Fatty Acid Hydrotreatment Using Hypercrosslinked Polystyrene-Supported Pd Catalysts to Produce Biofuels

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Current work is devoted to the search of novel technologies of biofuel production from non-eatable or waste cooking oils and fats. One of such technique is hydrofining which includes the following processes – hydrodeoxygenation, hydrocracking, hydrogenation – and allows producing 2nd generation biodiesel in form of linear saturated hydrocarbons or alcohols with carbon number of 15-22. Palladium-containing catalytic systems on the base of hypercrosslinked polystyrene (HPS) with different metal loading were studied in stearic acid hydrodeoxygenation and hydrogenation processes to obtain target products (heptadecane and stearyl alcohol) with high yield. It was revealed, that the most effective catalytic system in both processes was the catalyst 1%Pd/MN-270, which allows achieving the high products yield in hydrodeoxygenation process (selectivity regarding n-heptadecane was 99% at 100% substrate conversion) as well as in hydrogenation reaction (selectivity regarding stearyl alcohol was 93% at 100% substrate conversion) of stearic acid.

1. Introduction

Triglycerides are biomass components which due to their composition can be used as a source for production of oxygen-containing compounds such as fatty acids, fatty aldehydes and fatty alcohols. Nowadays one of the typical methods of triglyceride processing is synthesis of biodiesel in the form of fatty acid methyl esters (FAME) (Alonso et al., 2010).

The same time FAME production is connected with a number of technical and ecological challenges the major of which are: (i) the use of methanol as an alkylation agent; (ii) fuel property dependence on the type and composition of raw materials; (iii) underdevelopment of non-eatable oil processing technologies. The last problem causes the concurrence between the use of eatable oils for both of food and biodiesel production (Glisic and Orlović, 2014). With an economical point of view the biodiesel production causes doubts in its feasibility due to the volatility of vegetable oil prices and hence biodiesel price instability. Furthermore at now the prices both of biodiesel and petroleum diesel are almost equal and biomass processing products cannot effectively compete with petroleum industry (Rios et al., 2006). That is why the researcher's interest is focused on the investigation of processing of waste cooking oil (Filho et al., 2014) or agricultural biomass (Pirozzi et al., 2015)

These problems can find a solution in the development of new technologies of triglycerides conversion into various compounds. Nowadays there are two main processes to convert fatty acids and their derivatives: deoxygenation to produce diesel-like hydrocarbons (Hermida et al., 2015) and hydrogenation to form fatty alcohols(Beller et al., 2015) which can be used both as highly effective fuel and feedstock of chemical production. Both of the processes are conducted in the hydrogen medium in the presence of metal based catalysts such as Ni supported on zeolites (Ma and Zhao, 2014) and alumina (Kordulis et al., 2015), Pd deposited on zeolites (Ayodele et al., 2014), Pt embedded on titania (Srifa et al., 2014) or silica oxides (Manyar et al., 2010), Cu and Fe oxides (Kandel et al., 2015).

Recent studies of novel catalysts showed that noble metal-containing catalytic systems based on the polymeric matrix of hypercrosslinked polystyrene (HPS) had a high efficiency in hydrogenation (Sulman et al., 2012) and hydrodeoxygenation (Stepacheva et al., 2014) reactions. Current research is aimed on the investigation of biofuel production in the form of saturated hydrocarbons and fatty alcohols in the presence of palladium nanoparticles supported on HPS.

2. Materials and Methods

2.1 Materials
For catalyst synthesis the following substances were used as received: hypercrosslinked polystyrene MN-270 (Purolite, UK), $Na_2PdCl_4 \cdot 6H_2O$ (99.9 %, Sigma-Aldrich), tetrahydrofuran (98.0 %, Sigma-Aldrich), methanol (99.0 %, Sigma-Aldrich). Stearic acid (98.0 %, KhimMedServis, Russia) as a model compound and dodecane (99.9 % Sigma-Aldrich) as a solvent were used in the hydrotreatment reactions.

