PALLADIUM AND COPPER CATALYST FOR FURFURAL HYDROGENATION

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Abstract

The hydrogenation reaction of furfural was studied in a fixed bed catalytic reactor, operated in continuous flow, in isothermal conditions using a copper-palladium catalyst on a γ alumina support. The catalyst was characterized by determining its acid strength distribution using the diethyl amine thermodesorption method and textural characteristics. The Cu-Pd catalyst presented high efficiency in the furfural hydrogenation process giving a furfural conversion of ~ 98% and yielding in furfuryl alcohol (72.06%) and tetrahydrofurfuryl alcohol (25.78%).

Key words: Furfural, hydrogenation, acidity, catalysts

1. Introduction

Recently, furfural has recaptured attention as a potential source for biofuel and biochemicals. Bozell et al. considered it to be one of the most promising substances for sustainable production of fuels and chemicals in the 21st century [1]. Furfural, having a very flexible production, is the most commonly obtained industrial product. Furfural and its derivatives have been widely used in the plastics, pharmaceutical and agrochemical industries, as fungicides and insecticides, transport fuels, gasoline additives, aviation fuel, lubricants, resins, bleaching agents, drugs, flavor enhancers for food and beverages, and also for wood modification and book preservation [2,3].

Because of its high reactivity in condensation-polymerization reactions that can occur, furfural must be subjected to a hydrogenation process to improve its stability and reduce the number of reactive functional groups, like the carbonyl group. The hydrogenation process is complex, due to the series of parallel reactions, such as furan ring hydrogenation, the carbonyl group hydrogenation and also hydrogenolysis. This kind of reactions is favored by the acidic centers in the catalysts, leading to a decrease in the selectivity of furfural transformation. To improve the life of the catalyst used, the acidic characteristics must be kept in

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mind, because the selectivity of furfural hydrogenation process is influenced by the strength of the acidic centers of the catalyst [4].

As reported in literature, the main products obtained in the hydrogenation process of furfural are furfuryl alcohol (FA), tetrahydrofurfuryl alcohol (THFA), 2-methylfuran (MF), tetrahydro-2-methylfuran (THMF) as presented in Figure 1. It also shows the continuing of the hydrogenation process for the product earlier obtained, using different metal catalysts and in specific conditions for each product.

