CATALYTIC HYDROGENOLYSIS OF NATIVE AND ORGANOSOLV LIGNINS OF ASPEN WOOD TO LIQUID PRODUCTS IN SUPERCRITICAL ETHANOL MEDIUM

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Abstract

Catalytic hydrogenolysis in the medium of supercritical organic solvents is a promising way of wood lignins depolymerization into liquid products.

In this study, for the first time, the catalytic properties of bifunctional catalysts Ru/C, Pt/ZrO_2, $NiCuMo/SiO_2$, containing nanosized metal particles on acidic supports are compared in the processes of aspen wood and ethanol lignin hydrogenolysis in supercritical ethanol.

The most active catalysts are Ru/C and Pt/ZrO_2 which provide the high conversion of wood (to 78 wt%), significant yield of liquid products (to 50.6 wt%) and low yield of solid rest (to 22 wt%) at temperature 250 °C and H_2 pressure 9 MPa. These catalysts increase the yield of monomeric compounds in liquid products from 9.5 % to 42.9 % on mass of lignin.

GC-MS analysis shows that alkyl derivatives of methoxyphenols (mainly propyl syringol and propyl quaiacol) are dominated in liquid products. Solid products of aspen wood catalytic hydrogenolysis contain mainly cellulose (to 82.2 wt%). Therefore, the catalytic hydrogenolysis in supercritical ethanol in the presence of by functional catalysts Ru/C and Pt/ZrO_2 allows to fractionate the aspen wood biomass on cellulose and liquid products enriched with propyl siringol and propyl quaiacol.

In catalytic hydrogenolysis of ethanol lignin the yield of alkyl derivatives of methoxyphenols is lower compared to wood. This is probably due to the reduced content of reactive β-O-4 bonds in the structure of ethanol lignin compared to native lignin of aspen wood. As follows from the results obtained, native lignin of wood is easier depolymerized to monomeric compounds in the process of catalytic hydrogenolysis than ethanol lignin, isolated from wood.

According to GPC data, the catalysts shift to the region of lower molecular mass the molecular mass distribution of liquid products of aspen wood and ethanol lignin hydrogenolysis.

Keywords: aspen wood, hydrogenolysis, catalysts, bioliquids.

1. Introduction

Wood lignin, being a renewable source for producing valuable phenolic and aromatic hydrocarbons, remains a little used raw material [1-5]. The hydrolysis industry produces condensed lignin as a byproduct which is difficult to process into valuable chemicals. One of the promising method of lignin isolation is the extraction of lignocellulosic materials with organic solvent or its mixtures with water [6, 7]. The resulting organosolv lignins do not contain sulfur and have a higher reactivity compared to traditional technical lignins. However, when organosolv lignins are isolated the undesirable polymerization processes can occur, leading to a decrease in their yield and reactivity [8]. These circumstances make it urgent to develop methods of lignin depolymerization which eliminate the additional stage of its isolation from lignocellulosic material.

Catalytic hydrogenolysis of lignocellulosic biomass in the medium of supercritical organic solvents allows to combine the stages of lignin isolation and its catalytic depolymerization [9-11].

In particular, the influence of acid high silica zeolites catalysts on the depolymerization of aspen wood in supercritical ethanol medium at 270 °C was studied [12]. The most active catalyst with ratio Si/Al=30 produces 86 wt% of liquid products at 270 °C and pressure 6.4 MPa. They are mainly represented by compounds formed from wood polysaccharides: 5-HMF, furfural, levulinic acid, ethyl esters etc. The catalyst $NiCuMo/SiO_2$ gives the high yield of liquid products (near 90 wt%) in the depolymerization of aspen ethanol lignin in supercritical ethanol at 300 °C and 11.6 MPa [13]. This catalyst reduces the content of phenol and benzene derivatives and increases the content of esters, aldehydes and ketons in hexane soluble liquid products.

