# Hydrogenolysis of Sunflower Oil over Co-Mo Catalyst

**STELIANA CRISTEA[1], ION BOLOCAN[1], DORIN BOMBOS[1], MIHAELA BOMBOS[2], GABRIEL VASILIEVICI[2], TRAIAN JUGANARU[1]*, ROXANA CHIVU[3], CASEN PANAITESCU[1]**

[1] Petroleum-Gas University of Ploiesti, 39 Bucuresti, 100680, Ploiesti, Romania

[2] National Research Institute for Chemistry and Petrochemistry, ICECHIM, 202 Spl. Independentei, 060021, Bucharest, Romania

[3] Politehnica University of Bucharest, Faculty of IMST, 313 Splaiul Independentei, 060042, Bucharest, Romania

*Co-Mo/$\gamma$-$Al_2O_3$ catalyst was prepared by successive impregnation, the precursors of the two metal being cobalt nitrate and ammonium molybdate respectively. Acid strength distribution of the catalyst was determined by thermodesorption of diethyl amine in the temperature range 50-650°C. The main textural properties of Co-Mo/ ă-alumina catalyst, respectively the surface area, pore volume and size distribution of pores were determined by the BET method. Hydrogenolysis of sunflower oil to hydrocarbon fuel was performed on a fixed bed catalytic reactor, at a pressure of 20 – 50 atm, with volume hourly space velocities of sunflower oil (WHSV) of 0.1 – 0.3 $h^{-1}$ and molar ratio hydrogen/ sunflower oil of 10/1. The temperature varied in the range 375- 425$^0$C. The major compounds identified were $C_{16}$-$C_{18}$ hydrocarbons and straight and branched C≤ 17 hydrocarbons. Sunflower oil conversion was 100% and the yield values in hydrogenolysed product has changed with temperature, pressure and volume hourly space velocity.*

*Keywords: catalyst, hydrogenolysis, support acidity, sunflower oil, hydrocarbons*

The partially replacement of diesel with biodiesel drawbacks both in terms of oxidation stability [1] and of recovery of by-product glycerin [2,3]. Improving burning features of fossil fuels by emulsification adversely affects their rheological characteristics [4,5]. For this reason hydrotreating of vegetable oils in order to obtain biofuels has been approached by many authors in the last period [6-17]. Zhang and collaborators studied nanosized unsupported NiMoS and CoMoS catalysts in deoxygenation of vegetable oils. Thus the inherent impact of nickel and cobalt on the main deoxygenation routes has been investigated without the influence of catalyst supports. They showed that Ni and Co play a key role in enhancing the catalytic activities and selectivity of $MoS_2$. They have shown that Ni-promoted catalyst exhibits higher selectivity for hydrodeoxygenation reaction over hydrodecarbonylation/ decarboxylation, while Co-promoted catalyst prefers hydrodecarbonylation/ decarboxylation. Thus Ni-$MoS_2$ creates abundant sulfur vacancies that improve the hydrogenation ability, while Co-$MoS_2$ catalyst generated saturated edge centers, facilitating the hydrocracking [18]. Jerzy Walendziewski and collaborators studied the hydroprocessing of light gas oil - rape oil mixtures. The reactor feed was composed of 10 wt.% rapeseed oil / 90 wt.% gas oil and 20wt.% rape oil / 80wt.% gas oil. Hydroprocessing of both mixtures was performed at the same parameters. They have shown that it is possible to control vegetable oil hydrogenolysis in the presence of light gas oil fraction through the proper selection of the process parameters. The main reactions in the process were hydrogenolysis of ester bonds and hydrogenation of olefinic bonds from vegetable oils[19]. The deoxygenation of vegetable oils is a potential biofuel production process. Raw material commonly used in the manufacture of bio-diesel fuel is rapeseed oil. After the expiration of guarantee, strategic reserve state of sunflower oil can be an alternative feedstock for the production of biofuels. This paper addresses the study of hydrogenolysis process of sunflower oil over a Co-Mo/ $\gamma$-$Al_2O_3$ catalyst.

## Experimental part

The raw materials used in experiments were sunflower oil of technical grade, cobalt(II) nitrate hexahydrate puriss. p.a. (Sigma-Aldrich), ammonium heptamolybdate tetrahydrate (Sigma-Aldrich), $\gamma$-alumina granulated and electrolytic hydrogen purity from Linde Company. The main acids present in sunflower oil used in experiment was determined by GC analysis of methyl esters and are presented in table 1.