2.2 Catalyst Synthesis and Characterization
3 g of HPS-MN270 particle fraction with size below 70 μm were preliminary treated with acetone and dried at vacuum and following impregnated for 10 min with mixture consisting of 4 mL of tetrahydrofuran, 1 mL of methanol, and 1 mL of water with precalculated amount of Na_2PdCl_4. Then the resulting systems were dried at 70±2 °C for 30 min, treated with the solution of Na_2CO_3 with the concentration 2.76 g/L for 15 min, washed with distilled water and dried again for 1.5 h at 70±2 °C. All the synthesized catalysts were reduced with hydrogen at 300 °C for 3 h. Palladium-containing catalysts (Pd/MN-270) with the palladium content of 5, 3 and 1 wt.% were synthesized.
The catalyst specific surface area, porosity and pore size distribution were determined by the method of nitrogen low-temperature adsorption on the analyzer Beckman Coulter SA 3100 (Coulter Corporation, USA). X-ray photoelectron spectroscopy (XPS) data were obtained using Mg Kα (hv = 1,253.6 eV) radiation with an ES-2403 spectrometer modified with an analyzer PHOIBOS 100 produced by SPECS (Germany).

2.3 Stearic Acid Hydrodeoxygenation
Hydrodeoxygenation process was carried out in a stainless steel reactor-cell of Parr Series 5000 Multiple Reactor System equipped with magnetic stirrer with the total volume 50 mL. Catalyst with mass 0.1 g and 30 mL solution of stearic acid in dodecane with concentration 0.1 mol/L were inputted into the reactor-cell. Then the reactor was purged with hydrogen to remove air and heated up to working temperature (255 °C) under a constant hydrogen pressure (0.6 MPa). The process was carried out at constant stirring of 1700 rpm to eliminate the influence of external mass-transfer. During the reaction the samples of liquid phase were taken every 30 minutes and analyzed using GC-2010 chromatograph and GCMS-QP2010S mass spectrometer (SHIMADZU, Japan).

2.4 Stearic Acid Hydrogenation
Stearic acid hydrogenation was carried out in a stainless steel reactor-cell of Parr Series 5000 Multiple Reactor System with the total volume 50 mL. 0.1 g of catalyst and 30 mL solution of stearic acid in dodecane with concentration 0.1 mol/L were inputted into the reactor-cell. Then the reactor was purged with hydrogen to remove air and heated up to working temperature (150 °C) under a constant hydrogen pressure (3 MPa) at constant stirring of 1700 rpm. The liquid phase samples were taken every 30 min during the reaction and analyzed by GC-MS.

3. Results and Discussion

3.1 Catalyst Characterization
The XPS and low temperature nitrogen physisorption data for synthesized catalysts are presented in Table 1.

Table 1: Physic-chemical analysis of catalyst samples

Catalyst	Surface area, m^2/g	Area of micropores, m^2/g	E_b Pd 3d5/2, eV	Pd Forms
MN-270	1,490	1,120	-	-
1%-Pd/MN-270	1,200	900	335.2 (88 %)	Pd
			337.4 (11 %)	PdO
3%-Pd/MN-270	820	630	335.2 (82 %)	Pd
			337.4 (18 %)	PdO
5%-Pd/MN-270	610	380	335.2 (78 %)	Pd
			337.4 (22 %)	PdO

These data shows that the BET surface area decreases with the increase of the Pd content. The Pd content increase also results in the decrease of the volume of the pores with the diameter less than 6 nm, which can be ascribed to the small pore blockage with nanoparticles. At the same time, the volume of mesopores with diameters 6 – 50 nm significantly increases (especially, for 5 %-Pd/MN-270) which can be assigned to the changes in the micro and mesopore ratio.