In the presence of hydrogen or hydrogen-donor compounds, an increase in the yield of liquid products of lignin catalytic depolymerization can be expected due to intensification of the reactions of C–O and C–C bonds rupture. The reductive depolymerization of lignocellulosic biomass is carried out in organic solvents in the presence of metal-containing catalysts (Pd/C, Ru/C, Ni/C, Ni/Al_2O_3 etc) [14-16]. In the processes of biomass hydrogenolysis the low molecular weight soluble products are formed from hemicelluloses and lignin, while cellulose remains as a solid residue. The lower aliphatic alcohols with hydrogen donor properties are usually used as organic solvents. In the process of catalytic hydrogenolysis of biomass they extract the products of biomass depolymerization, alkylate and reduce the reactive intermediates, preventing their condensation [17]. Ethanol is a promising solvent, which can be obtained in the required quantities using existing industrial technologies [18].

The use of solid bifunctional catalysts on the basis of platinum metals and less expensive metals (Ni, Mo) on oxide (Al_2O_3, SiO_2) and carbon supports allows to intensify the depolymerization of lignin and to increase the yield of monomeric phenol derivatives [19-24]. Catalysts $NiCu/SiO_2$ and $NiCuMo/SiO_2$ were developed for the process of bio-oil

hydrodeoxygenation [25]. These catalysts were successfully used for depolymerization of aspen aceton lignin in the medium of supercritical butanol [26, 27]. The most active catalyst $NiCuMo/SiO_2$ increases by 2.4 times the yield of liquid products compared to non-catalytic process. The catalyst Ru/C is active in the processes of hydrogenolysis of birch ethanol lignin [28, 29], abies wood and ethanol lignin [30] and catalyst $Ni\text{-}Cu/ZrO_2$ – in the process of biodiesel and anisole hydrodeoxygenation [31].

In the present study, for the first time, the catalytic properties of bifunctional catalysts Ru/C, Pt/ZrO_2, $NiCuMo/SiO_2$, containing nanosized metal particles on acidic supports are compared in the processes of aspen wood and ethanol lignin hydrogenolysis in supercritical ethanol medium. Optimal process conditions providing the high yield of monomeric derivatives of phenol have been established.

2. Experimental

2.1. Initial wood materials

The air-dry sawdust (fraction 2–5 mm) of aspen wood (*Populus tremula*) with chemical composition (wt%): cellulose – 46.3, lignin – 20.4, hemicellulose – 24.1, ash – 0.5 and elemental composition (wt%): C – 49.9, H – 6.1, O – 44.0 was used in the experiments.

Ethanol lignin was isolated from aspen wood according to procedure described in [32] by extraction of wood fraction ≤ 1 mm with 60 % ethanol at 190 °C during 3 h. The soluble ethanol lignin was precipitated by cold water (–4 °C), separated from solution by filtration and dried at 50 °C until constant weight. The yield of ethanol lignin is 12.5 wt%, what corresponds to 56 wt% from lignin content in aspen wood.

2.2. Catalysts

Catalyst $NiCuMo/SiO_2$ was prepared by the sol – gel method described in [33]. Appropriate amounts of commercial nickel (II) carbonate basic hydrate, copper (II) carbonate basic and molybdenum (VI) oxide were mixed with the required amount of water solution of ammonia (25% of NH_3) and bidistilled water under constant stirring. Afterwards, the obtained suspension was filtered, left to dry in air overnight at 120 °C, and then calcined at 400 °C for 4 hours. The resulting mixed nickel-copper-molybdenum oxide systems were fractionated to 2-5 mm. The prepared granules were impregnated with ethyl silicate (with SiO_2 content of 32 wt.%), followed by drying of the samples at 120 °C for 12 hours and calcination at 500 °C for 2 hours. Then, the samples were reduced in a hydrogen flow at 500 ° C in a quartz reactor, kept at this temperature for 1 hour. Then they were cooled and passivated with a mixture of O_2 (2%)/N_2. The resulting catalyst contains

(wt%): Ni – 49, Cu – 6, Mo – 5. The surface area of the catalyst is 109 m^2 / g, the pore volume is 0.23 cm^3 / g, the average size of the metal particles is 10 nm [33].

