# THERMOCATALYTIC CONVERSION OF SPRUCE WOOD IN WATER-ETHANOL MIXTURES WITH RU/C CATALYST

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The study is devoted to the influence of the composition of the water-ethanol solvent on the process of thermocatalytic conversion of spruce wood using the bifunctional catalyst Ru/C. The experiments were carried out at different ratios of ethanol and water (95/5, 80/20, 50/50%) in an argon environment at a temperature of 225 °C and a pressure of 3.4–4.5 MPa. It was found that an increase in the proportion of water in the solvent to 50% leads to an increase in wood conversion from 49.5% to 67.4% in the presence of the Ru/C catalyst, and also contributes to obtaining a cellulose product with a minimum content of lignin (3.0%) and hemicelluloses (1.3%). The analysis of liquid products revealed an increase in the proportion of water-soluble oligosaccharides and a decrease in the yield of phenolic monomers when diluting ethanol with water. The results demonstrate the potential of using water-alcohol mixtures to optimize the processes of reductive catalytic fractionation of lignocellulosic biomass.

***Keywords***: thermocatalytic conversion, spruce wood, Ru/C catalyst, water-ethanol mixtures, lignocellulose, reductive fractionation

## INTRODUCTION

In recent decades, plant biomass has attracted increasing attention as a potential source of renewable energy and valuable raw materials for the chemical industry.[1] With population growth and increasing energy demand, the challenges of ensuring sustainable development are becoming increasingly pressing.[2] In this context, reductive catalytic fractionation (RCF) is a promising method for processing plant residues, which allows the efficient extraction of both energy and chemical components from the complex structure of biomass.[3] RCF converts lignocellulosic materials into hydrocarbons and other valuable chemical compounds, which not only facilitates the utilization of plant waste, but also reduces dependence on traditional fossil fuel sources.[4] This process can use various catalysts, which, depending on their nature and reaction conditions, can significantly affect the yield and selectivity of the target products.[5] An important part of reductive catalytic fractionation is the choice of feedstock, since different types of biomass have unique chemical compositions, which directly affects the catalytic processes. Typically, wood waste, agricultural residues, such as corn stalks or straw, and other organic materials are used.[6] The complex structure of lignocellulose makes it difficult to decompose, but this is precisely what ensures the creation of a variety of products during the catalytic process.[7]

Catalysts play a key role in RCF, as they not only accelerate reactions, but also determine the choice of target compounds. The most widely used metals are nickel, palladium, and platinum, which can catalyze hydrogenation and hydrodeoxygenation reactions.[8] However,

inexpensive alternatives, such as iron and cobalt, are also being actively explored,[9] which can significantly reduce the overall costs of the technology. Ultimately, the optimization of catalytic systems can lead to increased process efficiency, which will also be facilitated by the development of new technologies, such as nanocatalysts.

Also, the efficiency of RCF depends on the choice of the solvent, which not only ensures the transfer of reactants, but also participates in key depolymerization reactions and stabilization of intermediate products.[10] In this context, water-alcohol mixtures that combine the polarity of water and the dissolving power of alcohols are of particular interest. The use of ethanol in combination with water allows the creation of environments with controlled acidity and solvating power, which critically affects the hydrolysis of hemicelluloses, the destruction of lignin and the hydrodeoxygenation of products.[11] For example, ethanol promotes the dissolution of lignin and phenolic monomers, while water enhances the hydrolytic cleavage of carbohydrate components. Such mixtures also minimize the formation of toxic by-products compared to pure organic solvents and reduce energy costs due to milder process conditions. Recent studies confirm their effectiveness in biomass hydrogenation: the combination of alcohols with water improves the availability of active sites of the catalyst and stabilizes the radicals formed during the thermal decomposition of lignocellulose.[12] Despite the progress, the effect of the composition of water-alcohol mixtures on the selectivity of RCF remains poorly understood. The issues of how the ethanol/water ratio affects the balance between cellulose hydrolysis, preservation of its crystallinity and yield of phenolic monomers require detailed analysis. In addition, the role of bifunctional catalysts such as Ru/C under changing polarity conditions is not well understood.

