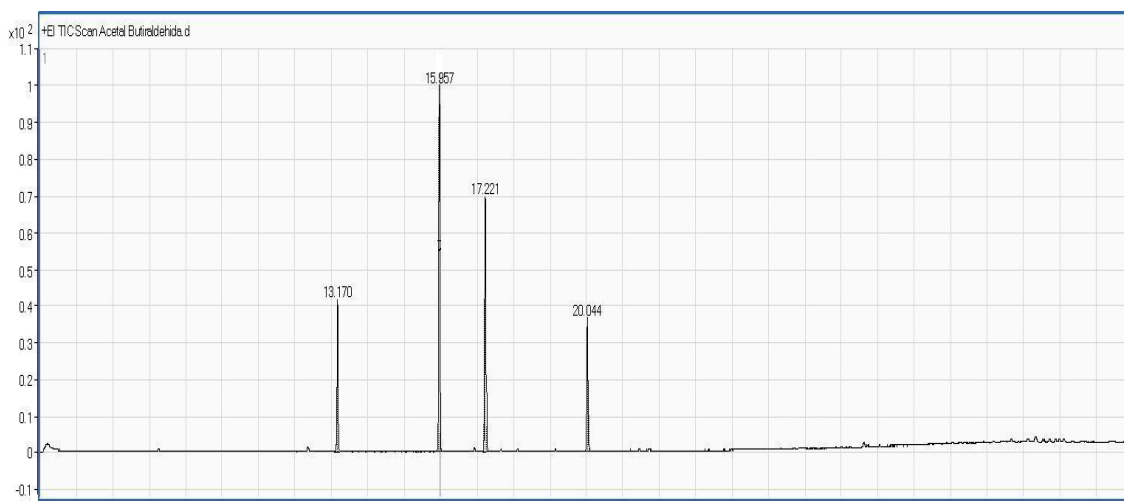


Fig. 1. GC-MS/MS analysis of glycerol butanal

## Transesterification of glycerol butanal acetal with methyl propionate

The method used to synthesize glycerol butanal propionate is described into previous papers [5, 6]. The GC/MS/MS analysis of distilled product indicated a chromatographic purity over 95% (fig. 2).

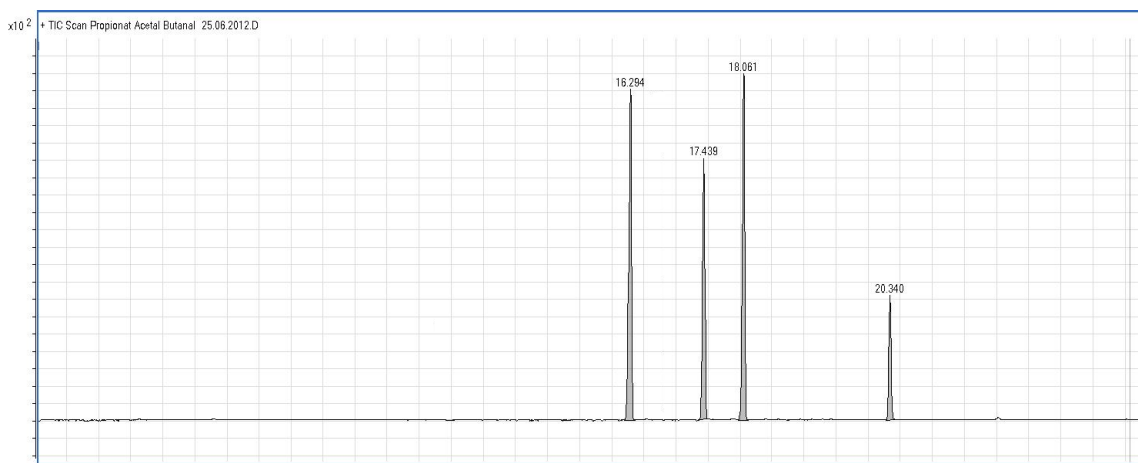


Fig. 2. GC-MS/MS analysis of glycerol butanal propionate

## Analysis of products

The reaction products were analyzed by a GC-MS/MS TRIPLE QUAD (Agilent 7890 A) with DB-WAX capillary column (30 m length, 0.25 mm internal diameter, 0.25  $\mu\text{m}$  film thickness) and helium a carrier gas at 1 mL/min. The temperature program was as follows: 70  $^{\circ}\text{C}$ , 5  $^{\circ}\text{C}/\text{min}$  up to 220  $^{\circ}\text{C}$ , hold time of 5 min. The GC injector and MS ion source temperatures were 250  $^{\circ}\text{C}$  and 150  $^{\circ}\text{C}$ , respectively. The transfer line temperature was 280  $^{\circ}\text{C}$ . The MS detector was operated in EI mode at 70 eV, with a m/z scanning range of 50–450 [5,6].

