

Catalytic Hydrogenolysis of Softwood Sawdust

Elena I. Shimanskaya, Mikhail G. Sulman, Irina Yu. Tiamina, Alexander I. Sidorov, Vladimir P. Molchanov, Esther M. Sulman

Tver State Technical University, A.Nikitin emb., 22, 170026, Tver, Russian Federation
shimanskaya-tstu@yandex.ru

The article presents the results of the process of hydrogenolysis of lignin obtained from softwood sawdust using 5% Pt/MN270 and 3% Pt/MN270 catalysts. Depending on the desirable products 2-propanol was chosen as the solvent showing the highest substrate conversion and product yield. Pt polymer-based catalyst provides high substrate conversion compared to Pd catalysts. This can be due to the higher surface area and the higher active metal concentration on the catalyst surface. Also, it is notable, that Pt-containing catalyst results in the lowest formation of oxygen-containing products. The highest conversion (90%) and the highest selectivity towards the oxygen-free hydrocarbons (92%) were achieved while using 5% Pt catalyst based on HPS.

1. Introduction

Recycling of industrial waste is one of the main problems for researchers now. Lignin is the most difficult to dispose of waste, which is formed in the process of chemical processing of wood in pulp and paper and hydrolysis plants. Food waste such as rice and buckwheat husks, sunflower husks, etc is also rich in lignin (Sluiter et al., 2010). However, due to its composition, lignin can be used as a potential source of important chemical compounds that can be used as biofuels (Gallezot, 2010)

This feature of lignin allows to solve the second important problem - the depletion of fossil energy sources (Lomovsky, 2015). The use of biofuels significantly reduces the number of harmful emissions and can solve the problem of environmental and energy security in a modern technological society (Anwar et al., 2014). Lignocellulosic biomass is the raw material for bioethanol (Farrell, 2006) and biodiesel production. (Kuznetsov, 2009). Currently, the main process of biofuel obtaining is to manufacture it on the basis of hydrotreated esters and fatty acids, but this process has drawbacks (Stepacheva et al., 2016). Due to the limited amount of used oils and fats and the absence of large amounts of non-edible oils, it is not appropriate to use different types of oils and fats as raw materials. Less developed area, but more attractive from an economic and environmental point of view is the transformation of lignin-containing biomass into bio-oil by pyrolysis which results in the formation of mainly high-boiling products with a high oxygen content (Bridgwater et al., 1990) to obtain fuel from which it is necessary to subject it to catalytic cracking and hydrotreating. However, pyrolysis itself requires quite a lot of energy costs.

The processes of direct catalytic hydrogenolysis of lignocellulosic biomass are of great interest (Karkas 2017). This method allows obtaining valuable chemical products under relatively mild conditions as a result of β -O-4-bond between polymer lignin units cleavage (Xu et al., 2014). And also allows reducing energy and economic costs for the synthesis of biofuels by reducing the duration and temperature of the process (Shimanskaya et al., 2018). Depolymerization of lignins by this method can be carried out in a variety of solvents (for example, water, methanol, ethanol, isopropanol, acetone (Warner et al., 2014). The reaction is carried out in the presence of various catalysts based on transition and noble metals fixed on different carriers (aluminosilicates, carbon materials) (Deepa et al., 2015)

The main limitation for the application of lignin hydrogenolysis processes are the processes of condensation and coke formation, which leads to the deactivation of catalysts. The literature presents studies of the process of hydrogenolysis of lignin to produce substituted phenols. Thus, the reaction is proposed to conduct ligninases by fragmentation of the polymer and the fragmented particles hydrogenolysis over Ni-catalyst with a

Paper Received: 28 March 2018; Revised: 30 July 2018; Accepted: 25 December 2018

Please cite this article as: Shimanskaya E., Sulman M., Tiamina I., Sidorov A., Molchanov V., Sulman E., 2019, Catalytic Hydrogenolysis of Softwood Sawdust, Chemical Engineering Transactions, 74, 229-234 DOI:10.3303/CET1974039

solvent as a hydrogen donor of propyl gallate and propyl silane with a yield up to 97% at 50% conversion (Song et al., 2013). Similar phenols were obtained in a 47% yield based on the lignin content in birch wood at a hydrogen pressure of 60 bar using Nickel carbide and tungsten on activated carbon catalysts with ethylene glycol as a solvent (Li et al., 2012). Hydrogenation of alkaline lignin was carried out in the presence of Pd/C catalyst at a hydrogen pressure of 1~5 MPa, which increased the total amount of hydroxyl, phenolic hydroxyl and hydroxyl alcohol to 64.23%, 37.10% and 89.67%, respectively, while carbonyl and carboxyl reduce separately to 43.50% and 53.41% (Jie-Wang et al., 2012). It was shown that model compounds of lignin can be converted with the release of the monomers up to 99%, but these reactions still need to be demonstrated on real feed lignin (Nichols et al., 2010).