Despite all the achievements, reductive catalytic fractionation still faces certain challenges. Among them, we can highlight the need for a deeper understanding of the reaction mechanisms, which requires long-term studies in the field of catalysis and interactions of various components, as well as the development of modifications to improve the stability of the catalysts and their resistance to deactivation. Future research also includes an assessment of the life cycle of RCF technologies and their impact on the environment, which will allow for a full understanding of their sustainability and competitiveness against traditional recycling processes.

The aim of this study was to establish the effect of a solvent based on water-ethanol mixtures of different concentrations in the process of reductive fractionation of spruce wood under argon, on the yield and composition of the products.

## EXPERIMENTAL

### Materials

Siberian spruce (*Pícea obováta*) wood used in this study contained cellulose (44.4), lignin (28.6), hemicelluloses (22.6), extractives (3.8), and ash (0.6% of weight of absolutely dry wood). The wood was ground into particles smaller than 1 mm in size, successively deresined with petroleum ether and acetone by a conventional ANSI/ASTM D 1105 method, and then dried at 24 °C to constant moisture content (4.3 wt%).[3]

In this study, we used ethanol (95%) (JSC "RFK"), $Ru(NO)(NO_3)_3$ (31.3% of Ru, Sigma-Aldrich), –N,O bistrifluoroacetamide (BSTFA + TMCS 99:1, Sigma-Aldrich), and ionol (>99%, Sigma-Aldrich).

### Preparation and study of Ru/C catalysts

The carbon supports containing acid sites were prepared by oxidizing a Sibunit-4 commercial mesoporous carbon material with an oxygen–argon mixture containing 20 vol% of $O_2$ in water vapors at temperatures of 400, 450, and 500 °C for 2 h using the technique described previously.[13]

The Ru (1%)/C and Ru (3%)/C catalysts were obtained by the incipient wetness impregnation of a carbon support with the $Ru(NO)(NO_3)_3$ aqueous solution, followed by drying first at room temperature for 2–3 h, and then at 60 °C for 12 h. The active component was reduced in a hydrogen flow (200 mL/min) at a temperature of 300 °C and a rate of 1 °C/min for 2 h. After cooling to room temperature in the hydrogen atmosphere, the catalyst was passivated with a mixture of 1% $O_2$ and nitrogen as described previously.[14]

### Catalytic conversion of spruce wood

The process of thermal conversion of crushed deresined wood was studied in a ChemRe SYStem R-201 autoclave (Republic of Korea) with a volume of 300 mL. 50 mL of ethanol (or water/ethanol mixture), 5.0 g of sawdust, and 0.5 g of 3% ruthenium catalyst were loaded into the reactor. Then, the autoclave was hermetically sealed, purged with argon to remove air, and filled. The hydrogenation was carried out at temperatures of 225 °C for 4.5 h under continuous stirring at a speed of 800 rpm. The operating pressure in the reactor ranged from 3.4 to 4.5 MP.

After completion of the reaction and cooling of the reaction mixture to room temperature, the gaseous products were collected in a gasometer, their volume was measured, and the composition was determined by gas chromatography (GC). The mixture of the liquid and solid products was quantitatively discharged from the autoclave by washing with ethanol and separated by filtration; then, the solid product was washed with ethanol until the solvent's discoloration and dried to a constant weight at 80 °C. Ethanol was removed from the liquid product by distillation on a rotary evaporator and the liquid product was brought to a constant weight by drying under vacuum (1 mmHg) at room temperature. The yields of the liquid ($\alpha_1$), solid ($\alpha_2$), and gaseous ($\alpha_3$) products and the spruce wood conversion ($Y_1$) were calculated using the equations:

