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Catalytic Hydrogenolysis of Lignin for the Synthesis of Biokerosene

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In this work, catalyst consisting of Ru deposited on hypercrosslinked polystyrene (HPS) was investigated in the process of hydrogenolysis of lignin isolated from different substrates. For sawdust, the maximum yield of the desired products was achieved with the use of acetic acid lignin, sunflower husk, and buckwheat husk when using the Klasson lignin. Analysis of hydrogenolysis products showed that the main substances formed in the process are benzene, phenol and their derivatives. In the process of hydrogenolysis of lignins at a pressure of 1 MPa hydrocarbons containing up to 9 hydrocarbon atoms were mainly obtained (78 %). Such hydrocarbons can be used as motor fuels. To increase the yield of hydrocarbons C_{9+}, experiments were conducted to vary the temperature and pressure. The optimal reaction conditions allowing obtaining the highest yield of the target products (C_{9+} hydrocarbons) were found to be the following: the processing time 1 h, the temperature of 300 °C, the partial pressure of hydrogen of 4 MPa, the stirring speed of 1500 rpm. The 3 % Ru/HPS catalyst showed high stability during hydrogenolysis (up to 5 consecutive cycles without regeneration).

1. Introduction

At present, jet fuel is not completely replaced by the fuel derived from biomass, partly because of the lack of cycloalkanes and aromatics in biofuels. Such molecules play a critical role in traditional jet fuels in terms of combustion characteristics and material compatibility. To date, this problem is solved by mixing biofuels with traditional oils. The production of 100 % biomass-based jet fuel requires a suitable bioresource for the synthesis of aromatic and cycloalkane fuel compounds (Feng and Catherine, 2017).

Lignin is the biomass component rich in benzene ring structures bound by ether bonds. Lignin is quite difficult to use because of its heterogeneity and resistance to chemical transformations. The simplest way of disposal of wood waste is thermal processing by direct burning, with the objective of obtaining a different product. The greatest amount of lignin is contained in wood. So, hardwood contains 20-30 % lignin, coniferous-up to 50 % by weight. The main functional groups of lignin are $-OCH_3$, -OH, -C=O and -COOH. Hydroxyl groups of lignin are divided into aliphatic (alcohol), located in the propane chain, and phenolic, associated with the benzene ring. The use of native lignin as fuel is impractical due to high humidity and the presence of large amounts of sulfur. But its composition makes lignin a very important raw material for further processing into biofuels.

The literature describes a large number of works on the processing of lignin-containing raw materials into chemical compounds that can be used as an alternative fuel. Biofuels, which currently meet the standards for use in aviation, including fuels based mostly on two processes: Fischer-Tropsch and hydro-processing of esters and fatty acids (Chiaramonti et al., 2016).

The study (Li et al., 2018) demonstrated that modified Ni/H-beta with active acid centers and hydrogen-related center can be an effective catalyst for the conversion of lignin into liquefied fuel. The catalyst has shown high efficiency in the conversion of Kraft lignin into liquefied fuel due to the synergistic effect of Lewis aluminum acid centers and Nickel-hydrogen bonding centers. With a Nickel content of 0.6 mmol/g, the Ni/H-beta catalyst gave a high yield of liquid products - 88.6 % at 300 °C. Most of the liquid products were dissolved in a mixture (73 % of 88.6 %), which mainly consisted of monomer and dimer decomposition products.

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The modified zeolite catalyst Zn-Ga was investigated in the work (Wang and Song, 2018). The combined action of Zn and Ga significantly improves the conversion of lignin, increases the yield of arenes along with the selectivity of benzene, toluene, ethylbenzene and xylene, which gives 37.4 wt. % yield of aromatic hydrocarbons from 62.2 wt. % selectivity at 400 °C and 3.0 MPa. The presence of methane has little effect on lignin conversion but improves arenes yield and selectivity.

The effect of solvent type, ethanol or water and Ru/C catalyst on lignin conversion by formic acid was studied in the work (Oregui-Bengoechea et al., 2018). The best results are obtained by using ethanol as a solvent at 300 °C and 10 h (i.e. 75.8 wt. % of oil and 23.9 wt. % of a solid substance). Ethanol gives a much larger amount of oil and fewer solids at 300 °C and 10 h. The main reasons for this positive effect of ethanol are 1) formation of ethers derived from ethanol, 2) C-alkylation of lignin fragments and 3) formation of more stable lignin derivatives. Ru/C exhibits significantly higher conversion activity compared to Ni-based catalysts, especially at 300 °C, which is associated with increased activity of Ru-centers to hydrogenolysis, hydrodeoxygenation and alkylation reactions.