Chapter 2 In this work catalysts consisting of platinum group metals deposited on hypercrosslinked polystyrene (HPS) were investigated in the process of hydrogenolysis of lignin isolated from softwood sawdust. These catalysts show high activity in the hydrogenation process and have high stability.

2. Experimental part

2.1 Extraction of lignin from softwood sawdust

Lignin was isolated after the hydrolysis of cellulose using the solution of the following composition: 24.7 wt % CH_3COOH + 5.3 wt % H_2O_2 + 2 wt % H_2SO_4 under standard conditions for 3 h. Then the lignin was filtered on a Buechner funnel and dried. The yield of lignin was 15 ± 1.5 wt %. With the help of infrared spectroscopy, the comparison of the isolated lignin with industrial one was carried out, the main peaks coincide.

2.2 The method of catalysts preparation

Catalysts were synthesized as follows: 3 g of the HPS brand MN270 (Purolite, USA) with the mean particle size of 80 μm was preliminary washed with water and acetone and dried to a constant mass in vacuum. Then it was treated with a solution of the calculated amount of metal precursor (hexachloroplatinic acid for Pt/MN270 and sodium chloropalladate for Pd/MN270) in a complex solvent THF – methanol-water at room temperature for 8-10 minutes. Then it was dried at 80 °C for 40 minutes and washed with sodium hydrocarbonate aqueous solution and water until the absence of chloride-anion reaction in the scouring waters. The washed catalysts were dried at 80 °C for 90 minutes and reduced at 300 °C for 3 hours. Thus, the following catalytic systems were synthesized: 3% Pd/MN270, 5% Pd/MN270, 3% Pt/MN270, 5% Pt/MN270.

2.3 The process of lignin hydrogenolysis

The process of hydrogenolysis was carried out for 4 hours in the reactor in a hydrogen atmosphere under the following conditions: substrate weight – 1.0 g, catalyst weight – 0.1 g, temperature – 300 °C, hydrogen partial pressure – 2 MPa, solvent volume – 30 mL. The following polar solvents were used: 2-propanol, water, and ethanol. Substrate conversion was calculated at the end of the reaction basing on the difference between the initial mass of the substrate and the dry weight of the residue.

2.4 Analysis of the reaction products

The liquid phase was sampled every 30 minutes. Analysis of samples of the liquid phase was carried out using gas chromatographic mass spectrometry using the chromatograph GC-2010 and the mass spectrometer GCMS-QP2010S (SHIMADZU, Japan). The analysis duration was 25 minutes with the following conditions: initial column temperature of 150 °C was maintained for 5 min, and then the temperature was increased up to 250 °C with the heating rate 5°K/min.

3. Results and Discussion

3.1 Noncatalytic hydrogenolysis of lignin

The process of hydrogenolysis of isolated lignin was first carried out in the absence of catalysts. Trace amounts of aromatic hydrocarbons were found in this study. There is no influence of pressure on the non-catalytic process. The similar conditions were created in the absence of hydrogen (in a nitrogen atmosphere). There is not much difference in the result.

3.2 Catalytic hydrogenolysis of lignin

Catalytic hydrogenolysis of lignin leads to the formation of the following products: phenol, 2-methylphenol, 2,6-dimethylphenol, 2-methoxyphenol, 2,4,6-trimethylphenol, 2-methoxy-5-2-methylphenol, 2-isobutyl phenyl, 4-methylbenzene-1,2-diol, 2,6-dimethylbenzene-1,4-diol, 2-methyl-6-propyl phenol, benzene, toluene, 4-

isopropylbenzene, 1-methoxy-4-methyl-2-isopropylbenzene, 1,4-dimethoxy-2-methylbenzene, 1-butyl-4-methoxybenzene, cyclohexane, as well as some carboxylic acids, esters, aldehydes, ketones and alcohols. The most important are oxygen-free compounds.

The highest yield was obtained using the catalyst 5% Pt/MN270. Figure 1 shows the dependency of the yield of liquid products on the type of catalyst.