The values of binding energies for Pd $3d_{5/2}$ reveal that all the samples contain palladium mostly in the form of Pd(0). There is a fraction of partially oxidized Pd species which can be explained by oxidation of Pd nanoparticles upon air exposure. According to XPS data, only 0.8, 1.7 and 3.0 % were accessible for the catalysts with the estimated amount of palladium 1, 3 and 5 wt. %. That indicates that the increase in palladium content leads to the decrease of its accessibility and it should considerably decrease the catalyst specific activity. Such shielding of the active metal can be possibly explained by the decrease of its specific surface. If the addition of 1 % mass palladium decreases the specific surface area by $\approx$ 15 % than the addition of 5% decreases it by $\approx$ 40 %. The factors pointed out should contribute to the change in the activity of 3 and 5 %-Pd/MN-270 catalyst compared to the sample with 1% palladium.

3.2 Hydrodeoxygenation Process

In all the experiments of stearic acid hydrodeoxygenation a high selectivity of the final product – *n*-heptadecane – formation ($\approx$ 95 – 98 mol.%), up to the full conversion of the initial substrate, was observed. The main by-product of the reaction was *n*- pentadecane. The total of these products was ($\approx$ 100 %) within the limits of determination error. Considering to the purity of the initial substrate (98 %) it appears that *n*-pentadecane forms due to the presence of palmitic acid in the initial substrate (Grossman and Ortega, 2008).

The comparison of the activity of 1%-Pd/MN-270, 3%-Pd/MN-270 and 5%-Pd/MN-270 catalysts was made by the comparison of substrate consumption kinetic curves. The reaction selectivity on these catalysts remained high (~99 %). From Figure 1 it is seen that the kinetic curves of the substrate consumption with 3 %-Pd/MN-270 and 5 %-Pd/MN-270 catalysts slightly deviate from each other (Figure 1, curves 2 and 3) and show only insignificant increase in the reaction rate comparing to the catalysis with 1 %-Pd/MN-270 (Figure 1, curve 1).
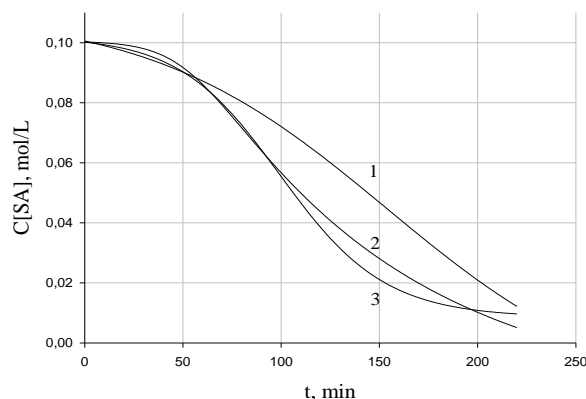

Figure 1: Stearic acid consumption depending on time for catalysts based on HPS MN-270 (1 – 1 %-Pd/MN-270; 2 – 3 %-Pd/MN-270; 3 – 5 %-Pd/MN-270)

A comparison of catalytic activity was made by TOF value (Table 2). It was founded that 1%-Pd/Mn-270 had the highest catalytic activity in comparison with both of HPS-based catalysts with higher metal loading and The reason for such a change is probably both the change of the catalyst specific surface area and mechanical blocking of the part of palladium nanoparticles in the catalyst.

Table 2: Activity and selectivity of HPS-based catalysts

Catalyst	TOF, s^{-1}	n-Heptadecane yield, %
1 %-Pd/MN-270	0.64	98.7
3 %-Pd/MN-270	0.32	98.5
5 %-Pd/MN-270	0.22	96.2

It is noteworthy that the selected catalyst (1 %-Pd/MN-270) remains its activity and selectivity regarding to the target product at the multiple usage (up to 20 times). Further experiments focused on the selection of

hydrodeoxygenation process optimal conditions showed that the following parameters allowed increasing of n-heptadecane yield up to 99.0 %: hydrogen partial pressure – 0.6 MPa; temperature – 255 °C; catalyst concentration - $3 \cdot 10^{-4}$ mol Pd/L; substrate concentration – 0.1 mol/L. Basing on the kinetic experiments it was founded that the apparent activation energy of hydrodeoxygenation process in the presence of 1 %-Pd/MN-270 catalyst was 85±5 kJ/mol.