Catalyst Ru/C was prepared using a graphite-like carbon support Sibunit (fraction 56–96 μm) according to the procedure [34]. The support was oxidized with moist air for 4 hours at 450 °C. Ruthenium was deposited by impregnating the carbon support in terms of moisture capacity with an aqueous solution of ruthenium nitrazyl nitrate $Ru(NO)(NO_3)_3$. The active component was reduced in a stream of hydrogen [35]. The surface area of the Ru / C catalyst is 371 m^2 / g, the pore volume is 0.53 cm^3 / g, the average particle size of Ru is 1 nm, and pH = 6.09 (at the point of zero charge) [28].

Catalyst Pt/ZrO_2 was prepared according to the procedure [36]. Zirconium hydroxide was obtained by slow precipitation from an aqueous solution of 1M $ZrO(NO_3)_2$ with an excess of NH_4OH. The precipitate was dried at 120 °C and treated with a 2M sulfuric acid solution. The resulting sulfated material was dried at 120 °C and calcined at 650 °C in an air stream. To prepare a bifunctional catalyst, the support was impregnated with a solution of H_2PtCl_6. The sample was dried at 120 °C and calcined at 450 °C in a stream of air. The Pt / ZrO_2 catalyst contains Pt – 1.0 wt.%, SO_4^{-2} – 5.9 wt.%, the rest is ZrO_2. The surface area of the catalyst is 110 m^2/g, and the pore volume is 0.09 cm^3/g, the particle size of Pt varies from 1 to 2 nm.

2.3. Hydrogenolysis of aspen wood and ethanol lignin

The processes of wood sawdust and ethanol lignin hydrogenolysis in supercritical ethanol were carried out in 300 ml autoclave (ChemRe SYStem R-201, the Republic of Korea) with stirring (800 rpm). Substrate (5.0 g), catalyst (0.5 g) and of ethanol (50 ml) were charged into the reactor. The air was removed from the autoclave by purging it with argon. Afterwards, hydrogen was supplied with an initial pressure of 4 MPa and the autoclave was heated at a rate of 10 °C/min to 250 °C. The duration of heat treatment at the final temperature was 3 h.

The scheme of the study of aspen wood and ethanol lignin hydrogenolysis and products analysis is presented in Fig. 1.

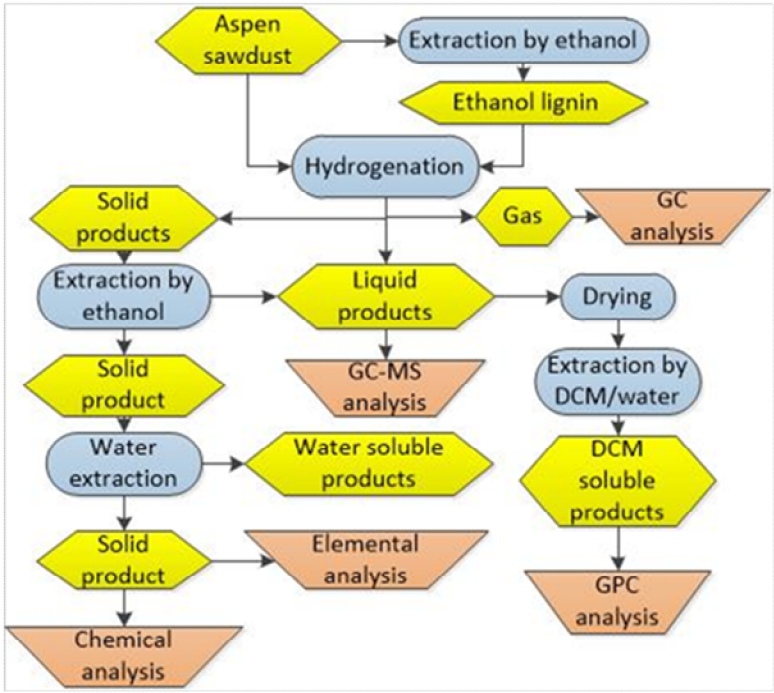

Fig. 1. Scheme of the study of aspen wood and ethanol-lignin hydrogenolysis and products analysis.