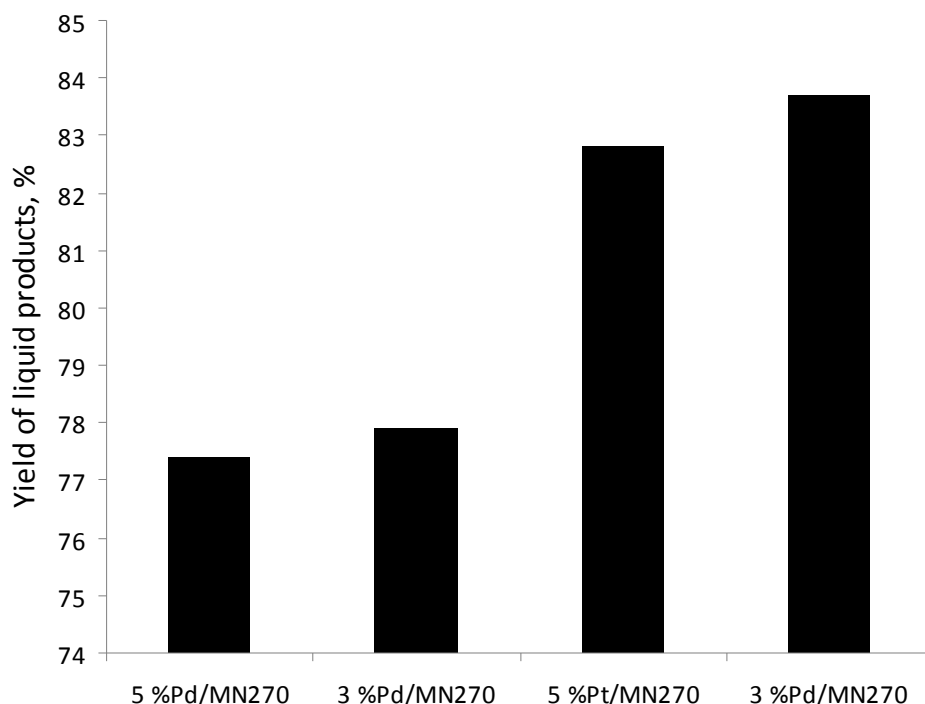


Figure 1: The dependence of the yield of liquid products on the catalyst

The data presented in Table 1 shows the selectivity of the studied catalysts. A catalytic system based on Pt shows higher selectivity compared to the catalytic systems based on Pd.

Table 1: Results of catalysts testing in the process of hydrogenolysis of lignin

Catalyst	The relative speed at 30 % conversion, C ⁻¹	Selectivity *, %	The conversion at maximum selectivity, %
5% Pd/MN270	3.45	87	89
3% Pd/MN270	3.40	87	89.6
5% Pt/MN270	3.55	92	90
3% Pt/MN270	3.53	92	91

*to oxygen-free compounds

The amount of metal does not affect the selectivity of the process, but rather the relative speed, so the maximum selectivity is achieved at a lower conversion. Figure 2 shows the dependence of selectivity on conversion for catalysts 5% Pt/MN270 and 3% Pt/MN270.

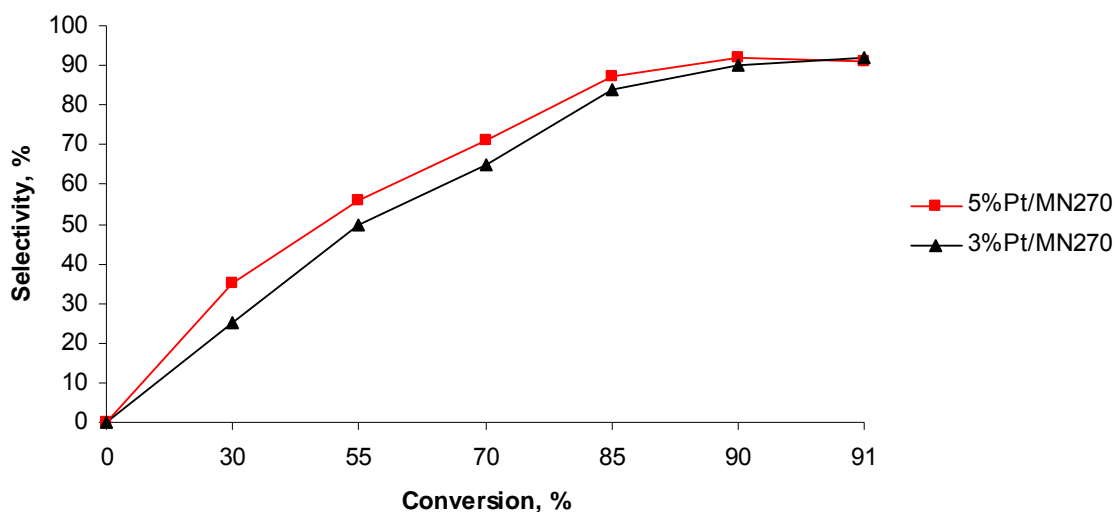


Figure 2: The dependence of selectivity on conversion for catalysts 5% Pt/MN270 and 3% Pt/MN270