3.3 Hydrogenation Process

In all the experiments of stearic acid hydrogenation the following main compounds were observed in the liquid samples: stearyl aldehyde, stearyl alcohol, n-heptadecane. Beside these compounds there were obtained the minor amounts of palmityc alcohol and n-pentadecane due to the presence of palmitic acid in the initial substrate. The analysis of kinetic curves for both of substrate consumption and product formation allowed suggesting the process behaviour by the consecutive way consisting of 3 stages: (i) aldehyde (intermediate product) formation; (ii) alcohol (target product) accumulation; (iii) hydrocarbon (side product) formation.

The comparison of the activity of 1 %-Pd/MN-270, 3 %-Pd/MN-270 and 5 %-Pd/MN-270 catalysts was made by the comparison of substrate consumption kinetic curves (Figure 2). From Figure 2 it is seen that 5 %-Pd/MN-270 catalyst (curve 3) has the highest substrate consumption rate.
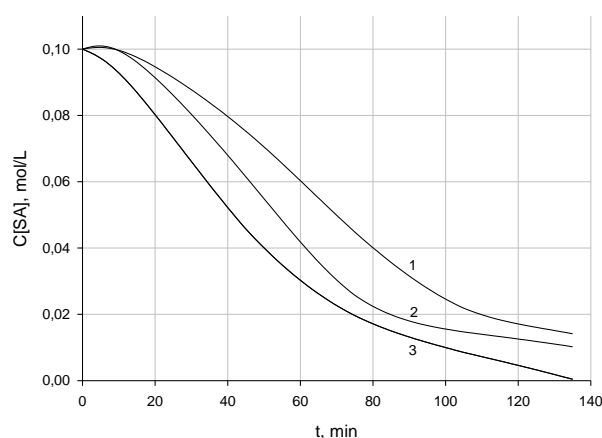

Figure 2: Stearic acid hydrogenation in the presence of catalysts based on HPS MN-270 (1 – 1 %-Pd/MN-270; 2 – 3 %-Pd/MN-270; 3 – 5 %-Pd/MN-270)

A catalyst choice was made basing on the both of catalytic activity (by TOF value) and selectivity regarding to the target product (stearyl alcohol) (Table 3). It was founded that 1 %-Pd/MN-270 was more preferable in comparison with catalysts with higher Pd content.

Table 3: Activity and selectivity of HPS-based catalysts in hydrogenation process

Catalyst	TOF, s^{-1}	Stearyl alcohol yield, %
1%-Pd/MN-270	1.20	93.4
3%-Pd/MN-270	0.58	92.0
5%-Pd/MN-270	0.59	91.3

Further experiments focused on the selection of hydrogenation process optimal conditions showed that the following parameters allowed increasing of stearyl alcohol yield up to 95.0 %: hydrogen pressure – 2.8 MPa; temperature – 150 °C; catalyst concentration - $3 \cdot 10^{-4}$ mol Pd/L; substrate concentration – 0.1 mol/L. Basing on the kinetic experiments it was founded that the apparent activation energy of hydrogenation process in the presence of 1 %-Pd/MN-270 catalyst was 60±5 kJ/mol.