The presence of hydrogen and the corresponding catalyst during the reaction is necessary in order to avoid the presence of free radical compounds, which usually lead to re-polymerization reactions. As for the stability of the resulting mixture, the molecular weight distribution of the oil does not change even after long-term storage (1-6 months) at the room temperature. The Ru/SiC catalyst can be regenerated by calcination without reducing catalytic activity (Yong et al., 2018). The resulting oil was extracted with hexane, which is the optimal lignin solvent for oil modernization. The extract was converted to aromatic hydrocarbons by hydrodeoxygenation at atmospheric pressure with MoO_3 catalyst (Wang et al., 2015).

Phenolic oil can be converted into a less viscous and dense oil, rich in long-chain alkanes, naphthenes and containing a small number of cycloalcohols with a small amount of oxygen (~1 %) and a lower molecular weight. This goal is achieved by catalytic hydrogenation/hydrodeoxygenation reaction (Chiaramonti, 2016). In (Hongliang et al., 2017) it was shown that triphthalate of metals can be used to replace conventional Lewis acids for hydrotreatment of lignin. Several model compounds of lignin and technical lignins have been used as reagents for more information on lignin conversion. A catalytic process involving hydrodeoxygenation (HDO) - corn lignin is extracted in dilute alkali, using Ru/Al_2O_3 and acid zeolite (H+-Y) as catalysts, C_7-C_{18} hydrocarbons are obtained, mainly C_{12}-C_{18} hydrocarbons of the cyclic structure. Most HDO processes are accompanied by the cleavage of both C-O-C and aliphatic C-C bonds in lignin, leading to the depolymerization of lignin to monomers, which usually contain 6-9 carbon atoms. Model lignin compounds were used.

The process of biomass hydrocracking on the $NiMo/Al_2O_3$ catalyst was studied in (Eller et al., 2016). According to the results of the experiment, the yield of target products reached 60 % (Zhang et al., 2016).

In the work (Lu et al., 2016), the process of hydrocracking of bio-alkanes for the production of bio-jet kerosene using bifunctional catalysts containing Pt on mesoporous molecular sieves MSM-41 with different Al content was studied. The introduction of Al in MCM-41 reduces the size of pores. However, at the same time, the volume of both total and average acid sites was increased, which increased the activity and selectivity of the catalyst. In addition, the activity of the catalyst is directly related to the Al content.

In this work catalyst consisting of Ru deposited on hypercrosslinked polystyrene (HPS) was investigated in the process of hydrogenolysis of lignin isolated from different substrates.

2. Materials and methods

2.1 Extraction of lignin from different substrates

Sunflower husks, softwood sawdust, and buckwheat husks were chosen as raw materials for the research. Lignin was isolated by three methods: sulfuric acid isolation (Klasson method), acetic acid method and alkaline method. Extraction of alkaline lignin from various substrates was carried out after preliminary hydrolysis of hemicellulose. Then lignin was boiled in a 2N NaOH solution for 3 h, then filtered on a Buchner funnel and dried at a temperature of 102 °C (Brown, 1967). Sulfuric acid lignin was obtained by the Klasson's method in Komarov modification (Obolenskaya et al., 1965). Initially, 1 g of the substrate was placed in the bux and kept in 25 mL of 72 % sulfuric acid at a temperature of 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, then lignin was filtered on a Buchner funnel and dried at a temperature of 102 °C. Acetic lignin was obtained using a solution of the following composition: 24.7 % weight CH_3COOH + 5.3 % weight H_2O_2 + 2 % weight H_2SO_4, the treatment was carried out under standard conditions for 3 h, then lignin was filtered on the Buchner funnel and dried at a temperature of 102 °C.