The synthesis of the catalyst was achieved by successive impregnation with aqueous solutions of the precursors of catalysts, applying the method of filling the pores. The precursors of the catalyst were cobalt nitrate and ammonium heptamolybdate tetrahydrate. Concentration of catalyst precursor of the impregnation solution was calculated according to the proposed metal content (2.6% Co and 10% for Mo). Reconditioning of the catalyst between impregnations was achieved by drying in an oven at 160°C for 4 h and the final conditioning was performed in the following sequence of steps: i) drying in the oven at 160°C for 6 h; ii) calcination at 450°C for 6 h and iii) activation in a hydrogen stream at 450°C for 6 h.

Chemical composition of catalyst used in the experimental program was determined by atomic absorption. Catalyst characterization was performed by determining the acid strength, textural characteristics and realization of SEM analysis.

**Table 1**
FATTY ACID COMPOSITION OF SUNFLOWER OIL ANALYZED BY GC–MS

| Fatty acids (Cn:m)* | C16:0 | C18:0 | C18:1 | C18:2 |
|---|---|---|---|---|
| Content (wt.%) | 19.0 | 5.2 | 35.1 | 38,6 |

*Cn:m: n, number of carbon atoms; m, number of C C double bonds in fatty acids

---

* *email: juganarut@yahoo.com; Tel: +40-244-57 31 71*

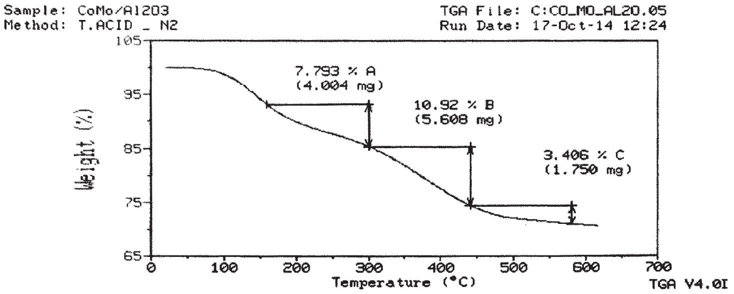

Fig. 1. Acid strength distribution of Co-Mo/ γ-$Al_2O_3$ catalyst

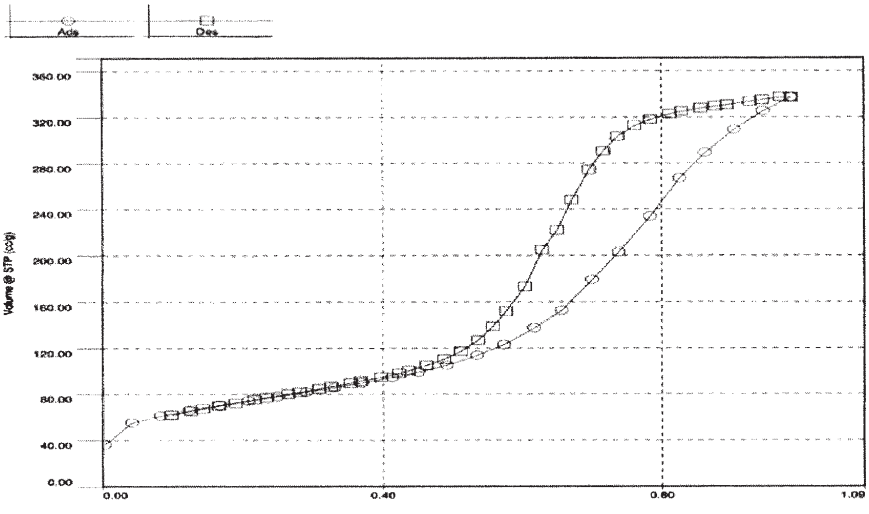

Fig.2. Adsorption / desorption isotherm of nitrogen for Co-Mo/γ-$Al_2O_3$ catalyst

The experimental program was performed in a continuous system and fixed bed catalytic reactor. The process was carried out in isothermal conditions. The temperature was automatically adjusted with an control system coupled with two fixed thermocouples, placed in the reactor jacket. A metallic jacket for the mobile thermocouple was also placed in the reactor axis, the sheath in which was axially placed in the central zone of the catalyst bed, in order to measure the reaction temperature.

Reaction conditions for catalyst were:

-pressure: 20 – 50 atm;

-temperature: 375 -425$^0$C ;

-weight hourly space velocities of sunflower oil (WHSV): 0.1 – 0.3 $h^{-1}$;

-molar ratio hydrogen/ sunflower oil (R):100/1.