$$a_1 = \frac{m_1(g)}{m_{init}(g)} \times 100\% \quad (1)$$

$$a_2 = \frac{m_s(g) - m_{cat}(g)}{m_{init}(g)} \times 100\% \quad (2)$$

$$a_3 = \frac{m_g(g)}{m_{init}(g)} \times 100\% \quad (3)$$

$$Y_1 = \frac{m_{init}(g) - m_s(g)}{m_{init}(g)} \quad (4)$$

where $m_l$ (g) is the liquid product mass, $m_{init}$ (g) – the mass of the initial wood, $m_s$(g) – the solid product mass, $m_{cat}$ (g) is the catalyst mass, and $m_g$ (g) – the gaseous products mass.

**Study of spuce wood hydrogenation products**

The ethanol-soluble wood conversion products were extracted with a mixture of dichloromethane and water, and separated into the aqueous and organic fractions. The organic phase was studied on an Agilent 7890A gas chromatograph, equipped with an Agilent 7000 A mass spectrometric detector, using an HP-5ms capillary column 30 m × 0.25 mm × 0.25 μm. The temperature of the injector and transfer lines was 305 °C and 310 °C, respectively. The initial oven temperature was set at 40 °C for 4 min, increased to 250 °C at a rate of 7 °C/min and then increased to 300 °C at a rate of 4 °C/min for 30 min. High-purity helium was used as the carrier gas, with a flow rate of 1 mL/min. The conditions for the mass spectrometer for the screening procedure were: full-scan mode (m/z 50–450 Da), electron ionization mode, ionization energy of 70 eV, ion source temperature of 230 °C. Compounds were identified based on comparison of mass spectra using the NIST MS Search 2.0 library, as well as an atlas of mass spectra and standard substances (guaicol (Acros Organics), methyl guaiacol, ethyl guaiacol, propyl guaiacol, propenyl guaiacol, vanillin, guaiacylacetone (Sigma-Aldrich)).

The content of glycols, monosaccharides and soluble oligosaccharides in the aqueous phase was analyzed using a Varian-450 GC gas chromatograph (Varian Inc., Palo Alto, CA, US), with a flame ionization detector on a VF-624 ms capillary column 30 m x 0.32 mm x 0.32 μm. Chromatography conditions: carrier gas – helium; injector temperature 250 °C; the initial column temperature – 50 °C, the temperature rose to 180 °C at a rate of 20 °C/min, exposure at 180 °C for 37 min, and then, the temperature rose to 250 °C at a rate of 20 °C/min and an exposure for 10 min. The detector temperature was 280 °C. The aqueous fraction was silylated by evaporating 1 mL of the solution with 0.01 mL internal standard 4 mg/mL (Sorbitol) to dryness and adding 100 μL of pyridine and 100 μL of –N,O-bis(trimethylsilyl)trifluoroacetamide (BSTFA); then kept at a temperature of 70 °C for 1 h. Calibration of GC and retention times mentioned were achieved using standard substances (ethylene glycol, glycerol (Merck), glucose, manose, galactose, xylose, arabinose (Panreac)). To measure the oligosaccharide content, the sample was completely hydrolyzed in sulfuric acid and then analyzed as usually; the oligosaccharide content was calculated as the difference between the detected carbohydrate amounts in the sample after this final hydrolysis and before it.

The composition of the gaseous products was determined by GC on a Khromatek Crystall-5000 chromatograph (Russia) with a thermal conductivity detector in a helium flow at a flow rate of 15 mL/min and a detector temperature of 170 °C. The CO and $CH_4$ analysis was carried out on a NaX zeolite column (3 m × 2 mm) in the isothermal mode at a temperature of 60 °C. The analysis of $CO_2$ and hydrocarbon gases was carried out on a Porapak Q column in the following mode: 60 °C for 1 min and then an increase in temperature to 180 °C at a rate of 10 °C/min.