3.4 Mathematical modeling

For mathematical description of kinetic curves transformation method was used (Schmidt and Sapunov, 1982). The kinetic curves of stearic acid consumption were superimposed onto one curve (Figure 3) that was chosen as a standard by linear transformation of time base (multiplication of time by coefficient η). Numerical values of coefficient η correspond to the change in catalytic activity of the studied catalysts.
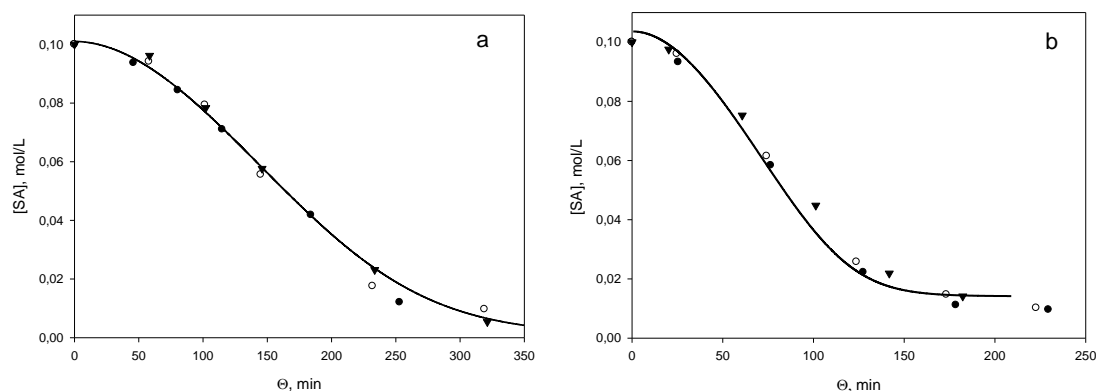
Figure 3: Generalized curves of stearic acid consumption for hydrodeoxygenation (a) and hydrogenation (b) processes (signs – experimental; line – calculated)

Toestimateaconfidencelimitfortheexperimentaldataobtainedattimelineartransformation (Figure 3) weattemptedtofinda mathematical description for generalized kinetic curve in the form of differential equation. According to the kinetic equation of stearic acid consumption Eq(1) the dependence of reaction rate on catalyst concentration can be expressed as a cofactor Eq(2).

$$\frac{d[SA]}{dt} = -F([SA],[cat]) \tag{1}$$

$$\frac{d[SA]}{dt} = -F_1([cat])F_2([SA]) \tag{2}$$

Whilechoosingkineticcurvefor one of the catalysts $[cat]_0$ as a "standard" Eq(3) the curves for other catalysts will be defined by the Eq(4) considering transformation coefficient η.

$$\frac{d[SA]}{dt} = -F([SA],[cat]_0) \tag{3}$$

$$\frac{d[SA]}{dt} = -\frac{F_1([cat]_i)}{F_1([cat]_0)} F([SA],[cat]_0) \equiv -\eta F([SA],[cat]_0) \tag{4}$$

$$\frac{d[SA]}{dt\eta} = -F([SA],[cat]_0) \tag{5}$$

Therefore according Eq(5) kineticcurvesmustbecongruentin coordinates [SA] ~ η*t at equal initial substrate concentration.

Eq(6) is a mathematical equation described stearic acid consumption for both hydrodeoxygenation and hydrogenation process (Figure 3, lines) with a high determination coefficient $R^2 = 0.987$. The constant values was found to be as following: for hydrodeoxygenation process $k_f = 0.005$ min^{-1}, $k(I) = 2.2$ min^{-1}, $K = 0.011$; for hydrogenation process $k_f = 0.01$ min^{-1}, $k(I) = 2.7$ min^{-1}, $K = 0.023$; $\tau = \eta \cdot t$.

$$\frac{d[SA]}{dt} = -\frac{\eta \cdot k(I) \cdot (1 - \exp(-k_f \cdot \tau)) \cdot [K] \cdot [SA]}{(1 + K \cdot [SA])} \tag{6}$$

4. Conclusions

The study of the influence of Pd-containing catalysts based on HPS on stearic acid hydrogenation and hydrodeoxygenation showed that for both of the processes the most effective catalyst was 1 %-Pd/MN-270 allowed obtaining high target product yield: up to 99.8 % of n-heptadecane and up to 95 % of stearyl alcohol. It was founded that HPS-based catalysts remained catalytic activity and selectivity regarding to the target

product in multiple uses. A mathematical modeling for studied processes was done basing on linear transformation of time coordinate and the constant values were defined.

References

Alonso D.M., Bond J.Q., Dumesic J.A. 2010, Catalytic conversion of biomass to biofuels, Green Chemistry, 12, 1493–1513.

Ayodele O.B., Abbas H.F., Ashri Wan Daud W.M., 2014, Hydrodeoxygenation of Stearic Acid into Normal and Iso-Octadecane Biofuel with Zeolite Supported Palladium-Oxalate Catalyst, Energy Fuels, DOI: 10.1021/ef501325g.