The composition of the reaction mixtures was performed by the method of gas chromatography coupled with mass spectrometry, equipped with capillary column with a length of 30m having a diameter of 0.250mm, whose fixed phase was polyethylene glycol (PEG) and Helium as mobile phase.

## Results and discussions

Acid strength distribution of the catalyst was determined, as well as in a previous paper [20], by termodesorption of diethyl amine in the temperature range 20-700°C. Thermal analyzes (ATG, DSC) was performed on a DuPont Instruments' Thermal Analyst 2000/2100 "coupled with a module "951 Thermogravimetric Analizer".

Figure 1 shows the distribution of acidity center for catalyst Co-Mo / γ-$Al_2O_3$ (A - concentration of centers with weak acidity, B - concentration of centers with medium acidity, C - concentration of centers with high acidity).

In figure 1 is observed a high content in weak acid centers (1.067meq./g), a higher concentration of medium acid centers (1.495 meq./g) and a concentration of strong acid centers over three times smaller than medium acid centers (0.467meq./g).

The adsorption isotherm for the catalyst prepared is shown in figure 2.

Adsorption curve contains more areas for the catalyst than for the catalytic support[15]. Thus, in the area of low relative pressure p /po, the volume of nitrogen adsorbed by the catalyst is lower than for catalyst support, being associated with a monolayer adsorption of nitrogen on the surface.

At relative pressures close to 1.0 is observed an increase in the volume adsorbed and the presence of a small hysteresis loop, this last area being associated with condensation of nitrogen in the spaces between the particles.

Textural characteristics of the catalyst was determined by BJH method cumulative desorption pore volume, and are presented in table 2. The surface area of the catalyst Co-Mo/γ-$Al_2O_3$ has a typical value for γ-alumina-based catalysts.

Figure 3 shows that the Co-Mo/γ-alumina catalyst possesses a well-defined large pore size with maximum distribution centered around 55A°. This result could indicate that the monomodal pore structure of Co-Mo/γ-alumina catalyst has been induced during the catalyst preparation process.

Generally, main textural properties of Co-Mo/γ-alumina catalyst prepared as described above consist of large surface area, high pore volume and monomodal mesopore size distribution indicating a good accessibility of the catalytic sites.

**Table 2**
TEXTURAL CHARACTERISTICS OF THE CATALYST PREPARED

| Catalyst | Specific Surface, ($m^2$/g) | Total Pore Volume, ($cm^3$/g) | Medium Pore Diameter, (nm) |
|---|---|---|---|
| Co-Mo/γ-$Al_2O_3$ | 373.765 | 0.566 | 5.480 |