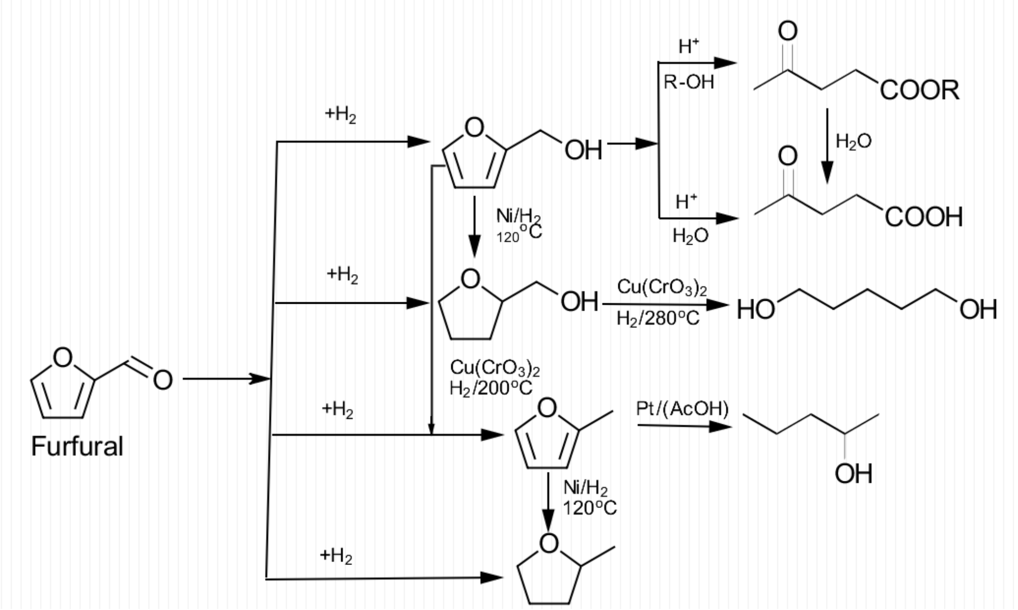

Fig 1. Possible reactions in the furfural hydrogenation process

Liquid-phase transfer hydrogenation of furfural using Cu based catalyst was performed by María M. Villaverde et al. [5]. The experiments were carried out using different Cu loadings (20%w, 30%w, 40%w), in a temperature range 110°C-150°C, using as H donor 2-propanol. They found that the Cu-Mg-Al catalyst containing 40%w Cu presented the best results, with a 100% conversion of furfural to FA at 150˚C, after 8 hours of reaction, thus showing that the rate of transfer hydrogenation increases with the Cu amount.

In their research, Á. O'Driscoll et al. [6] studied the influence of different metals and supports on monometallic and bimetallic catalysts activity for the liquid phase hydrogenation of furfural to FA. Metals like copper, palladium, nickel and platinum were used to prepare 1%w and 2%w monometallic catalysts by wet impregnation method, on supports like SiO_2, β zeolite, TiO_2, active carbon, Al-SBA-15. They found that out of all the metals and supports tested, Pt and SiO_2 gave the best conversion of furfural and the best FA selectivity, thus selecting Pt to be further tested in bimetallic catalysts. The bimetallic catalysts were prepared by surface reaction and the second metals used were selected by their electronegativity because if the second metal (the promoter) is more electropositive then the first metal the interactions with the carbonyl group in furfural increases [7]. The $0.6\%Pt0.4\%Sn/SiO_2$ catalyst presented a 47% furfural conversion and almost 100% selectivity to FA at 100˚C and 20 bar hydrogen pressure, using toluene as solvent.

The influence of Sn was also studied on a R-Ni/AlOH catalyst by Rosiansono et al. [8]. The catalyst was prepared by a simple method at low temperature. The Ni-Sn(3.0)/AlOH presented the best results at 453 K temperature for one hour, and a hydrogen pressure of 3MPa, using methanol as solvent, obtaining a >99% furfural conversion and a 98% yield in FA.

Jiménez-Gómez et al. [9] studied a series of Cu/CeO_2 catalysts for the gas phase hydrogenation of furfural. The catalysts were prepared using a co-precipitation method and had Cu/Ce molar ratios between 0.2 and 6. Because of the strong metal-cerium interaction the catalysts presented high stability and great catalytic behavior, the most efficient proving to be $Cu\text{-}CeO_2\text{-}6$ catalyst, where a furfural conversion of 83% was achieved after 5 hours of time on stream (TOS) at a temperature of 190ºC. The only products obtained were MF and FA, the majority product being influenced by the TOS, thus MF was the majority product at shorter reaction times, while the yield in FA increases at higher reaction times due to formation of carbonaceous deposits which determine the hydrogenolysis of the alcohol to MF.

Noble metals like Pd and Pt have also captured the attention of researchers, being used to obtain catalysts for furfural hydrogenation. S. Bhogeswararao and D. Srinivas [10] tested a series of Pt and Pd based catalysts on a γAl_2O_3 support for furfural hydrogenation. The Pd based catalysts favored the hydrogenation of the furan ring, yielding in THFA, while the Pt catalyst favored the C=O group hydrogenation, yielding in FA. The reactions were carried out at 25ºC. With temperature increase the Pd catalyst enabled the decarbonylation of furfural, resulting in a yield in furan of 82%.

The main objective of this research was to design an efficient catalyst for selective hydrogenation of furfural to oxygenated furan derivatives having a low oxygen content and good stability. Copper and palladium based catalysts supported on $\gamma Al_2O_3$with controlled acidity were synthesized. Addition of copper aimed to improve the hydrogenation of the furfural carbonyl group, while the palladium was employed for the furan ring saturation.