The solid wood product was analyzed for the hemicelluloses, cellulose, and lignin contents. The residual lignin content was determined by hydrolysis with 72% $H_2SO_4$ at 98 °C.[15] The composition and concentration of monosaccharides in the solution obtained by hemicellulose hydrolysis with 4% sulfuric acid were determined by GC.[16] The cellulose content was calculated from a difference between the wood weight (or the solid residue) and the hemicelluloses and lignin contents.

The GC study was carried out with a Varian-450 GC gas chromatograph (Varian Inc., Palo Alto, CA, US), with a flame ionization detector, and a VF-624ms capillary column with a length of 30 m, an inner diameter of 0.32 mm, and helium as a gas carrier at an injector temperature of 250 °C. Before the analysis, the solution was derivatized to produce trimethylsilyl derivatives according to the procedure described previously.[17] Sorbitol was used as an internal standard. The peaks were identified from retention times of the tautomeric forms of monosaccharides.

The elemental compositions of wood and the products of its conversion were determined on a

Thermo Quest HCNS-O EAFLAS HTM 1112 analyzer.

## RESULTS AND DISCUSSION

Table 1 presents the data on the effect of the ethanol/water ratio and the type of catalyst on wood conversion and product distribution. The highest conversion (67.4%) was achieved using 50/50% ethanol/water with the Ru/C-ox catalyst. Increasing the proportion of water in the solvent leads to an increase in the yield of liquid products (up to 62.5% in experiment 7) and a decrease in the proportion of solid residue. The Ru/C-ox catalyst demonstrates superiority over Sib-4, which is due to its bifunctional properties combining acid and metal centers.

Table 1
Effects of spruce wood thermal conversion conditions on the degree of conversion and product yield

| № | Catalyst | Ethanol/water ratio, % | Degree of wood conversion,* wt% | Yield of liquid products ("lignin oil"), wt% | Gas yield, wt% | Yield of solid products, wt% |
|---|---|---|---|---|---|---|
| 1 | Ru/C-ox (3%) | 95/5 | 49.5 | 23.0 +19.6 | 6.9 | 50.5 |
| 2 | Sib-450 | 95/5 | 42.0 | 20.4 + 19.6 | 2.5 | 58.0 |
| 3 | w/o cat | 95/5 | 33.3 | 15.6 + 17.7 | 1.2 | 66.7 |
| 4 | Ru/C-ox (3%) | 80/20 | 57.3 | 25.8 + 26.7** | 4.8 | 42.7 |
| 5 | Sib-4 | 80/20 | 45.4 | 23.0 + 20.7 | 1.7 | 54.6 |
| 6 | w/o cat | 80/20 | 40.6 | 21.3+ 18.0 | 1.3 | 59.4 |
| 7 | Ru/C-ox (3%) | 50/50 | 67.4 | 26.4 + 35.8 | 5.2 | 32.6 |
| 8 | Sib-4 | 50/50 | 63.5 | 24.2 + 34.1 | 4.2 | 38.5 |
| 9 | w/o cat | 50/50 | 57.5 | 22.7 + 32.7 | 2.1 | 42.5 |