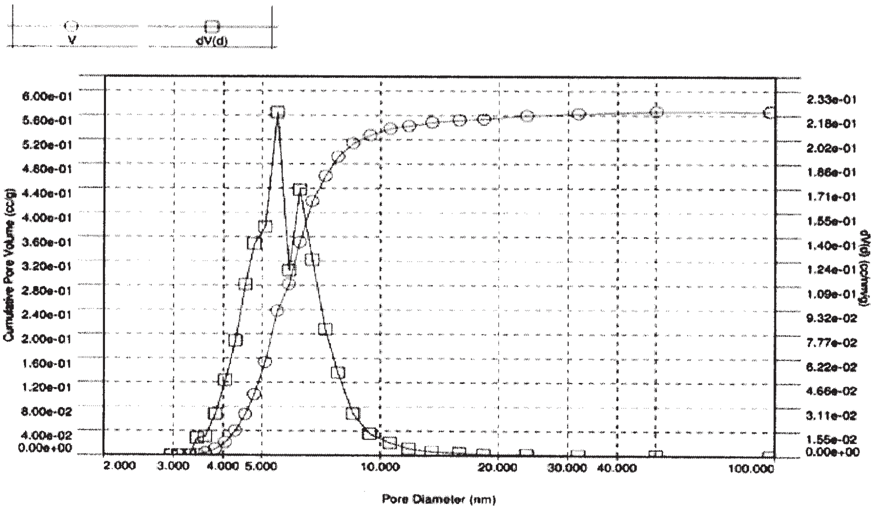

Fig. 3. Pore size distributions of Co-Mo/γ-alumina

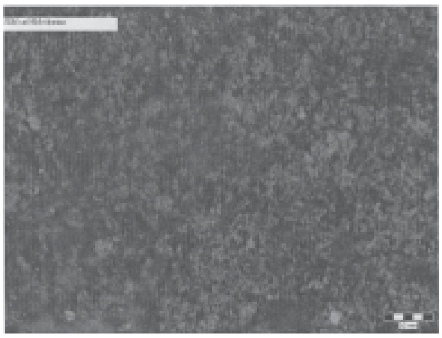

Fig. 4. *SEM* image of Ni-Mo/γ-$Al_2O_3$ *catalyst*

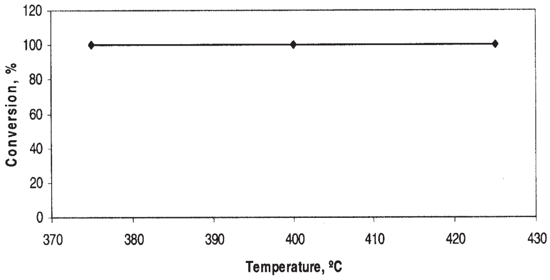

Fig. 5. Influence of temperature on the sunflower oil conversion at 30 bar, VHSW 0.3 $h^{-1}$ and hydrogen/ triglycerides molar ratio of 100/1

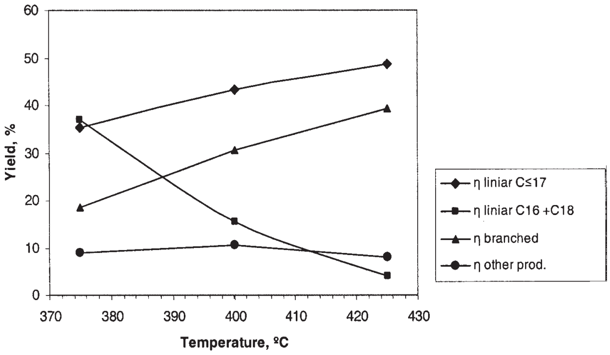

Fig.6. Influence of temperature on the products yield at 30 bar, VHSW 0.3 $h^{-1}$ and hydrogen/ triglycerides molar ratio of 100/1

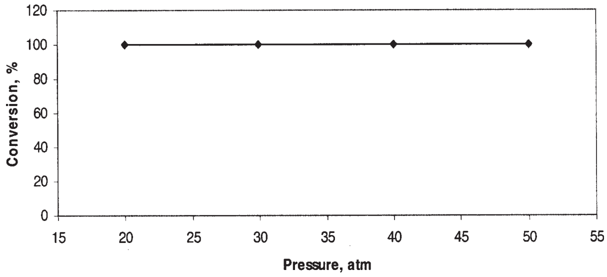

Fig. 7. Influence of pressure on the sunflower oil conversion at 375ºC, VHSW 0.3 $h^{-1}$ and hydrogen/ triglycerides molar ratio of 100/1

*SEM* image analysis for the characterization of the *catalyst* are shown in figure 4. It shows a high dispersion of species deposited on the catalyst support.

The major compounds identified at sunflower oil hydrogenation were straight hydrocarbons with less than 17 carbon atoms (C≤17) obtained by hydrocracking, straight hydrocarbons with 16 and 18 carbon atoms (C16+C18) obtained by hydrogenolysis of triglycerides and branched hydrocarbons obtained by isomerization of straight hydrocarbons.

Variation of triglycerides conversion with temperature was studied at 30 bar, VHSW of 0.3 $h^{-1}$ and hydrogen/ triglycerides molar ratio of 100/1. From figure 5 it is observed that the conversion of sunflower oil was total throughout the temperature range studied.

The straight hydrocarbons with less than 17 carbon atoms were obtained at higher yield of 35% on the area of temperature studied. Increasing of the temperature favors improving of the yield in straight hydrocarbons with less than 17 carbon atoms. Thus, increasing temperature from 375°C to 425°C favors increasing efficiency in straight hydrocarbons with less than 17 carbon. The yield in straight hydrocarbons with 16 and 18 carbon atoms decreases with increasing temperature from the value of approx. 37% at 375°C, to 4% at a temperature of 425°C. The yield in branched hydrocarbons increases with increasing of the temperature of approx. 18% at a temperature of 375°C to approx. 39%, temperature of 425°C. The yield in other products stayed at approx. constant value of less than 10% over the whole range of temperature studied (fig. 6). Note that the increase of temperature, on the field studied, favors hydrocracking and hydroisomerization reactions.

Variation of triglycerides conversion with pressure was studied at 375°C, VHSW of 0.3 $h^{-1}$ and hydrogen/ triglycerides molar ratio of 100/1. From figure 7 it is observed that sunflower oil conversion was total throughout the temperature range studied.