2. Materials and methods

Materials

The raw materials used in the experiments were furfural p.a (Sigma-Aldrich), $Cu(NO_3)_2 \cdot 3H_2O$ p.a (Sigma-Aldrich), $PdCl_2$ p.a (Sigma-Aldrich), granulated γ alumina and electrolytic hydrogen purity from Linde Company.

Catalyst preparation

The Cu-Pd/γAl_2O_3 catalyst was prepared by successively impregnating the γAl_2O_3 support with aqueous solutions of the Cu and Pd precursors, applying the pore-filling method. The aqueous solutions were prepared at the desired concentration according to the desired metal content (3%Cu and 0.5%Pd/ γAl_2O_3). The first metal to be deposited on the γAl_2O_3 support was Pd, then Cu. Between the impregnations, the catalyst was dried at 160˚C for 4 hours and at the end dried at 160˚C for 6 hours and calcinated at 450˚C for 6 hours. The catalyst reduction was done using an aqueous solution containing the equivalent amount of sodium borohydride.

Catalyst characterization

The catalyst characterization was performed by determining the textural properties (such as surface area, pore volume, average pore diameter, pore size distribution) using an Autosorb 1 Quantacrome Nova 2200 Analyzer and determining the acid strength distribution by applying the diethyl amine thermodesorption method using a DuPont Instruments Thermal Analyst 2000/2100&951TGA coupled with a Thermogravimetric Analizer module 951.

The porous structure of the γAl_2O_3 support and catalyst was characterized by N_2 adsorption-desorption. The BET equation was used to determine the surface area while the pore distribution and size were determined by applying the BJH method.

Furfural hydrogenation

The furfural hydrogenation process was carried out in a fixed bed catalytic reactor, operated in continuous flow, in isothermal conditions. The temperature was controlled using an automatic system coupled with two fixed thermocouples, situated in the reactor jacket. In order to measure the reaction temperature, on the reactor's axis was placed a metallic jacket for the mobile thermocouple.

The reaction conditions were as follows: the reaction was carried out at various temperatures in the range of 135-220ºC, pressures between 20 and 60 bar, a hydrogen/furfural molar ratio of 10:1 and a $0.15h^{-1}$ liquid hourly space velocity (LHSV).

The reaction products were characterized by GC-MS (Varian -3800). Operational parameters for the GC method were: column VF-5ms 30m X 0.25mm, ID DF=0.25; the oven program was set at 175°C with a temperature gradient of 16°C/min, the carrier gas used was He and the injector temperature was 155ºC.

For the MS method the parameters were: collision cell QQQ: Flow Quench Gas (He) 2.2 mL/min with collision gas flow of 1.5 mL/min, a 70eV electron energy and the source temperature was 230ºC.

3. Results and discussions

To determine the acid strength distribution of the materials, the diethyl amine thermodesorption method was applied in the temperature range 20-600°C. The diethyl amine thermodesorption curves for the γAl_2O_3 support, 0.5%Pd/ γAl_2O_3 and for the catalyst 3%Cu-0.5%Pd/ γAl_2O_3 are presented in Figure 2 a, b and c.

The mass losses recorded on the thermodesorption curves at temperatures between 150-300ºC (zone A) are attributed to the diethyl amine desorption from the weak acidic centers, between 300-440ºC (zone B) the desorption of diethyl amine from the acidic centers with medium acidity and between 440-580ºC (zone C) are attributed to the thermodesorption from strong acidic centers. Total acidity is defined as the mass of desorbed amine from acidic centers, expressed as mEg/gram of catalyst (mEg/g_{cat}).