## Diesel blends characterization

The European standards used for diesel blends characterization were: EN ISO3104 (kinematic viscosity (40  $^{\circ}\text{C}$ )), EN ISO 3016 (pour point), EN ISO 2719 (flash point) and EN ISO 3675 (density at 15 $^{\circ}\text{C}$ ).

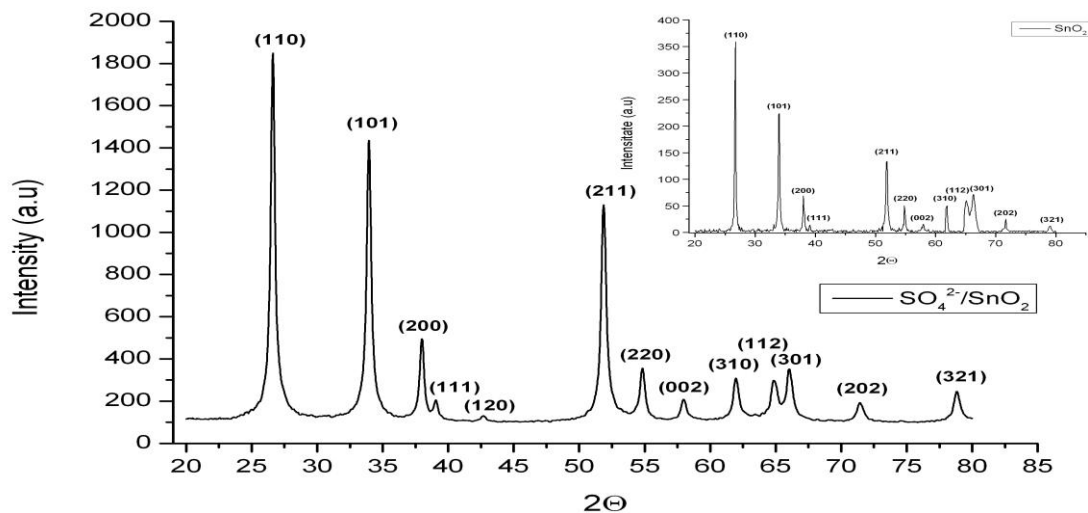
## Results and Discussion

### Catalyst characterization

Figure 3 shows XRD patterns of sulfated tin oxide and tin oxide [5]. All samples display the following plans 110, 101, 200, 211, 220, 002, 310, 112, 301, 202, and 321 which are characteristic of pure  $\text{SnO}_2$  phase with tetragonal lattice (JCPDS no. 41-1445). Moreover, no other peaks of metallic tin and other tin oxides were observed. The synthesis of pure tetragonal  $\text{SnO}_2$  phase is very important for the formation of strong acidic sites in sulfated tin oxide [5, 12].

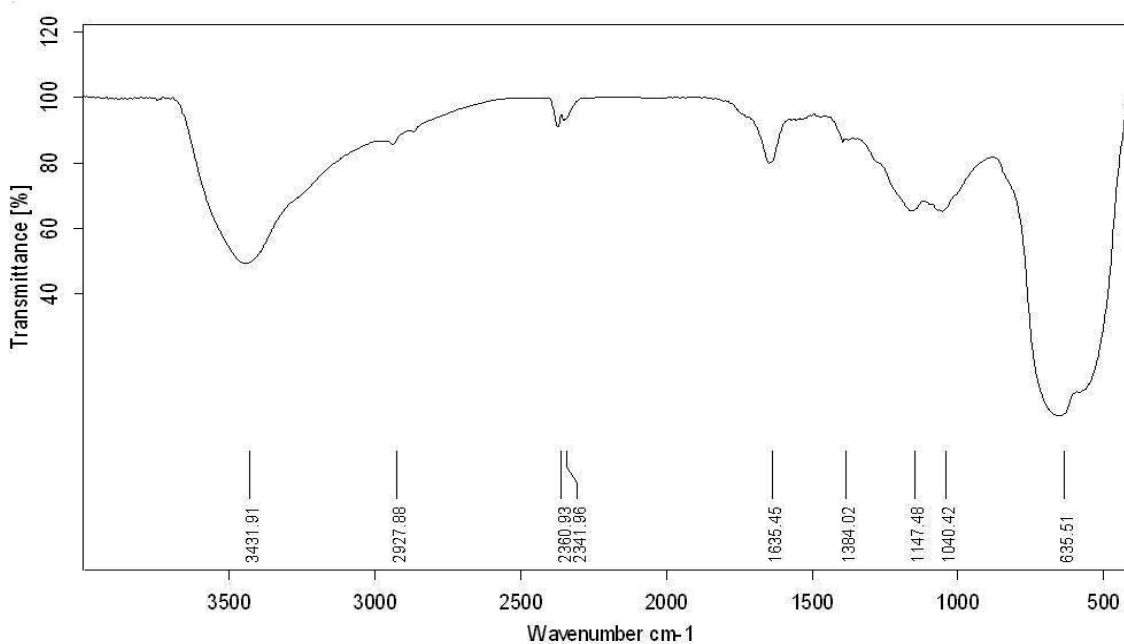
In order to study the effect of sulfate content on the crystallization degree, the crystallite size was calculated for the most intense peak at  $2\theta$  of 26.63 (101). The values obtained show a