2.2 The process of lignin hydrogenolysis

The hydrogenolysis process was carried out in a six-cell Parr Series 5000 Multiple Reactor System in a hydrogen medium. The reactor allows conducting a series of parallel experiments under different conditions. The isolated lignin was loaded into the cell of a six-cell reactor, a solvent (isopropanol) was added, and then a measured amount of catalyst was added. The reactor was purged with nitrogen, and then it was heated to the required temperature with constant stirring, after which the working pressure of hydrogen was achieved. The conversion of the substrate was calculated at the end of the reaction based on the difference between the initial weight of the substrate and the dry mass of the residue. Previously, a comparison of synthesized and commercial catalysts in the process of hydrogenolysis of industrial lignin was carried out, it showed that polymer catalysts based on HPS allow achieving the higher conversion of raw materials and selectivity of hydrocarbons (Shimanskaya et al., 2018). The highest selectivity to oxygen-free hydrocarbons (96 %) at maximum conversion (68 %) of lignin-containing material was achieved in the presence of the catalyst 3 % Ru/HPS. This catalyst showed high stability during hydrogenolysis (up to 5 consecutive cycles without regeneration). Therefore this polymer catalyst was chosen for the present research. The process was carried out with the following conditions: the processing time is 1 h, the temperature of 300 °C, the partial pressure of hydrogen of 4 MPa, the stirring speed of 1,500 rpm (Figure 1).

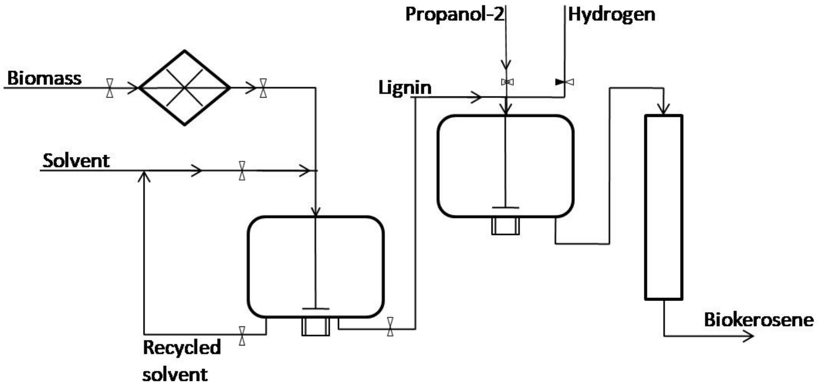

Figure 1: The scheme of the process of lignin hydrogenolysis

2.3 Analysis of the reaction products

Samples of the liquid phase were taken in all experiments every 30 minutes. The samples were analyzed using GC-2010 chromatography and GCMS-QP2010S mass spectrometer (SHIMADZU, Japan). The analysis was carried out for 25 minutes under the following conditions: the initial column temperature 150 °C, withstand 5 min, then raised the temperature to 250 °C at a heating rate of 5 °C / min; injector temperature: 280 °C. Quantitative analysis of liquid hydrogenolysis products was performed using the internal standard method.

3. Results and Discussions

In order to evaluate the influence of the method of lignin extraction from the raw material, three different types of isolation methods were used. Table 1 presents the yield of lignin from softwood sawdust, sunflower husk and buckwheat husk by acetic acid, sulfuric acid (Klasson method) and alkali.

Table 1: The results of lignin isolation from different substrates

Substrate	Method of isolation		
	Klasson method	acetic acid method	alkaline method
softwood sawdust	21.0 ± 1.7 %	15.0 ± 1.5 %	6.3 ± 0.3 %
sunflower husk	43.0 ± 1.5 %	17.0 ± 1.8 %	12.0 ± 1.3 %
buckwheat husk	23.0 ± 0.9 %	18.0 ± 1.2 %	10.0 ± 1.5 %

It is well seen that Klasson method allows producing the highest yield of lignin (21.0 %, 43.0 %, and 23.0 % from softwood sawdust, sunflower husk, and buckwheat husk respectively) in comparison with the other used methods. This may be due to the strongest effect of the sulfuric acid on the hydrolysis of cellulosic and hemicellulosic components of the feedstock. Moreover, the highest content of lignin was obtained while using sunflower husks as a raw material. Such high value (over 40 %) can be explained by the lowest content of cellulose and hemicelluloses in sunflower husks. Meanwhile, in order to evaluate the influence of the type of feedstock and the extraction method, further experiments on the lignin hydrogenolysis were performed for all extracted materials.

Figure 2 shows the results of hydrogenolysis of different types of lignin depending on the substrate and the method of isolation. The experiments conditions were the following: the processing time is 1 h, the temperature of 300 °C, the partial pressure of hydrogen of 3 MPa, the stirring rate of 1,500 rpm.