Based on the diethyl amine thermodesorption curves, the acid strength distribution of the materials was determined and presented in Table 1. As observed from the values obtained, for the γAl_2O_3 support the strong acidic centers are found at the lowest concentration, with the weak acidic centers having a higher concentration than the ones for medium and strong acidic centers. After impregnating the support with the Pd precursor, as expected, the concentration of medium and strong acidic centers raises slightly compared with the γAl_2O_3 support, but the total acidity has a lower value compared with the one of the support. After adding the Cu precursor, the medium acidic centers are found at the lowest concentration while the weak acid centers concentration raises considerably, with its value being higher than the concentration of the strong acidic centers and much higher than the one of the medium acidic centers.

Figure 3 presents the pore size distribution of the materials. As observed from the BJH desorption method, the materials present big, well defined pores with a maximum distribution for the 3%Cu-0.5%Pd/γAl_2O_3 catalyst centered at about 95 Å. The specific surface area of the catalyst is typical for γAl_2O_3 supported catalysts with values higher than 200m^2/g. With the precursors addition to the support the value of the surface area decreases from 232.34m^2/g to 224.01 m^2/g for the 3%Cu-0.5%Pd/γAl_2O_3. Also the pore volume decreases from 0.530 cm^3/g to 0.486 cm^3/g. The medium pore diameter of the 3%Cu-0.5%Pd/γAl_2O_3 catalyst is 9.58 nm which puts the catalyst in the mesoporous category. The textural characteristics of the materials are presented in Table 1.

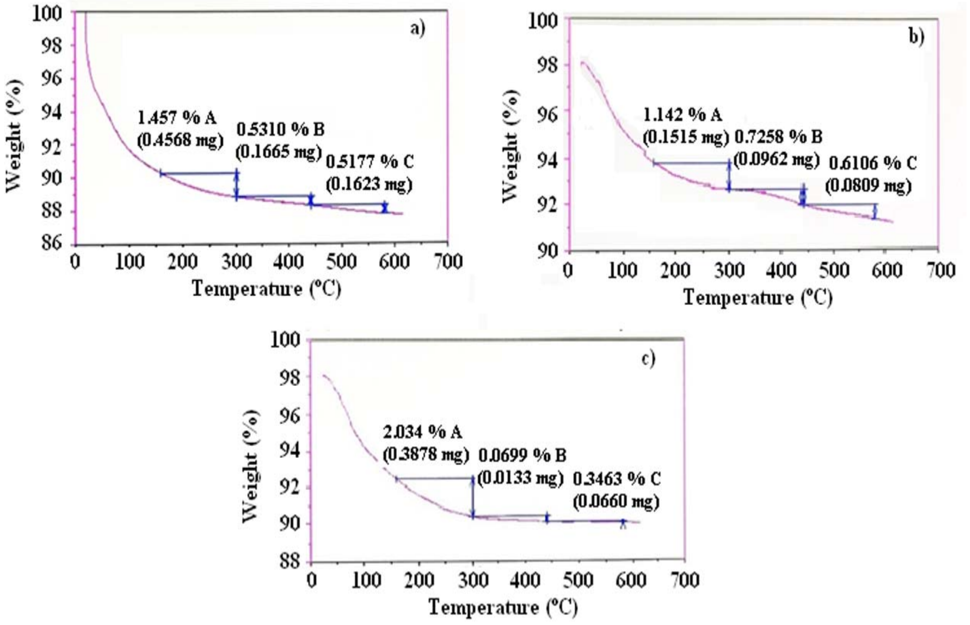

Fig. 2. Diethyl amine thermodesorption curves for: a) γAl_2O_3 support, b) 0.5%Pd/γAl_2O_3 and c) 3%Cu-0.5%Pd/γAl_2O_3