noticeable decrease in crystallite size from 174.09 Å for SnO<sub>2</sub> to 29.33 Å for SO<sub>4</sub><sup>2-</sup>/SnO<sub>2</sub>. This decrease can be explained by the fact that, during calcination the sulphate groups remains bound to the support surface inhibiting the growth of crystallites. This observation is consistent with the literature data [5, 13].



**Fig. 3.** X-ray diffraction patterns of SO<sub>4</sub><sup>2-</sup>/SnO<sub>2</sub> and SnO<sub>2</sub>

The FT-IR spectrum of SO<sub>4</sub><sup>2-</sup>/SnO<sub>2</sub> is presented in Fig. 4. As can be seen, SO<sub>4</sub><sup>2-</sup>/SnO<sub>2</sub> exhibit 2 typical bands between 1147 and 1040 cm<sup>-1</sup> associated with the vibration of sulfate anions. The characteristic band of sulfate promoted superacids is recorded at 1384 cm<sup>-1</sup> [14]. The broad absorption peak at 3431 cm<sup>-1</sup> and the sharp one at 1635 cm<sup>-1</sup> are assigned with the vibrations of the water molecules on the surface of the solid. The band around 635 cm<sup>-1</sup> is due to the vibrations of Sn-O-Sn bonds [5, 15].



**Fig. 4.** FT-IR spectra of SO<sub>4</sub><sup>2-</sup>/SnO<sub>2</sub>

The TG analysis of sulfated tin oxide exhibits two weight-loss steps: the first step from 25 to 355 °C is associated with water desorption, while the second step between 356 and 800 °C is attributed to the decomposition of sulfate species on the sample [16]. These results are similar with the literature data [5, 17]. The total acidity of the solid sample was measured by thermogravimetric analysis of adsorbed n-butylamine. The obtained data are: 45.10 % weak acid site and 54.90 % intermediate and strong acid sites. The total number of acid sites expressed as mmol n-butylamine/g catalyst is 1.06.

### Optimization of glycerol acetal ester synthesis

To determine the optimal parameters for glycerol acetal, the following three impact factors were studied: the influence of different amounts of catalyst, mole ratios of reactants and reaction time. The first step, glycerol acetalisation with n-butanol was realized using different amounts (from 0.5 to 3.5 wt. %, with respect to glycerol) of  $\text{SO}_4^{2-} / \text{SnO}_2$  superacid catalyst. From the obtained results (Table 1) it can be observed that the yield increased with the increasing of catalyst amount, reaching the maximum value at 2.5 wt.% catalyst, probably due to the increasing of total number of available acid sites. A higher growth catalyst mass does not significantly influence the yield. The influence of reaction time on the glycerol acetal yield has a continuously increasing trend (Table 1.). The experiments were performed at different time periods between 0.5 h and 3 h. The glycerol acetal yield reached its maximum value of 96.83 % after 2 h. Afterwards, there was no considerable change in the glycerol derivative yield. The results of acetalization of glycerol with various n-butanol molar ratio indicates that an excess of carbonyl compound enhances the glycerol acetal yield. This behavior can be attributed with the occupancy of carbonyl compound over the active sites and the availability of alcohol molecules for further ketalisation [18]. For the transesterification reaction of glycerol acetal the optimal parameters were established in a previous article [6].