* into liquid and gaseous products; ** yield of water fraction of products

The dilution of ethanol with water significantly affected wood conversion, yield and composition of products. Wood conversion increased with a simultaneous increase in the water content in the water-ethanol solvent from 33% by weight to 57.5% by weight in experiments without a catalyst. In catalytic experiments, conversion increased from 49.5% by weight to 71% by weight on the Ru/C-ox catalyst and from 42.0% by weight to 62.5% by weight on pure Sib-4 (Table 1). In all experiments, an increase in conversion was accompanied by an increase in the proportion of the liquid fraction of wood thermal transformation products. As can be seen from the results presented in Table 2, an increase in the water content in the solvent led to a sharp decrease in the content of lignin and hemicelluloses in the composition of the solid cellulose product. The maximum purity of the cellulose product was achieved at 50% water concentration in the water-alcohol solvent; in the experiments without catalysts, the lignin and hemicellulose content decreased from 19.8% by weight and 14% by weight to 15% by weight and 4.8% by weight, respectively. In the experiments in the presence of Ru/C-ox, the purest cellulose product was obtained with a lignin and hemicellulose content of 3.0% by weight and 1.3% by weight, respectively. The composition of the solid residue shows that an increase in the proportion of water in the solvent improves the purity of cellulose. At 50% water and Ru/C-ox, the cellulose content reaches 95.7%, while lignin and hemicelluloses decrease to 3.0% and 1.3%, respectively. This is explained by the increased hydrolytic cleavage of hemicelluloses and the destruction of lignin in a more polar environment.

The obtained results on the composition of the solid cellulose product are consistent with the results of its analysis by the X-ray diffraction method. As can be seen from the nature of the diffraction pattern profile (Fig. 1), an increase in the water concentration in the water-alcohol solvent and the presence of catalysts led to the formation of a cellulose product with a more ordered structure. At the same time, the crystallinity index (CI) increased from 0.50 for the original wood to 0.68 for the solid cellulose residue obtained in a 50% water-alcohol solvent in the presence of the Ru/C-ox catalyst.

Table 2
Composition of the solid product of wood thermal conversion

| № | Catalyst | Ethanol/water ratio, % | Cellulose, wt% | Hemicelluloses, wt% | Lignin, wt% |
|---|---|---|---|---|---|
| 1 | Ru/C-ox (3%) | 95/5 | 82.6 | 9.9 | 9.2 |
| 2 | Sib-450 | 95/5 | 74.0 | 9.8 | 14.2 |
| 3 | w/o cat | 95/5 | 66.2 | 14.0 | 19.8 |
| 4 | Ru/C-ox (3%) | 80/20 | 92.3 | 3.2 | 7.5 |
| 5 | Sib-4 | 80/20 | 89.0 | 1.7 | 9.3 |
| 6 | w/o cat | 80/20 | 77.8 | 3.2 | 19.0 |
| 7 | Ru/C-ox (3%) | 50/50 | 95.7 | 1.3 | 3.0 |
| 8 | Sib-4 | 50/50 | 90.2 | 2.8 | 7.0 |
| 9 | w/o cat | 50/50 | 80.2 | 4.8 | 15.0 |