The straight hydrocarbons with less than 17 carbon atoms were obtained at higher yield of 30% on the area of temperature studied. At low levels of pressure (between 20 and 30 atm), increasing of the pressure favors diminishes of the yield in straight hydrocarbons with less than 17 carbon atoms. At pressure values between 30 and 40 atm, yield in straight hydrocarbons with less than 17 carbon is maintained at approx. constant, and to more than 40 atm. yield in straight hydrocarbons with less than 17 carbon diminishes again. The yield in straight hydrocarbons with 16 and 18 carbon atoms varies after a symmetrical curve with the curve of the yield in straight hydrocarbons with less than 17 carbon atoms. Thus, at low levels of

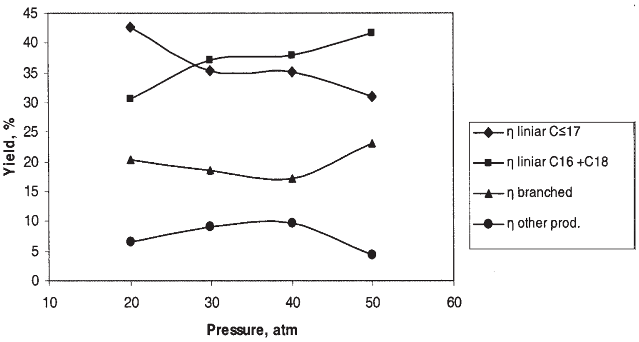

Fig. 8. Influence of pressure on the products yield at 375°C, VHSW of 0.3 $h^{-1}$ and hydrogen/ triglycerides molar ratio of 100/1

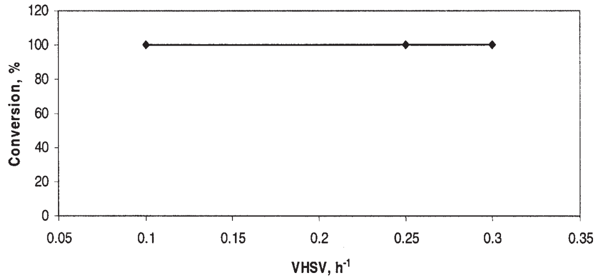

Fig. 9. Influence of volumic hourly space velocity on the sunflower oil conversion at 425°C, 50 atm. and hydrogen/ triglycerides molar ratio of 100/1

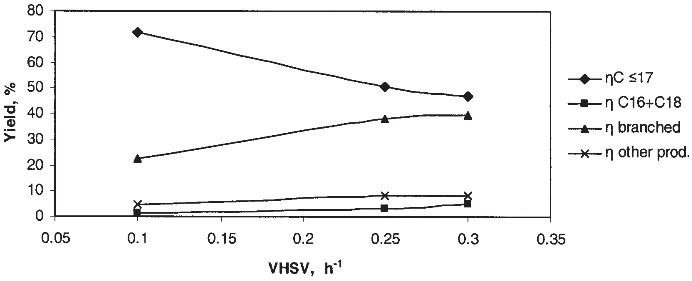

Fig. 10. Influence of volumic hourly space velocity on the products yield at 425°C, 50 atm. and hydrogen/ triglycerides molar ratio of 100/1

pressure (between 20 and 30 atm), increasing of the pressure favors increase of the yield in straight hydrocarbons with 16 and 18 carbon and at higher value more than 40 atm., yield in straight hydrocarbons with 16 and 18 carbon increases again. The yield in branched hydrocarbons decreases with increasing of the pressure up to 40 atm and then increases with increasing pressure. The yield in other products shows a small variation, with a maximum at a pressure of 40 atm (fig. 8). Note that the increasing of pressure to values greater than 40 atm favors hydrogenolysis and hydroisomerization reactions.

Variation of triglycerides conversion with volumic hourly space velocity was studied at 42°C, 50 atm. and hydrogen/ triglycerides molar ratio of 100/1. From figure 9 it is observed that sunflower oil conversion was total throughout the volumic hourly space velocity range studied.

The yield in straight hydrocarbons C≤ 17 shows alues between approx. 47% and 72% and the yield in straight hydrocarbon C16+C18 shows values between approx. 1% and 5%. The variation in yield of straight hydrocarbons C≤ 17 with weight hourly space velocity of sunflower oil and in the yield in branched hydrocarbons have a symmetrical curve. Thus, the increase of yield in branched hydrocarbons is accomplished by decreasing yield in straight hydrocarbons C≤ 17, which shows that branched hydrocarbons are obtained by isomerisation of straight hydrocarbons C≤ 17. The yield of hydrogenolysed products (C16-C18 hydrocarbons) with weight hourly space velocity of sunflower oil presented a nearly linear variation, its low values indicating their high reactivity in reactions of hydrogenolyzing ( fig. 10).