**Table 1.** Parameters optimization of glycerol condensation with n-butanol

Time reaction (h)	Catalyst loading (wt.% of glycerol)	Molar ratio glycerol: n-butanol	Glycerol butanol yield (%)
0.5	2.5	1.10	64.21
1	2.5	1.10	81.76
2	2.5	1.10	96.83
3	2.5	1.10	96.91
2	0.5	1.10	66.86
2	1.5	1.10	89.65
2	2.5	1.10	96.83
2	3.5	1.10	96.60
2	2.5	1.05	90.20
2	2.5	1.10	96.83
2	2.5	1.15	96.98

### Diesel blends characterization

Fuel properties of diesel blends containing 1, 3, 6 and 9 wt. % of glycerol butanol propionate (named as *Diesel* (standard diesel fuel), *GAP 1* (diesel blend with glycerol butanol propionate 1 wt. %) *GAP 3*, (diesel blend with glycerol butanol propionate 3 wt.%) *GAP 6* (diesel blend

with glycerol butanal propionate 6 wt.%) and **GAP 9** (diesel blend with glycerol butanal propionate 9 wt.%), respectively, were studied. Results are presented in Table 2. Kinematic viscosity and density are two important parameters required by diesel fuel standards because viscosity affects the atomization quality, size of fuel drop and penetration [19], while density influences resistance to self-ignition, diesel index and calorific value [20].

The data presented in Table 2 shows a slightly increasing trend with the addition of glycerol acetal ester in diesel blends, which can be explained by the fact that density of glycerol acetal ester is slightly higher compared with standard diesel. Density increases from 0.842 g / m<sup>3</sup> for standard diesel to a maximum of 0.847 g/cm<sup>3</sup> for diesel blend containing 9 wt. % glycerol butanal acetal. Contrary, the addition of glycerol acetal decrease viscosity of standard diesel fuel from 2.72 mm<sup>2</sup>/s to 2.66 mm<sup>2</sup>/s. The next parameter tested was flash point. As can be seen in Table 2 this fuel property was improved with 6 °C when 9 wt. % of glycerol butanal propionate was added in diesel fuel. The last parameter analyzed was the pour point. From the data obtained, the best performance of -21 °C was achieved when 9 wt.% of glycerol derivative was added to diesel.

**Table 2.** Characteristics of the diesel fuel blends components

Blends	Density at 15°C (kg/m <sup>3</sup> )	Viscosity at 40°C (mm <sup>2</sup> /s)	Flash point (°C)	Pour point (°C)
<i>Diesel</i>	842	2.72	60.1	-10
<i>GAP 1</i>	843	2.66	62.2	-13
<i>GAP 3</i>	845	2.67	64.6	-16
<i>GAP 6</i>	846	2.69	62.1	-19
<i>GAP 9</i>	847	2.71	66.1	-21

## Conclusions

The conclusions of the study are the followings:

- The synthesis of glycerol butanal propionate was realized in two steps. First step, acetalisation of glycerol with butanal was performed using SO<sub>4</sub><sup>2-</sup>/SnO<sub>2</sub> solid superacid catalyst, while the second step transesterification of glycerol acetal butanal with methyl propionate was carry out over sodium methoxide 30%.
- The optimal reaction parameters for glycerol acetal synthesis were studied ;
- Fuel properties of diesel blends containing different amounts of glycerol additive were tested. The results indicate that the addition of glycerol butanal propionate in diesel increase density and flash point and decrease viscosity and pour point.

## Acknowledgement

The work has been funded by the Sectoral Operational Programme Human Resources Development 2007-2013 of the Ministry of European Funds through the Financial Agreement POSDRU/159/1.5/S/134398