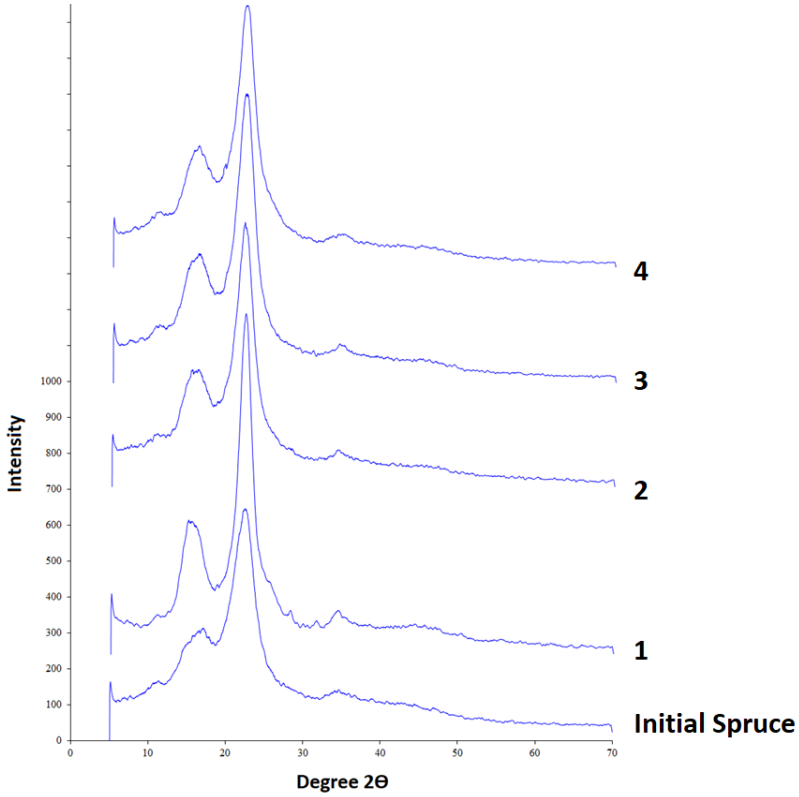


Figure 1: X-ray diffraction data: 1 – solid residue + catalyst Ru/C-ox (3%), ethanol/water ratio 50/50; 2 – solid residue + catalyst Sib-4, ethanol/water ratio 50/50; 3 – solid residue + catalyst Ru/C-ox (3%), ethanol/water ratio 80/20; 4 – solid residue + catalyst Ru/C-ox (3%), ethanol/water ratio 95/5

The analysis of gaseous products by gas chromatography showed that an increase in the water content in the water-alcohol solvent does not significantly affect the yield of gaseous products (Table 3). The presence of catalysts contributes to a greater formation of gaseous products, but in general their yield is insignificant and did not exceed 7% by weight. The main gaseous product was carbon dioxide in all experiments. In the presence of catalysts, cracking of the main structural components of wood increased significantly, which resulted in a sharp increase in the yield of methane, compared to experiments without a catalyst. The analysis of gaseous products revealed the predominance of $CO_2$ (60–94% of the total gas yield). In the presence of Ru/C-ox, an increase in the yield of methane is observed (up to 30% in experiment 4), which is associated with catalytic cracking of hydrocarbon fragments. However, the total gas yield does not exceed 7%, which confirms the efficiency of the process in the direction of liquid and solid products.

A significant increase in the yield of liquid products with an increase in the water concentration to 50% in the water-alcohol solvent was accompanied mainly by an increase in the proportion of water-soluble substances in the composition of the liquid products of wood thermal conversion (Tables 1, 5). These results are consistent with the data on elemental analysis of the liquid fraction of wood thermal conversion products (Table 4). As can be seen from the table, an increase in the water content in the solvent leads to a decrease in the proportion of carbon in the products and an increase in the proportion of oxygen in the experiments without catalysts. This indicates an increase in the solvating capacity of the solvent with an increase in the water content and promotes the transition of saccharides into solution, which contain significantly more oxygen compared to soluble phenolic fragments. In the presence of catalysts, the hydrodeoxygenation process was enhanced, as indicated by a decrease in the proportion of oxygen and an increase in the proportion of carbon in the products of wood thermal conversion (Table 4). The elemental composition of the liquid fraction demonstrates a decrease in the carbon content (from 67.4% to 58.8%) and an increase in oxygen (from 26.4% to 36.4%) with an increase in the proportion of water. This indicates the transition of polar oxygen-containing compounds (oligosaccharides) into solution. Ru/C-ox catalysts partially compensate for this effect due to hydrodeoxygenation.

Increasing the water content in the water-ethanol solvent contributed to an increase in the proportion of C-5 and C-6 oligosaccharides in the composition of water-soluble products in all experiments (Table 5). In the catalytic experiments, the proportion of monomeric products increased sharply compared to experiments without catalysts (Table 5). The yield of water-soluble products increases with an increase in the proportion of water, reaching 50.7% in experiment 7. The main components are C-5 and C-6 oligosaccharides, which confirms the efficiency of hemicellulose hydrolysis in an aqueous medium.