Beller H.R., Lee T.S., Katz L., 2015, Natural products as biofuels and bio-based chemicals: fatty acids and isoprenoids, Natural Products Reports, DOI: 10.1039/c5np00068h.

Filho S.C.S., Silva T.A.F., Miranda A.C., Fernandes M.P.B., Felício H.H., Calarge F.A., Santana J.C.C., Tambourgi E.B., 2014, The Potential of Biodiesel Production from Frying Oil Used in the Restaurants of São Paulo city, Brazil, Chemical Engineering Transactions, 37, 577-582.

Glisic S.B., Orlović A.M., 2014, Review of biodiesel synthesis from waste oil under elevated pressure and temperature: Phase equilibrium, reaction kinetics, process design and techno-economic study, Renewable and Sustainable Enzergergy Reviews, 31, 708-725.

Grosman A, Ortega C., 2008, Capillary condensation in porous materials: hysteresis and interaction mechanism without pore blocking/percolation process, Langmuir, 24, 3977–3986.

Hermida L., Abdullah A.Z., Mohamed A.R., 2015, Deoxygenation of fatty acid to produce diesel-like hydrocarbons: A review of process conditions, reaction kinetics and mechanism, Renewable and Sustainable Energy Reviews, 42, 1223-1233.

Kandel K., Chaudhary U., Nelson N.C., Slowing I.I., 2015, Synergistic Interaction between Oxides of Copper and Iron for Production of Fatty Alcohols from Fatty Acids, ACS Catalysis, 5, 6719-6723.

Kordulis C., Bourikas K., Gousi M., Kordouli E., Lycourghiotis A., 2015, Development of nickel based catalysts for the transformation of natural triglycerides and related compounds into green diesel: a critical review, Applied Catalysis B, Environmental, DOI: 10.1016/j.apcatb.2015.07.042.

Ma B., Zhao C., 2014, High-grade diesel production by hydrodeoxygenation of palm oil over a hierarchically structured Ni/HBEA catalyst, Green Chemistry, DOI: 10.1039/C4GC02339K.

Manyar H.G., Paun C., Pilus R., Rooney D.W., 2010, Highly selective and efficient hydrogenation of carboxylic acids to alcohols using titania supported Pt catalysts, Chemical Communications, 46, 6279-6281.

Pirozzi D., Ausiello A., Fagnano M., Fiorentino N., Sannino F., Toscano G., Zuccaro G., 2015, Innovative Methods for the Production of II Generation Biodiesel by Exploitation of Agricultural Biomasses Through the Use of Oleaginous Yeasts, Chemical Engineering Transactions, 43, 253-258.

Rios L.A., Restrepo G.M., Valencia S.H., Franco A.C., Echeverri D.A.Z. 2006, La hidrogenacion selectiva de aceites naturales a traves de catalizadores heterogeneos, Scientia et Technica Ano XII, 31, 221-226.

Schmidt R., Sapunov V.N., 1982, Non-Formal Kinetics. Monographs in Modern Chemistry. Verlag Chemie Weinheim, Deerfield Beach-Florida, Basel, Germany

Srifa A., Faungnawakij K., Itthibenchapong V., Assabumrungrat S., Thompson J.M., Hardacre C., 2014, Roles of monometallic catalysts in hydrodeoxygenation of palm oil to green diesel, Chemical Engineering Journal, DOI: 10.1016/j.cej.2014.09.106.

Stepacheva A.A., Nikoshvili L.Zh., Sulman E.M., Matveeva V.G., 2014, Hydrodeoxygenation of stearic acid for the production of "green" diesel, Green Process and Synthesis, 3, 441–446.

Sulman E.M., Nikoshvili L.Zh., Matveeva V.G., Tyamina I.Yu., Sidorov A.I., Bykov A.V., 2012, Palladium Containing Catalysts Based on Hypercrosslinked Polystyrene for Selective Hydrogenation of Acetylene Alcohols, Topics in Catalysis, 55, 492-497.