## References

1. Karinen, R.S., Krause, A.O.I. – New biocomponents from glycerol, *Appl. Catal. A* 2006; **306** (7), pp. 128–33.
2. Ferreira, P., Fonseca, I.M., Ramos, A.M., Vital, J., Castanheiro, J.E. – Valorisation of glycerol by condensation with acetone over silica-included heteropolyacids, *Applied Catalysis B: Environmental* 2010; **98**, pp. 94–99.
3. Goncalves, V.L.C., Pinto, B.P., Silva, J.C., Mota, C.J.A. – Acetylation of glycerol catalyzed by different solid acids, *Catal. Today*, 2008; 133–135, pp. 673–677.
4. Mota, C.J., da Silva, C.X.A., Rosenbach, N., Costa, J., da Silva, F. – Glycerine derivatives as fuel additives: the addition of glycerol/acetone ketal (solketal) in gasolines, *Energy Fuels* 2010; **24**, pp. 2733–6.
5. Oprescu, E.E., Stepan, E., Dragomir, R.E., Radu, A., Rosca, P. – Synthesis and testing of glycerol ketals as components for diesel fuel, *Fuel Processing Technology* 2013; **110**, pp. 214–217.
6. Oprescu, E.E., Dragomir, R.E., Radu, E., Radu, A., Velea, S., Bolocan, I., Stepan, E., Rosca, P. – Performance and emission characteristics of diesel engine powered with diesel-glycerol derivatives blends, *Fuel Processing Technology* 2014; **126**, pp. 460–468.
7. Crotti, C., Farnetti, E., Guidolin, N. – Alternative intermediates for glycerol valorization: iridium-catalyzed formation of acetals and ketals. *Green Chem* 2010; **12**, pp. 2225–31.
8. Malaya, R.N., Zhongshun, Y., Wensheng, Q., Hassan, S. G., Marc-Andre, P., Chunbao (Charles), X. – Catalytic conversion of glycerol to oxygenated fuel additive in a continuous flow reactor: Process optimization, *Fuel* 2014; **128**, pp. 113–119.
9. Güemez, M.B., Requies, J., Agirre, I., Pedro, L.A., Barrio, V.L., Cambra, J.F. – Acetalization reaction between glycerol and n-butyraldehyde using an acidic ion exchange resin. Kinetic modeling, *Chemical Engineering Journal* 2013; **228**, pp. 300–307.
10. Jinbo, N., Wu, M., Yang, Z., Bu, C., He, Q. – Effective  $\text{SO}_4^{2-}/\text{TiO}_2\text{-ZrO}_2$  for preparation and hydrolysis of 1,3-propanediol acetals. Reaction Kinetics, *Mechanisms and Catalysis*, 2010; **100**, pp. 337–346.
11. Subhash, P.C., Zubaidha, P.K., Shubhada, W.D., Keshavaraj, A., Ramaswamy, A.V., Ravindranathan T. – Use of solid superacid (sulphated  $\text{SnO}_2$ ) as efficient catalyst in facile transesterification of ketoesters, *Tetrahedron Letters* 1996; **37**, pp. 233–236.
12. Furata, S., Matsushashi, H., Arata, K. – Catalytic action of sulfated tin oxide for etherification and esterification in comparison with sulfated zirconia, *Applied Catalysis* 2004; **269**, pp. 187–191.
13. Dunchen, Y., Sen, L., Yonglai, Z., Chengyang, Y., Yan, D., Xiao, F. S. – Mesoporous sulfated tin oxide and its high catalytic activity in esterification and Friedel-Crafts acylation, *Catalysis Letters* 2006; **108**, pp. 155–158.
14. Waqif, M., Bachelier, J., Saur, O., Lavalley, J.C. – Acidic properties and stability of sulfate-promoted metal oxides, *Journal of Molecular Catalysis* 1992; **72**, pp. 127–138.
15. Punnoose, A., Hays, J., Thurber, A., Engelhard, M.H., Kukkadapu, R.K., Wang, C., Shutthanandan V., Thevuthasan S. – Development of high-temperature ferromagnetism in  $\text{SnO}_2$  and paramagnetism in  $\text{SnO}$  by Fe doping, *Physics Review B* 2005; **72**, pp. 054402–054416.
16. Guierrez-Baez, R., Toledo-Antonio, J.A., Cortes-Jacome, M.A., Sebastian, P.J., Vazquez, A. – Effects of the  $\text{SO}_4$  Groups on the Textural Properties and Local Order Deformation of  $\text{SnO}_2$  Rutile Structure, *Langmuir* 2004; **20**, pp. 4265–4271.
17. Hino, M., Kurashige M., Matsushashi, H., Arata, K. – The surface structure of sulfated zirconia: Studies of XPS and thermal analysis, *Thermochimica Acta* 2006; **41**, pp. 35–41.
18. Serafim, H., Fonseca, I.M., Ramos, A.M., Vital, J., Castanheiro, J.E. – Valorization of glycerol into fuel additives over zeolites as catalysts. *Chemical Engineering Journal* 2011; **178**, pp. 291–296.
19. Alptekin, E., Canakci, M. – Determination of the density and the viscosities of biodiesel-diesel fuel blends, *Renew. Energ* 2008; **33** (12), pp. 2623–2630
20. Tat, M. E., van Gerpen, J. H. – The specific gravity of biodiesel and its blends with diesel fuel, *J. Am. Oil Chem. Soc.* 2000; **77** (2), pp. 115–119.

## Esteri de tip acetali ai glicerinei ca aditivi pentru biodiesel

### Rezumat

*Lucrarea prezinta studii privind valorificarea glicerinei ca aditiv pentru biodiesel. Aditivul pe baza de glicerol se obtine in doua etape: condensarea glicerolului cu n-butanal in prezenta unui catalizator superacid de tip  $SO_4^{2-}/SnO_2$  si apoi transesterificarea acetal glicerolului cu propionat de metil. Au fost studiatii parametrii de performanta ai catalizatorului folosit precum si proprietatile de aditiv ale ester acetalului de glicerina.*