Table 3
Yield and composition of gaseous products

| № | $CO_2$, wt% | CO, wt% | $CH_4$, wt% | Sum, wt% | $CO_2$, wt% | CO, wt% | $CH_4$, wt% |
|---|---|---|---|---|---|---|---|
| 1 | 4.2 | 1.2 | 1.5 | 6.9 | 60.9 | 17.4 | 21.7 |
| 2 | 1.5 | 0.5 | 0.5 | 2.5 | 60.0 | 20.0 | 20.0 |
| 3 | 0.9 | 0.2 | 0.1 | 1.2 | 75.0 | 16.7 | 8.3 |
| 4 | 2.1 | 0.7 | 1.2 | 4.0 | 52.5 | 17.5 | 30.0 |
| 5 | 0.9 | 0.3 | 0.5 | 1.7 | 52.9 | 17.6 | 29.5 |
| 6 | 1.0 | 0.2 | 0.1 | 1.3 | 76.9 | 15.4 | 7.7 |
| 7 | 3.0 | 0.9 | 0.3 | 4.2 | 71.4 | 21.4 | 7.2 |
| 8 | 3.0 | 0.2 | - | 3.2 | 93.7 | 6.3 | - |
| 9 | 1.7 | 0.1 | - | 1.8 | 94.4 | 5.6 | - |

Table 4
Elemental analysis of the liquid fraction of spruce wood thermal conversion products

| № | C, wt% | H, wt% | O, wt% |
|---|---|---|---|
| 1 | 67.4 | 6.2 | 26.4 |
| 2 | 66.8 | 6.0 | 27.2 |
| 3 | 64.8 | 5.5 | 29.7 |
| 4 | 65.0 | 5.6 | 29.4 |
| 5 | 64.4 | 5.3 | 30.0 |
| 6 | 64.1 | 5.1 | 30.8 |
| 7 | 63.4 | 5.2 | 31.4 |
| 8 | 62.5 | 5.0 | 32.5 |
| 9 | 58.8 | 4.8 | 36.4 |

Table 5
Effect of spruce wood thermal conversion conditions on the yield and composition of water-soluble products*

| Substance | № of exp./Content, wt% | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 |
| Ethylene glycol | 6.4 | 3.6 | 0.4 | 3.8 | 1.8 | 0.8 | 6.6 | 1.1 | 0.6 |
| Glycerol | 4.2 | 2.8 | 0.3 | 2.8 | 1.4 | 0.6 | 4.4 | 0.5 | 0.4 |
| 1,2.5-Pentanetriol | 2.0 | 0.6 | - | 1.2 | 0.2 | - | 2.2 | 0.2 | - |
| Glucose | 3.2 | 2.4 | 0.4 | 2,3 | 1.5 | 0.8 | 3.7 | 1.2 | 1.5 |
| Manose | 5.4 | 3.2 | 0.6 | 4.5 | 2.6 | 1.0 | 5.9 | 3.3 | 2.7 |
| Oligosaccharides C-5 | 1.8 | 3.0 | 7.9 | 8.3 | 7.7 | 7.6 | 6.4 | 17.4 | 15.8 |
| Oligosaccharides C-6 | 2.0 | 12.0 | 15.8 | 14.8 | 15.2 | 17.3 | 18.3 | 22.1 | 20.2 |
| Unidentified substances | 1.5 | 1.4 | 0.8 | 2.4 | 1.8 | 1.2 | 3.2 | 2.6 | 1.4 |
| Sum | 30.1 | 29.2 | 26.2 | 40.1 | 32.2 | 29.3 | 50.7 | 49.0 | 44.6 |