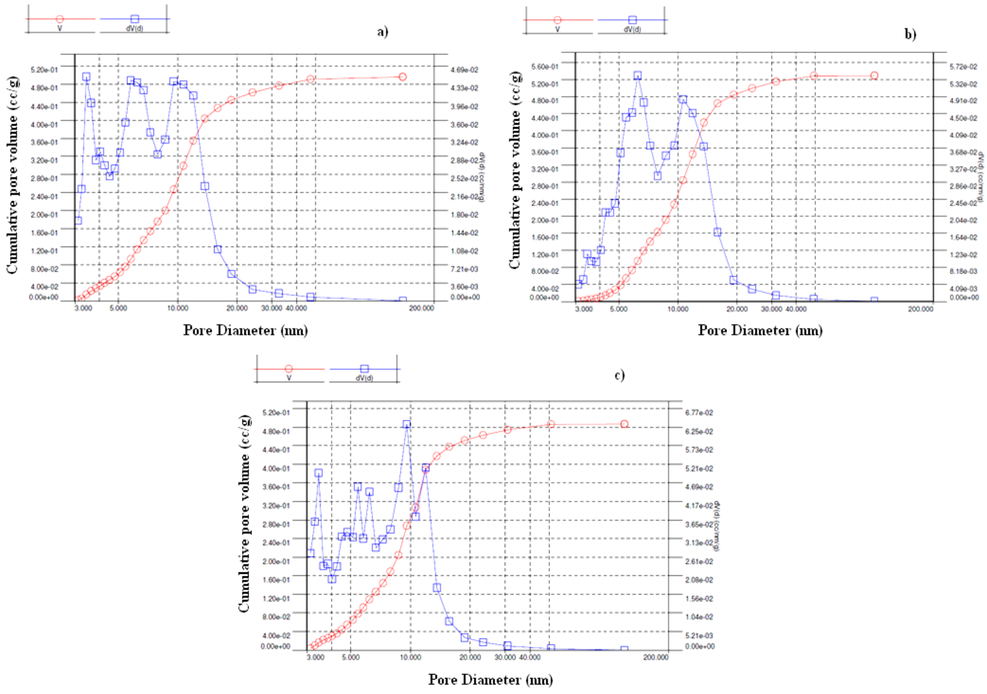

Fig. 3. Pore size distribution for: a) γAl_2O_3 support, b) 0.5%Pd/γAl_2O_3 and c) 3%Cu-0.5%Pd/γAl_2O_3 by BJH desorption method

Table 1.

Acid strength distribution and textural characteristics for γAl_2O_3 support, 0.5%Pd/ γAl_2O_3 and 3%Cu-0.5%Pd/ γAl_2O_3

Materials	S_{BET} (m2/g	Pore volume (cm3/g)	Medium pore diameter (nm)	Acid strength distribution (mEg/g_{cat})			
				Weak	Medium	Strong	Total
γAl_2O_3	232.34	0.530	3.44	0.199	0.072	0.070	0.341
0.5%Pd/ γAl_2O_3	230.11	0.496	6.24	0.156	0.099	0.083	0.338
3%Cu-0.5%Pd/γAl_2O_3	224.01	0.489	9.58	0.278	0.009	0.047	0.334

For furfural hydrogenation the 3%Cu-0.5%Pd/γAl_2O_3catalyst presented a high activity in the parameters ranges that were studied. As can be seen from figure 4, furfural conversion varies according to a parabolic curve with a maximum of 97.84% at 180˚C, for a pressure of 40 bar and a 0.15 h^{-1}LHSV. At temperatures higher than 180˚C the conversion starts to decrease, possibly due to the formation of gums that block the pores of the catalyst, deactivating it. The presence of strong acidic centers at relatively high concentrations (0.334 mEg/g) favors the condensation reactions with the formation of gums, mostly at temperatures higher than 180˚C.

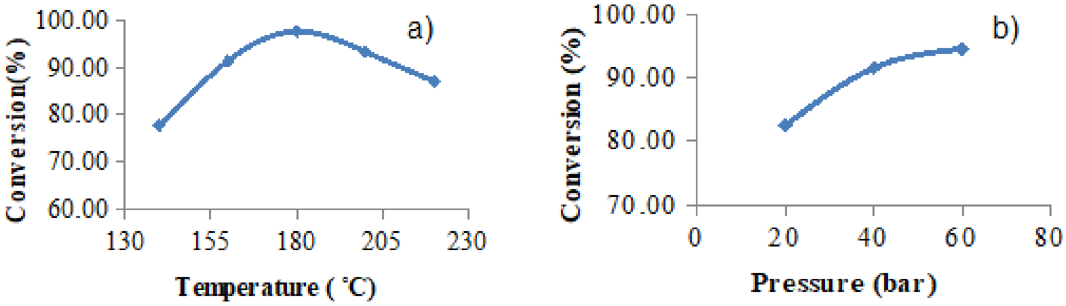

Fig. 4. Temperature and pressure influence on the furfural conversion: a) influence of temperature at 40 bar; b) influence of pressure at 160 °C.