To understand the difference between the activities of investigated catalyst the physicochemical studies have been conducted. The oxidation state of metals and binding energy were determined by X-ray photoelectronic study, determination of the specific surface area and porosity of catalysts was carried out by low-temperature nitrogen adsorption. The higher activity of the Pd-containing catalysts can be explained by the greater access of the substrate to the catalytic active centres.

Table 2: Results of catalysts testing in the process of hydrogenolysis of lignin

Catalyst	S_{BET} , m^2/g	$S_{\text{t-plot}}$, m^2/g	Binding energy, eV	The state of the metal
5% Pd/MN270	649.48	94.23 *	337.8 ± 0.1	Pd ⁰ Pd ⁺²
		553.24 **		
		647.47 ***		
		72.22 ¹⁾		
3% Pd/MN270	705.40	630.28 ²⁾	337.6 ± 0.1	
		702.50		
		453.13 *		
5% Pt/MN270	968.36	492.24 **	74.1 ± 0.1	Pt ⁰ Pt ⁺²
		945.37 ***		
		470. *		
		650.42 *		
3% Pt/MN270	1015.78	1120.60 ***	71.3 ± 0.1	

* surface area of macropores

** surface area of micropores

*** total t-plot surface area

3.3 The solvent effect

In order to study the solvent influence on lignin processing, three solvents (ethanol, 2-propanol, and water) were used in the presence of the 5% Pt/MN270 catalyst. The substrate conversion values were 45% in a water medium, 90% in 2-propanol and 57% in ethanol. While the hydrogenolysis was carried out in a water medium the highest yield of phenolic compounds was obtained. It can be explained by the higher polarity of water in comparison with the other solvents used. However, we focused on the production of hydrocarbons, thus, depending on the desirable products 2-propanol was chosen as the solvent showing the highest substrate conversion and product yield.

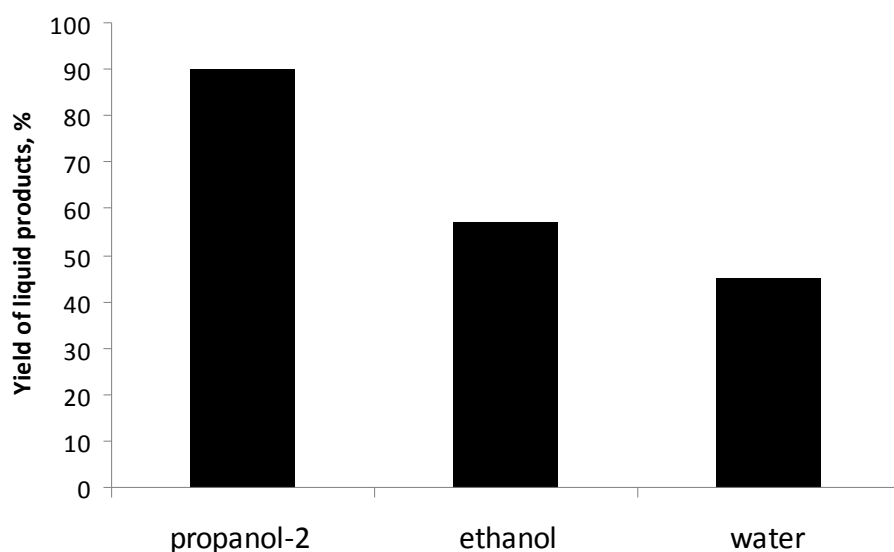


Figure 3: The solvent effect on the process of hydrogenolysis

4. Conclusions

Among the products obtained during hydrogenolysis of lignin-containing raw materials fuel-like aromatic and cyclic hydrocarbon (benzene, toluene, and cyclohexane), as well as phenolic compounds are the most promising. The latter can be used as additives to conventional fuels and fuels derived from biomass. Moreover, a number of cyclic and aromatic hydrocarbons may also be used in various fields of fine chemicals production as solvents and reagents. The use of the catalytic system based on platinum group metals allows obtaining a high yield of valuable products. Moreover, the synthesized polymer-based catalysts showed high stability in the hydrogenolysis process (up to 5 consecutive cycles without any regeneration).

