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Catalytic Hydrogenolysis of Different Types of Lignin Obtained from Sawdust Softwood

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The article presents the results of the process of hydrogenolysis of lignin obtained by three different methods from softwood sawdust: alkaline, sulfuric acid, acetic acid. It is shown that the isolation process has a strong impact on the conversion of feedstock and on the yield of products. The maximum conversion of 67.5 % was observed in the case of acetic lignin in propanol-2 as a solvent, and the highest yield of liquid products (38.5 wt.%) was obtained in the case of using an alkali lignin. On the basis of the conducted researches it was shown that the catalytic system 3 % Ru/MN 270 is more active in the process of hydrogenolysis than 3 % Pd/MN270, but Pd requires a lower temperature and pressure for the process. When using both catalysts a large number of derivatives of phenol, which can be used as alternative fuel are formed. The optimal process conditions are: 3 % Ru/MN270 - temperature 300 ° C, partial hydrogen pressure of 4 MPa, the ratio of substrate/catalyst is 20:1, for 3 % Pd/MN270 temperature 250 °C, the partial pressure of hydrogen of 2 MPa, the volume of solvent 30 mL, the ratio of substrate/catalyst 15/1.

1. Introduction

Currently, due to the gradual decrease in global oil reserves, the tendency of searching for new ways of obtaining of hydrocarbon fuels is increasing. In order to make a full transition to alternative fuels, it is necessary to change the types of engines, which will entail high costs (Bi et al., 2015).

Therefore, the most relevant direction is the development of additives to existing fuels that will reduce carbon dioxide emissions into the atmosphere, as well as use of alternative sources of raw materials for fuel without changing the engine type (Peiyan et al., 2015).

The use of non-food renewable raw materials, in particular, waste from the pulp and paper industry, will solve two important environmental problems at once, such as the creation of new alternative fuels and waste processing with the production of industrially important chemicals (Alonso et al., 2010).

The content of native lignin in the plant biomass reaches 35 wt.%. Due to its chemical composition and structure (Solimene et al., 2016), lignin can be considered as a promising, renewable raw material for the production of alkylaromatic (Yang et al., 2017) and saturated hydrocarbons (Borges et al., 2009), which can be used as components of motor and aviation fuels (Chiaramonti et al., 2016).

Hydrogenation of lignin-containing raw materials is one of the promising methods for producing such hydrocarbons. Current researches on the processing of lignin aimed at its thermal degradation (slow and rapid pyrolysis and gasification) (Bozell et al., 2014). Along with the use of combustible gaseous products, thermal methods lead to the formation of so-called bio-oils - complex mixtures containing phenolic derivatives, aromatic hydrocarbons and olefins.

However, direct use of bio-oil is not possible due to the high oxygen content and fuel properties - density, ash content, heat value (Bulushev et al., 2011). Currently, there is a growing interest in the combined processes of lignin conversion into liquid fuel. One of these processes is hydrotreating.

Typically, the lignin hydrotreating process will include solvolization and hydrogenation reactions that are carried out in various solvents (especially in polar ones) in the presence of metal-based catalysts such as CoMo and NiMo deposited on activated carbon (Horacek et al., 2012), platinum-based catalysts on aluminum (Saiadi et

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al., 2015), palladium deposited on HZSM-5 zeolite (Jan et al., 2015) and ruthenium deposited on TiO_2 (Kloekhorst et al., 2015). In this work, during the hydrotreating of lignin, catalytic systems based on hypercrosslinked polystyrene containing ruthenium and palladium catalytic systems were tested.

Softwood sawdust was used as a substrate. The substrate was obtained from the sawmill of Sandovsky district of Tver region. Three types of lignin obtained from sawdust of softwood were used for hydrogenolysis experiments: alkaline lignin, sulfuric acid lignin and acetic lignin.

With the aim of improving of conversion and selectivity different catalytic systems, representing the active nanoparticles of metals, stable in hypercrosslinked polystyrene were applied. These systems show high activity in hydrogenation processes (Tsyurupa et al., 2003), which justifies their use in the hydrogenolysis process (Qingquan et al., 2010).

2. Experimental part

2.1 Extraction of lignin from softwood sawdust

In laboratory conditions, the extraction of alkali lignin from softwood sawdust was carried out after pre-hydrolysis of hemicelluloses. Then the lignin was boiled in 2n NaOH solution for 3 h, then was filtered on a Buechner funnel and dried at a temperature of 102 °C (Brown et al.,1967). The yield of alkali lignin (black powder) was about 6.3 ± 0.3 wt %.