Also, at a temperature of 160˚C and 0.15 h^{-1} LHSV, with the increase in pressure the furfural conversion increases, reaching a maximum value of ~94.5% at 60 bar. It can be noted a diminution of the curve slope variation which represents the furfural conversion with the pressure at values higher than 40 bar.

The products obtained from the furfural hydrogenation with 3%Cu-0.5%Pd/γAl_2O_3 catalyst were FA and THFA, with FA as the majority component obtained. Figures 5 and 6 show the temperature and pressure influence on the yield in FA and THFA.

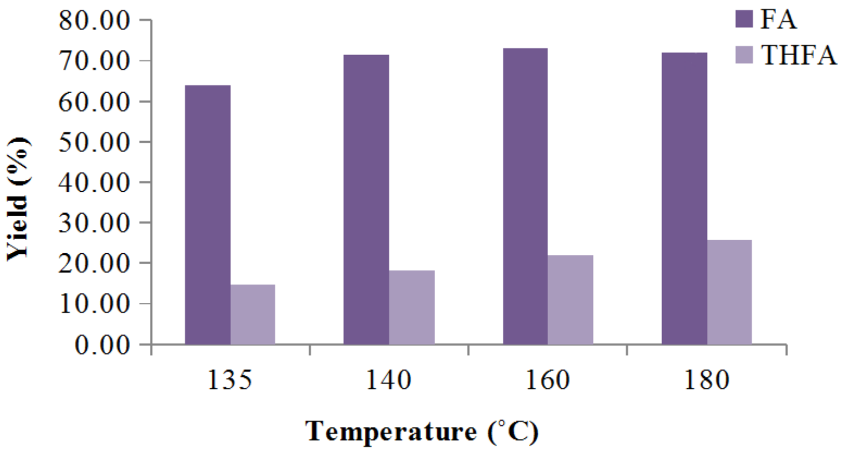

Fig. 5. Temperature influence on the yield in FA and THFA, at 40 bar pressure and 0.15h^{-1} LHSV

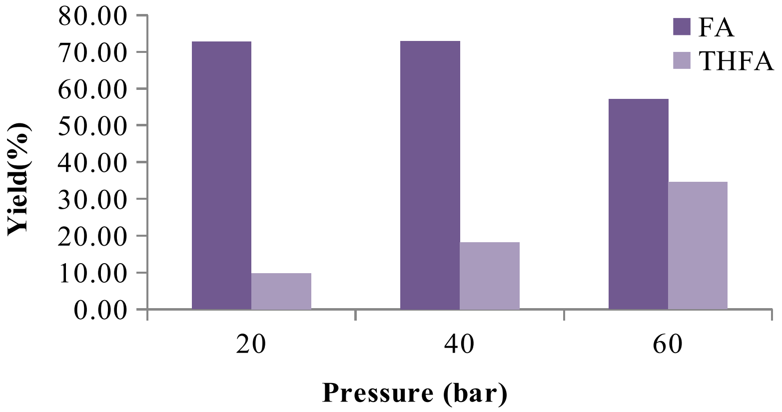

Fig. 6. Pressure influence on the yield in FA and THFA, at 160˚C and 0.15h^{-1} LHSV

The yields in FA and THFA increase with temperature, with a maximum yield in FA of 72.97% at 160˚C and 25.78% maximum yield in THFA at 180˚C. With the pressure increase the yield in FA decreases while the yield in THFA increases with a maximum of 34.54% at 160˚C, 60 bar and 0.15h^{-1} LHSV. The diminishing of the yield in FA at temperatures above 160°C is due both to its hydrogenation to THFA and to the condensation reactions of FA to resins, reactions favored by the presence of strong acid centers.