* product yield calculated as carbohydrates in a wood sample

Table 6
Effect of conditions of thermal conversion of spruce wood in water-ethanol solvent on the yield and composition of phenol-derivative monomers*

| Substance | № of exp./Content, wt% | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 |
| Guaiacol | | - | - | - | - | - | - | - | - |
| Methyl guaiacol | 0.19 | - | - | - | - | - | - | - | - |
| Ethyl guaiacol | 1.58 | 0.35 | 0.21 | 0.61 | 0.13 | 0.13 | 0.28 | - | - |
| Propyl guaiacol | 12.63 | 0.45 | 0.22 | 2.76 | 0.29 | 0.21 | 2.2 | 0.35 | 0.31 |
| Propenyl guaiacol | 7.11 | 1,72 | 1.53 | 2.81 | 0.62 | 0.57 | 0.95 | 0.51 | 0.43 |
| Vanillin | - | - | - | 0.08 | 0.06 | 0.09 | 0.16 | 0.09 | 0.08 |
| Guaiacylacetone | 0.17 | 0.06 | 0.05 | 0.10 | - | - | - | - | - |
| Propanolguaiacol | - | - | - | 0.26 | 0.11 | - | 0.09 | 0.08 | - |
| Sum | 21.68 | 2.58 | 2.01 | 7.62 | 1.13 | 1.0 | 4.68 | 1.03 | 0.82 |

* yield of monomers calculated as lignin in a wood sample

GC-MS analysis of the phenol fraction of the liquid products revealed a low content of monomeric methoxyphenols in the experiments without a catalyst. As can be seen from the data in Table 6, an increase in the proportion of water in the solvent negatively affected the yield of phenolic monomers. With an increase in the water concentration to 20% in an aqueous-ethanol solvent, the yield of monomeric methoxyphenols in the presence of the Ru/C-ox catalyst decreased from 21.7 wt% (experiment 1) to 7.6 wt% (experiment 4), *i.e*., by almost 3 times. With a further increase in the proportion of water to 50%, the yield of methoxyphenol monomers sharply decreased by 4.6 times compared to experiment 1. In experiments with the Sib-4 catalyst, the yield of monomeric methoxyphenols did not differ significantly compared to the experiments without a catalyst. It is likely that the stabilization of methoxyphenol monomer radicals by hydrogen occurred predominantly at the metal sites of the Ru/C-ox catalyst.

The decrease in the yield of methoxyphenol monomers during the thermal catalytic conversion of wood over the Ru/C catalyst with increasing water concentration in the aqueous ethanol solvent is likely due to a decrease in the concentration of hydrogen atoms with dilution and, concurrently, the competition between phenolic and carbohydrate radicals for active metal sites on the surface of the bifunctional Ru/C-ox catalyst. It should be noted that propanol guaiacol was identified in the products of experiments Nos. 1, 4, 7, 8, and 9; however, its yield in all cases was less than 0.08 wt% of the lignin mass in the wood sample. Because of the low yield, data on this compound were not included in the final table. Thus, the decrease in the yield of phenolic monomers from 21.68% to 0.82% with an increase in the proportion of water is associated with the competition of radicals for the active centers of Ru/C-ox and a decrease in the concentration of hydrogen, which limits the

stabilization of phenolic fragments and shifts the process towards the carbohydrate direction.

## CONCLUSION

The nature of the solvent has a significant effect on the thermal conversion of wood, as well as the yield and composition of the products formed. An increase in the concentration of water in the aqueous-alcoholic solvent promotes depolymerization of the cellulose component and, as a consequence, increases the conversion and content of monomeric, oligomeric saccharides and their derivatives in the products of thermal and thermocatalytic transformations of wood. In the presence of Ru/C-ox and Sib-4 catalysts, which have active acid centers, the degree of polymerization of the structural components increases. The stabilization of monomeric radicals of phenolic and carbohydrate nature by hydrogen atoms occurs primarily on the metal Ru centers of the bifunctional catalyst Ru/C-ox. However, when diluting the aqueous-alcoholic solvent with water, the concentration of the resulting hydrogen atoms decreases and, simultaneously, the competition between phenolic and carbohydrate radicals for the metal active centers of the catalyst increases. Due to the insufficient number of atoms for stabilization of phenolic radicals, the yield of methoxyphenol monomers decreases.

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