## Conclusions

Hydrogenolysis of sunflower oil was performed on Co-Mo/γ-$Al_2O_3$ granular *catalyst* prepared by successive impregnation, using a fixed bed catalytic reactor in continuous systems.

The reaction mixture was analyzed by chromatography, and the major compounds identified at sunflower oil hydrogenation were C16-C18 hydrocarbons, straight and branched C≤ 17 hydrocarbons.

Acid strength distribution of the catalyst was determined by termodesorption of diethyl amine in the temperature range 20-700°C.

The main textural properties of Co-Mo/γ-alumina catalyst consist of large surface area, a relative high pore volume and mono-modal mesopore size distribution indicating a good accessibility of the catalytic sites.

The activity of prepared catalyst was high and the sunflower oil conversion was total throughout the range of parameters studied

The yield in hydrogenolysed products varies with temperature, pressure and volume hourly space velocity.

## References

1. CURSARU, D., NEAGU, M., BOGATU, L., Rev. Chim. (Bucharest), **64**, no. 4, 2013, p. 438

2. DUŞESCU, C., BOLOCAN, I., Rev. Chim. (Bucharest), **63**, no.3, 2012, p.305

3. DUŞESCU, C., BOLOCAN, I., Rev. Chim. (Bucharest), **63**, no. 7, 2012, p.732

4. DUŞESCU, C., BOMBOS, D., JUGANARU, T., POPOVICI, D., BOLOCAN, I., Rev. Chim. (Bucharest), **60**, no. 7, 2009, p. 719

5. BOMBOS, D., BOMBOS M., BOLOCAN, I., VASILIEVICI, G., DUŞESCU, C., ZAHARIA E., Rev. Chim. (Bucharest), **61**, no.9, 2010, p. 862

6. KUBICKA D., BEJBLOVA M., VLK J. Top Catal 53 (2010), 168

7. KUBICKA D, SIMACEK P., ZILKOVA N., Top Catal 52(2009), 161

8. VILJAVA T.R., KOMULAINEN R.S., KRAUSE A.O.I., ApplCatal A 209(2001),33

9. VERIANSYAHB, HAN J.Y., KIM S.K., HONG S.A., KIMY. J., LIM J., SHU Y.W., OH S.G., KIM J., Fuel 94 (2012) 578–585

10. HORACEK J, TIŠLER Z, RUBAŠ V, KUBICKA D., Fuel 121 (2014), 57–64

11. GARCÍA-DÁVILA J., OCARANZA-SÁNCHEZ E., ROJAS-LÓPEZ M., MU OZ-ARROYO J.A., RAMÍREZ J., MARTÍNEZ-AYALA A.L., Fuel 135 (2014), 380–386

12. KRAR M. , KOVACS S, KALLO D., HANCSOK J. Bioresource Technology 101 (2010), 9287–9293

13. KUBICKA D., HORACEK J. Applied Catalysis A: General 394 (2011) 9–17

14. ŞENOL O.I., VILJAVA T.R., KRAUSE A.O.I. Catalysis Today 106 (2005) 186–189

15. ŞENOL O.I., RYYMIN E.M., VILJAVA T.R., KRAUSE A.O.I., Journal of Molecular Catalysis A: Chemical 268 (2007) 1–8

16. BEZERGIANNI S. , DIMITRIADIS A., MELETIDIS G., Fuel 125 (2014) 129–136

17. M. TOBA, Y. ABE, H. KURAMOCHI, M. OSAKO, T. MOCHIZUKI, Y. YOSHIMURA, Catal. Today 164 (2011) 533–537.

18. HAIPING ZHANG, HONGFEI LIN, YING ZHENG, APPLIED CATALYSIS B: Environmental, 160–161, (2014), 415-422

19. JERZY WALENDZIEWSKI, MAREK STOLARSKI, RAFAŁ ŁU NY, BARTŁOMIEJ KLIMEK, Fuel Processing Technology, 90, Issue 5, (2009), 686-691

20. CRISTEA S., BOLOCAN I., BOMBOS D., BOMBOS M., JUGANARU T., Rev. Chim. (Bucharest) **66,** no. 3 , 2015, p.404

---

Manuscript received: 21.10.2014