Sulfuric acid lignin was obtained by the Klasson method. Initially, 1 g of sawdust was placed in a bux and kept in 25 mL of 72 % sulfuric acid at 25 °C for 1.5 h, then the mixture was transferred to a flask of 250 mL, 200 mL of water was added and boiled with a reflux for 3 h, after which the lignin was filtered on a Buhner funnel and dried at 102 °C (Chen et al., 2010). The yield of sulfuric acid lignin (dark brown powder) reached 21.0 ± 1.7 %.

Acetic lignin was obtained using the solution of the following composition: 24.7 wt % CH_3COOH + 5.3 wt % H_2O_2 + 2 wt % H_2SO_4, the treatment was carried out under standard conditions for 3 h, after which the lignin was filtered on a Buechner funnel and dried at a temperature of 102 °C (Chen et al., 2011). The yield of acetic lignin (dark brown powder) was less than 15 ± 1.5 wt %. The dependence of the yield of lignin on the isolation method shown in Figure 1.

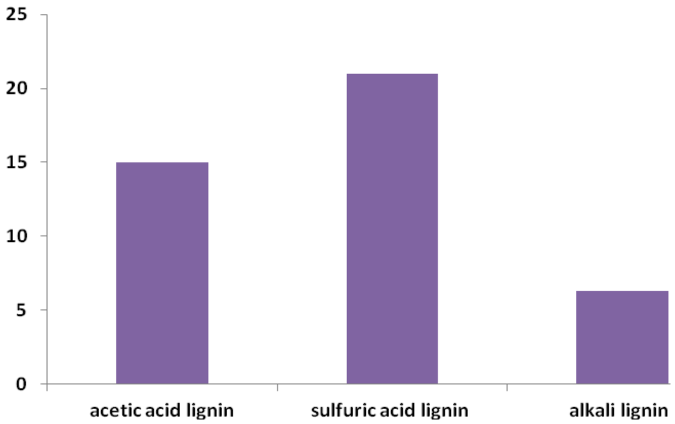

Figure 1: The dependence of the yield of lignin on the isolation method

2.2 The method of catalysts preparation

The catalysts were synthesized by impregnation of HPS brand MN270 (Purolite Inc. UK) by water capacity with aqueous solutions of precursors (ruthenium hydrochloride (Ru(OH) Cl_3 (Manaenkov et al., 2014) and sodium tetrachloride ($Na_2[PdCl_4]$) in a complex solvent: tetrahydrofuran + methanol + water at a ratio of 4:1:1 at room temperature (Sapunov et al., 2013).

The catalyst was dried at a temperature of 70 °C and treated with a mixture of sodium hydroxide and hydrogen peroxide at 80 °C. Then the catalysts were washed with water until disappearance of the reaction to the chloride-anions in the washing water and dried at 85 °C. The catalysts were reduced in a current of hydrogen at atmospheric pressure and an average temperature of about 300 °C for 2 h (Matveeva et al., 2017) and catalysts with a content of 3 % of metal were synthesized.

2.3 The process of lignin hydrogenolysis

The process of hydrogenolysis was carried out in active mode, the Parr Series 5000 Multiple Reactor System in an isopropanol media. Such parameters as hydrogen partial pressure (from 2 to 4 MPa), temperature (from 200 to 300 °C) and substrate/catalyst ratio were varied. The reactor was introduced with samples of lignin and catalysts, then 50 mL of solvent (2-propanol or ethanol) was added, the mixture was blown three times with nitrogen, and then heated to the operating temperature in the atmosphere of nitrogen.

Then the reactor was blown with hydrogen and the reaction was carried out at the working values of the hydrogen pressure. The reaction was carried out with intensive stirring (1,500 rpm) to eliminate intra-diffusion braking for 3 h. Sampling was carried out every 30 min. To determine the degree of lignin conversion, the dry residue was dried and weighed after the end of the reaction (Shimanskaya et al., 2018).

2.4 Analysis of the reaction products

Analysis of reaction products is carried out on gas chromatograph GC-2010 equipped with a mass spectrometer under the following conditions: the temperature of the sample - 260 °C, column temperature (HP - 1, length 100.0 m) - 50 °C, carrier gas pressure - 192.9 kPa, flow rate-20 mL/min by the following program: holding by 8 min at 50 °C, then heating to 280 °C, the total analysis time - 45 min.