Pressure growth favors hydrogenation of FA to THFA, relatively low values of yield to THFA are due to a relatively high concentration of acid centers and especially of strong acid centers.

4. Conclusions

The 3%Cu-0.5%Pd/γ-Al2O3 catalyst presents a specific high surface area and pore diameters specific to mesoporous catalysts. The furfural hydrogenation process was carried out in a fixed bed catalytic reactor, operated in continuous flow and isothermal conditions, temperature 135-220˚C, pressure 20-60 bar and a 0.15 h^{-1} LHSV. The main products obtained were furfuryl alcohol and tetrahydrofurfuryl alcohol. The catalyst was most efficient at 180˚C, 40 bar pressure giving a maximum furfural conversion of 97.84% with a 72.06% yield in furfuryl alcohol and 25.78% yield in tetrahydrofurfuryl alcohol. The yield in tetrahydrofurfuryl alcohol increases with pressure, reaching a maximum value of 35.57% at 160˚C and a 60 bar pressure.

A lower yield in THFA than in FA is due to an inappropriate ratio between Cu and Pd metal centers but also to an inadequate acid strength distribution.

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REFERENCES

[1] Bozell J.J., Petersen G.R., Technology development for the production of biobased products from biorefinery carbohydrates—the US Department of Energy's "Top 10" revisited, *Green Chemistry*, 12, (2010), 539–554.

[2] Yan K., Wu G., Lafleur T., Jarvis C., Production, properties and catalytic hydrogenation of furfural to fuel additives and value-added chemicals, *Renewable and Sustainable Energy Reviews*, 38, (2014), 663–676.

[3] Eseyin A.E., Steele P.H., An overview of the applications of furfural and its derivatives, *International Journal of Advanced Chemistry*, 3, (2015), 42-47.

[4] Bomboş D., Velea S., Bomboş M., Vasilievici G., Roşca P., Hydroconversion of Furfural Derivates on Ni-Co-Mo Catalysts, *Revista de Chimie*, 10, (2016), 67-71.

[5] Villaverde M.M., Garetto T.F., Marchi A.J., Liquid-phase transfer hydrogenation of furfural to furfuryl alcohol on Cu–Mg–Al catalysts, *Catalysis Communications,* 58, (2015), 6–10.

[6] O'Driscoll Á., Leahy J.J., Curtin T., The influence of metal selection on catalyst activity for the liquid phase hydrogenation of furfural to furfuryl alcohol, *Catalisys Today*, 279(2), (2017), 194-201.

[7] Merlo A.B., Vetere V., Ramallo-Lopez J.M., Requejo F.G., Casella M.L., Liquid-phase furfural hydrogenation employing silica-supported PtSn and PtGe catalysts prepared using surface organometallic chemistry on metals techniques, *Reaction Kinetics, Mechanisms and Catalysis*, 104(2), (2011), 467-482.

[8] Rodiansono, Astuti M.D., Santos U.T., Shimazu S., Hydrogenation of biomass-derived furfural over highly dispersed-aluminium hydroxide supported Ni-Sn (3.0) alloy catalysts, *Procedia Chemistry*, 16, (2015), 531 – 539.

[9] Jiménez-Gómez C.P., Juan A.C., Márquez-Rodríguez I., Moreno-Tost R., Santamaría-González J., Mérida-Robles J., Maireles-Torre P., Gas-phase hydrogenation of furfural over Cu/CeO2catalysts, *Catalysis Today*, 279(2), (2017), 327-338.

[10] Bhogeswararao S., Srinivas D., Catalytic conversion of furfural to industrial chemicals over supported Pt and Pd catalysts, *Journal of Catalysis*, 327, (2015), 65-77.