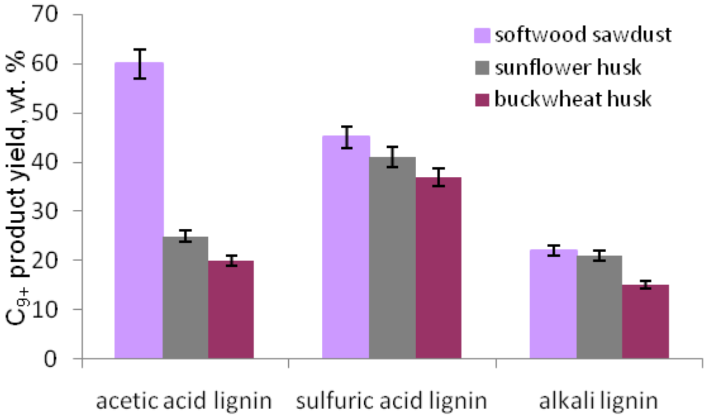

Figure 2: The yield of hydrocarbons C_{9+} depending on the type of isolation for different types of lignin

For sawdust, the maximum yield of lignin 21.0 ± 1.7 % (Table 1) was achieved by Klasson method, but the maximum yield of the desired products - 60% was achieved with the use of acetic acid lignin (Figure 2). While using sulfuric and alkali lignin mainly hydrocarbons $<C_9$ were obtained. Also, carboxylic acids, esters, aldehydes, ketones, and alcohols were obtained. For sunflower husk, the maximum yield of lignin 43.0 ± 1.5 % was achieved by Klasson method, and the maximum yield of the desired products – 41 % was achieved with the use of the Klasson lignin. While using acetic and alkali lignin mainly hydrocarbons $<C_9$ were obtained. For buckwheat husk, the maximum yield of lignin 23.0 ± 0.9 % was achieved by Klasson method, and the maximum yield of the desired products – 37 % was achieved with the use of the Klasson lignin. While using acetic and alkali lignin mainly hydrocarbons $<C_9$ were obtained.

To increase the yield of hydrocarbons C_{9+}, experiments to vary the temperature and pressure were conducted. Figure 3 shows the influence of hydrogen pressure on the yield of hydrocarbons C_{9+} using sulfuric acid lignin as the most optimal feedstock. With an increase in the hydrogen pressure at a temperature of 300 °C to 2 MPa, the yield of the required hydrocarbons increases by 30 %, at a pressure of 3 MPa to 40 %, at a pressure of 5 MPa decreases to 35 %.

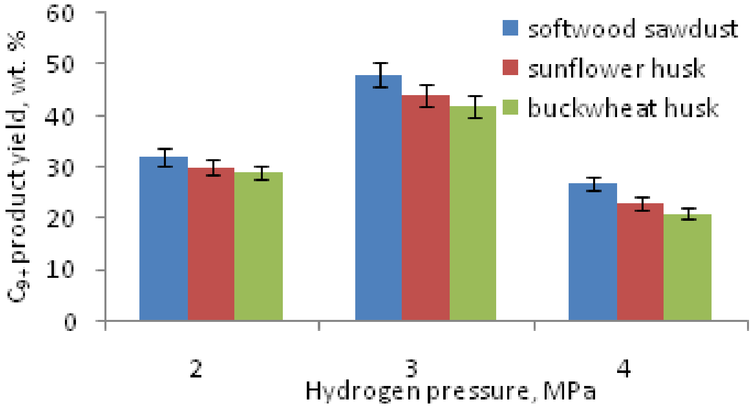

Figure 3: The yield of hydrocarbons C_{9+} depending on the hydrogen pressure

At the selected pressure, the temperature was varied from 200 to 400 °C (Figure 4). The optimum temperature was found to remain 300 °C since the condensation of the products increases with temperature.

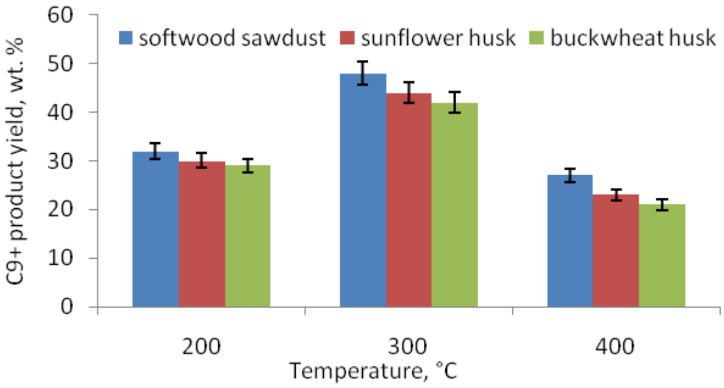

Figure 4: The yield of hydrocarbons C_{9+} depending on the temperature

The maximum temperature of the experiment was chosen based on the stability of the catalytic system. The stability of the polymeric matrix at the temperature of the experiment was investigated using the thermogravimetry method. Pre-weighted to a constant mass of 10^{-7} g the sample was placed on TG 209 F1 (NETZSCH, Germany) thermoscales, after which the heat treatment program was started. The area of change in the weight of the sample on the TG curve corresponds to the thermal degradation of the polymer matrix of hypercrosslinked polystyrene corresponding to a temperature of 435 °C (Figure 5).