3. Results and discussions

The extraction method has a significant impact on the degree of lignin conversion and yield of liquid products. Maximum conversions 67.5 and 67.0 wt.% were obtained in experiments with acetic lignin using 2-propanol and ethanol, respectively in the presence of 3 % Ru/MN270 (Figure 2). The highest yields of low boiling liquid products 38.5 and 38.0 wt. % were obtained in experiments with alkaline lignin while using 3 % Ru/MN270 and 3 % Pd/MN270 as shown in Figure 3. Sulfuric acid lignin showed the lowest degree of conversion and yield of liquid products in the presence of both catalytic systems in all solvents. The results of catalytic testing in the process of different types of lignin hydrogenolysis shown in Table 1.

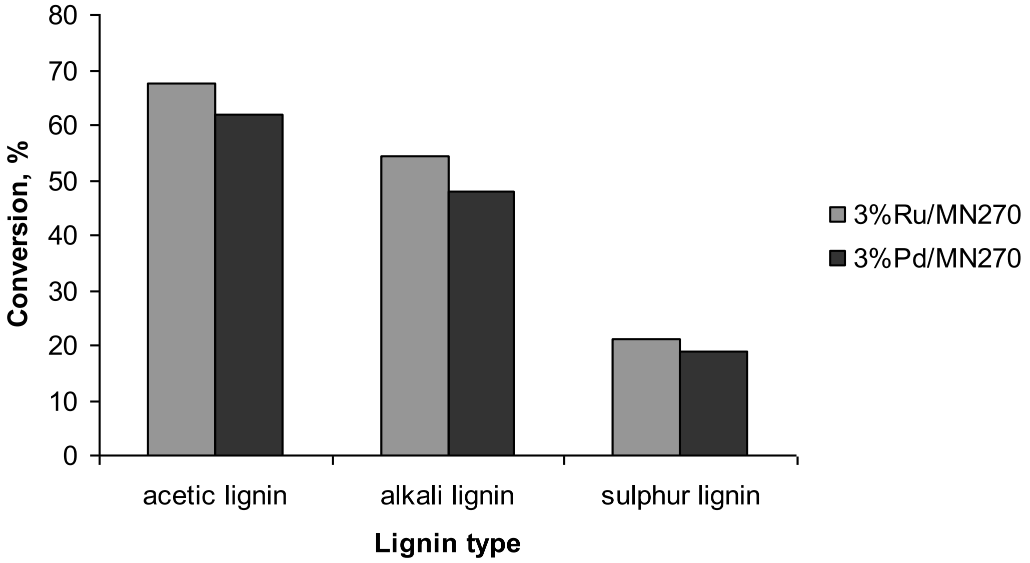

Figure 2: The dependence of the conversion of the substrate on the lignin type

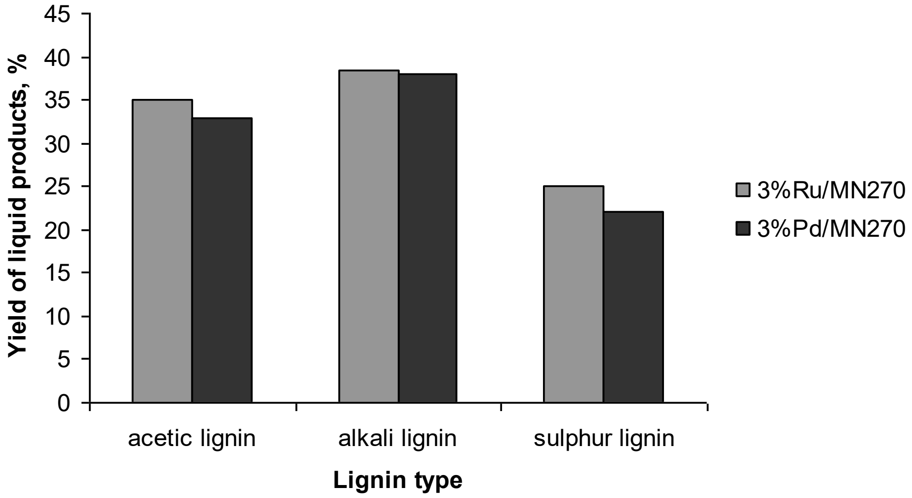

Figure 3: The dependence of the yield of liquid products on the lignin type

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 with maximum selectivity, %
3 %Pd/MN270	3.40	87.0	89.6
3 %Ru/MN270	3.55	92.0	90.0

*by phenol

The highest yield of liquid products and a high degree of conversion was obtained when the reaction was carried out in the environment of propanol-2, because it is thermally unstable and decomposes with evolution of hydrogen. This type of hydrogen-donor solvents was lately widely used in the processes of hydrotreating of the biomass, including lignin. Among the products obtained during the hydrotreatment of lignin, aromatic hydrocarbons (benzene, toluene, cyclohexane) and phenolic compounds that can be used as additives to traditional fuels and fuels derived from biomass are the most promising for the production of fuels. In addition, a number of cyclic and aromatic hydrocarbons can also be used in various fields of fine organic synthesis as solvents and reagents. The main liquid products obtained during hydrogenolysis are phenol, cresol, cyclohexane, benzene, furfuryl alcohol as shown in Table 2.