Pt polymer-based catalyst provides high substrate conversion compared to Pd catalysts. This can be due to the higher surface area and the higher active metal concentration on the catalyst surface. Also, it is notable, that Pt-containing catalyst results in the lowest formation of oxygen-containing products (phenols and methylcyclohexane). The highest conversion (90%) and the highest selectivity towards the oxygen-free hydrocarbons (92%) were achieved while using 5% Pt catalyst based on HPS.

Acknowledgments

This study was funded by the RSF project, grant number 18-79-00303.

References

- Anwar Z. Gulfranz M., Irshad M., 2014, Agro-industrial lignocellulosic biomass a key to unlock the future bio-energy: a brief review, *Journal of Radiation Research and Applied Sciences*, 7(2), 163-173.
- Bridgwater A.V., Grassi G., *Biomass pyrolysis liquids upgrading and utilization*, 1990, Elsevier applied science, London.
- Deepa A.K., Dhepe P.L., 2015, Lignin depolymerization into aromatic monomers over solid acid catalysts, *ACS Catal*, 5, 365-379.
- Farrell A.E., Plevin R.J., Turner B.T., Jones A.D., O'Hare M., Kammen D.M., 2006, Ethanol can contribute to energy and environmental goals, *Science*, 311, 506-508.
- Gallezot P., 2010, Alternative value chains for biomass conversion to chemicals, *Topics in catalysis*, 53 (15-18), 209-1213.
- Jie-wang Y., Gui-Zhen F., Chun-de J., 2012, Hydrogenation of Alkali Lignin Catalyzed by Pd/C, *APCBEE Procedia*, 3, 53 – 59
- Karkas M. D., 2017, Lignin Hydrogenolysis: Improving Lignin Disassembly through Formaldehyde Stabilization, *ChemSusChem*, 10, 2111– 2115.
- Kuznetsov B.N., Sharypov V.I., Kuznetsova S.A., Tarabanko V.E., Ivanchenko N.M., 2009, The study of different methods of bio-liquids production from wood biomass and from biomass/polyolefine mixtures, *International Journal of Hydrogen Energy*, 34, 7051–7056.

- Li C., Zheng M., Wang A., Zhang T., 2012, One-pot catalytic hydrocracking of raw woody biomass into chemicals over supported carbide catalysts: simultaneous conversion of cellulose, hemicellulose, and lignin, *Energy Environ. Sci.*, 5, 6383-6390.
- Lomovsky O., Bychkov A., Lomovsky I., Logvinenko V., Burdukov A., 2015, Mechanochemical production of lignin-containing powder fuels from biotechnology industry waste, *Thermal Science*, 19, 219-229.
- Nichols J. M., Bishop L. M., Bergman R. G., Ellman J. A., 2010, Catalytic C-O Bond Cleavage of 2-Aryloxy-1-arylethanol and its Application to the Depolymerization of Lignin Related Polymers, *Am. Chem. Soc.*, 132, 12554-12555.
- Shimanskaya E.I., Rebrov E., Filatova A.E., Matveeva V.G., Sulman M.G., Sulman A.M., 2018, Catalytic hydrogenolysis of different types of lignin obtained from sawdust softwood *Chemical Engineering Transactions*, 70, 361-366.
- Sluiter J.B., Ruiz R.O., Scarlata C.J., Sluiter A.D., Templeton D.W., 2010, Compositional analysis of lignocellulosic feedstocks. 1. Review and description of methods, *Journal of agricultural and food chemistry*, 58, 9043-9053.
- Song Q., Wang F., Cai J., Wang Y., Zhang J., Yu W., Xu J., 2013, Lignin depolymerization (LDP) in alcohol over nickel-based catalysts via a fragmentation-hydrogenolysis process, *Energy Environ. Sci.*, 6, 994-1007.
- Stepacheva A.A., Matveeva V.G., Sulman E.M., Sapunov V.N., 2016, Fatty acid hydrotreatment using hypercrosslinked polystyrene-supported Pd catalysts to produce biofuels *Stepacheva, A.A., Chemical Engineering Transactions*, 52, 625-630.
- Warner G., Hansen T.S., Riisager A., Beach E.S., Barta K., Anastas P.T., 2014, Depolymerization of organosolv lignin using doped porous metal oxides in supercritical methanol. *Bioresour. Technol.*, 161, 78-83.
- Xu C., Arancon R.A., Labidi J., Luque R., 2014, Lignin depolymerization strategies: towards valuable chemicals and fuels. *Chem. Soc. Rev.*, 43(22), 7485-7500.