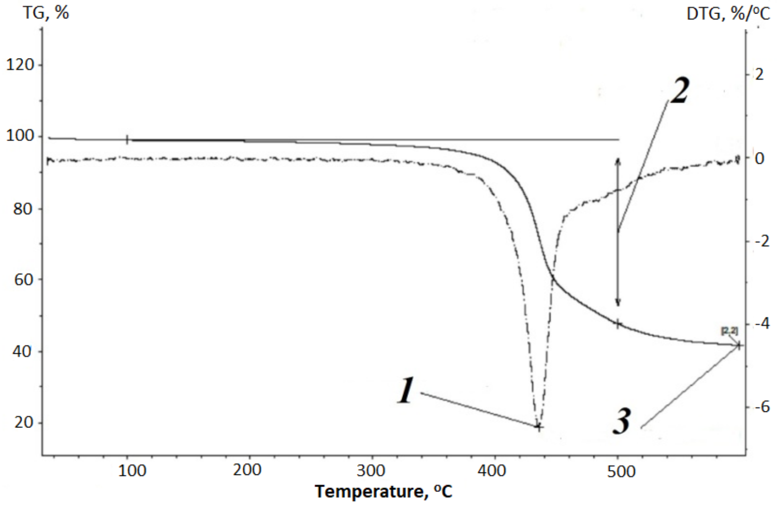

Figure 5: The results of termogravimetric investigation of HPS sample (1- peak: 435.5 °C, 2 - change in mass: 51.45 %, 3 - residual weight: 41.69 % (599.0 °C)).

The stability of the used catalytic system was studied in five consecutive cycles. It was found that the re-use of the 3 % Ru/HPS catalyst without regeneration did not lead to a decrease in the C_{9+} hydrocarbons yield at the optimal reaction conditions. It is noteworthy, that while using the catalyst in the lignin hydrogenolysis no sufficient changes in the catalyst structure and composition took place (Table 2).

Table 2: The results of catalyst characterization

Catalyst	Surface area, m^2/g	Pore volume, mL/g	Mean particle diameter, nm	Ru state
3 % Ru/HPS	900 ± 10	0.95 ± 0.1	4.3 ± 0.2	RuO_2
3 % Ru/HPS after 5 cycles	850 ± 10	0.91 ± 0.1	4.7 ± 0.2	RuO_2

4. Conclusions

From the selected raw materials, lignin was isolated in various ways: by the Klasson method, acetic acid, and alkaline methods. The following lignin yields were obtained: from softwood sawdust 21.0 ± 1.7 %, 15.0 ± 1.5 %, 6.3 ± 0.3 %, from sunflower husk 43.0 ± 1.5 %, 17.0 ± 1.8 %, 12.0 ± 1.3 %, from buckwheat husk 23.0 ± 0.9 %, 18.0 ± 1.2 %, 10.0 ± 1.5 %. Then the process of hydrogenolysis of the isolated lignin in the presence of 3 % Ru/HPS catalytic system was carried out. Analysis of hydrogenolysis products showed that the main substances that can be used as fuels are benzene, phenol and their derivatives.

To use hydrogenolysis products as jet fuels, they must contain oxygen-free hydrocarbons C_9-C_{15}. In the process of hydrogenolysis of lignins at a pressure of 2 MPa mainly hydrocarbons containing up to 9 hydrocarbon atoms (78 %) were obtained. Such hydrocarbons can be used as motor fuels. To increase the yield of hydrocarbons C_{9+}, experiments were conducted to vary the temperature and pressure. With an increase in the hydrogen pressure at a temperature of 300 °C to 2 MPa, the yield of the required hydrocarbons increases by 30 %, at a pressure of 3 MPa to 40 %, at a pressure of 5 MPa decreases to 35 %. At the selected pressure, the temperature was varied from 200 to 400 °C. The optimal temperature was 300 °C since the condensation of the products increases with temperature. For sawdust, the maximum yield of the desired products was achieved with the use of acetic acid lignin, sunflower husk, and buckwheat husk when using the Klasson lignin.

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