Table 2: Main products of lignin hydrogenolysis

Catalyst	Conversion, %	Main products
3 %Pd/MN270	28.0	phenol (60 %), benzene (18 %), cyclohexane (9 %), furfuril alcohol (5 %)
3 %Ru/MN270	23.0	phenol (76 %), benzene (13 %), cyclohexane (6 %), furfuril alcohol (5 %)

Two synthesized catalysts, 3 %Pd/MN 270 and 3 %Ru/MN 270 were used in the hydrogenolysis reaction. Commercial lignin and lignin isolated from sawdust in the laboratory were used as raw materials. Lignin, isolated independently, was analysed by IR spectrometry (Fernandez-Rodriguez et al., 2016). It was found that most peaks of industrial lignin coincide with peaks of lignin isolated in the laboratory.

For 3 %Pd/MN 270 the following optimum conditions were found: temperature 250 °C, the partial pressure of hydrogen of 1 MPa, the volume of solvent - 30 ml, the ratio of substrate/catalyst - 15/1. For 3 %Ru/MN 270, the optimum process conditions were: temperature 300 °C, partial pressure of hydrogen 4 MPa, substrate/catalyst ratio 20:1, solvent volume 30 mL (Figure 4). The results of catalysts testing under optimal conditions are presented in table 1.

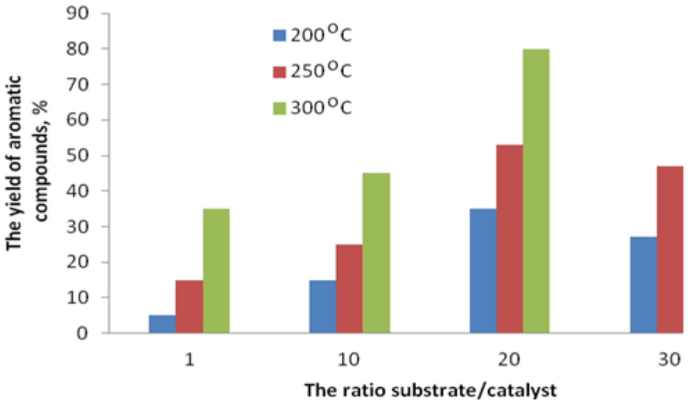

Figure 4: The dependence of the yield of aromatic compounds on the ration substrate/catalyst (3 % Ru/MN270) at different temperatures

The difference in selectivity is probably due to the different catalyst surface, the different state of the metal on the surface and the greater access of the substrate to the catalytic active centres in the case of 3 % Ru/MN270 as shown in Table 3.

Table 3: Physical and chemical characteristics of catalysts

Catalyst	S_{BET}, m^2/g	$S_{t\text{-}plot}$, m^2/g	Binding energy, eV	The state of the metal
3 %Pd/MN270	705.0	75.0*	335.0 (77.5 %)	Pd^0
		630.0**	337.4 (22.5 %)	PdO
3 %Ru/MN270	839.1	157.5*	462.6 (3.8 %)	RuO_2
		699.2 **	463.3 (96.2 %)	$RuO_2•nH_2O$

* surface area of macropores
** surface area of micropores

4. Conclusions

It was found that the method of its separation from soft wood sawdust has a very strong influence on the conversion of lignin in catalytic hydrogenolysis and on the yield of liquid products. In this work three methods of extraction were used: alkaline, sulfuric acid, acetic acid. The maximum conversion of 67.5 was observed in the case of acetic lignin in propanol-2 as a solvent, and the highest yield of liquid products (38.5 wt %) was obtained in the case of using an alkali lignin. On the basis of the conducted researches it was shown that the catalytic system 3 % Ru/MN 270 is more active in the process of hydrogenolysis than 3 % Pd/MN270, but Pd requires a lower temperature and pressure for the process. When using both catalysts a large number of derivatives of phenol, which can be used as alternative fuel are formed. The optimal process conditions are: 3 % Ru/MN270 - temperature 300 °C, partial hydrogen pressure of 4 MPa, the ratio of substrate/catalyst is 20:1, for 3 % Pd/MN270 temperature 250 °C, the partial pressure of hydrogen of 2 MPa, the volume of solvent 30 mL, the ratio of substrate/catalyst 15/1.

Acknowledgments

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