At the end of the experiment, the autoclave was cooled to room temperature, the volume of gaseous products was determined and their analysis was performed by gas chromatography. Liquid and solid products were removed from the autoclave by washing with ethanol. The resulting mixture of liquid and solid products was separated by filtration. The solid residue was extracted with ethanol in a Soxhlet apparatus. The ethanol extract was combined with the filtrate, an aliquot was taken from the resulting mixture for analysis by gas chromatography-mass spectrometry (GC-MS). The yield of liquid products (α_1, wt.%) was calculated according to Eq. (1):

$$\alpha_1 = \frac{m_l\ (g)}{m_w\ (g)} \times 100\%, \qquad (1)$$

Where: m_l is the mass of liquid products (g), m_w is the mass of the wood (g).

In the experiments with wood, the solid residue was extracted with water in a Soxhlet apparatus and was dried at 80 °C to constant weight. The yield of water soluble products (α_2, wt.%) was calculated according to Eq. (2):

$$\alpha_2 = \frac{m_{sr1}(g) - m_{sr2}\ (g)}{m_w\ (g)} \times 100\%, \qquad (2)$$

Where: m_{sr1} is the mass of the solid residue after extraction with ethanol (g), m_{sr2} is the mass of the solid residue after extraction with water (g).

The yield of solid products (α_3, wt.%) was calculated according to Eq. (3)

$$\alpha_3 = \frac{m_{sr2}\ (g) - m_{cat}\ (g)}{m_w\ (g)} \times 100\%, \qquad (3)$$

Where: m_{cat} is the mass of the catalyst (g).

Wood conversion (χ_w) was calculated according to Eq. (4):

$$\chi_w = \frac{m_w\,(g) + m_{cat}\,(g) - m_{sr2}(g)}{m_w\,(g)} \times 100\%, \quad (4)$$

The liquid products of wood hydrogenolysis, after removal of the ethanol, were extracted with dichloromethane (DCM) and water according to the procedure [37]. After removal of the dichloromethane soluble products were analyzed by gel permeation chromatography (GPC).

2.4. Analytical methods

GC-MS analysis

An aliquot of the liquid products soluble in ethanol was analyzed by gas chromatography–mass spectrometry (GC–MS) using an Agilent 7890A chromatograph fitted with an Agilent 7000A Triple Quad mass-selective detector (Agilent, USA) by recording the total ion current. The chromatographic separation of products was performed using an HP-5MS capillary column (30 m × 0.25 mm i.d) in the temperature-programmed mode while raising the temperature from 40 to 250 °C at of 3 °C/min. Identification of chromatographic peaks was carried out according to the NIST MS library and the literature data on bio-oils composition. To quantify the yield of monomer compounds, the standard substances, such as phenol, guaiacol, vanillin, syring aldehyde, 4-methylphenol, (Sigma – Aldrich), ethyl palmitate (Tokyo Chem. Ind.) were used. The response factor for each standard compound was defined relative to the internal standard [38]. Phenanthrrene was used as an internal standard.

GPC analysis

The average molecular weight (Mw), number average molecular weight (Mn) and the polydispersity (D) of liquid products were determined by gel permeation chromatography using an Agilent 1260 Infinity II Multi-Detector GPC / SEC System with a triple detection: refractometer, viscometer and light diffusion. Separation was performed on a PLgel Mixed-E column using 250 ppm BHT stabilized tetrahydrofuran as the mobile phase. Column calibration was carried out using polydispersed polystyrene standards (Agilent, USA). The eluent feed rate was 1 ml / min and the sample volume was 100 µl. Before analysis, the samples were dissolved in THF (1 mg / ml) and filtered through a 0.45 µm membrane PTFE filter (Millipore). Data collection and processing was performed using Agilent GPC / SEC MDS software.

GC analysis

The composition of the gaseous products of thermal conversion was determined with the use of gas chromatograph by Crystal 2000 M (Khromatek, Russia) with a thermal conductivity detector. Carrier gas helium (flow rate 15 ml / min). The temperature of the detector is 170 °C. For analysis of CO and CH_4, a column with NaX zeolite (3m * 2 mm) was used in isothermal mode at a temperature of 60 °C. Analysis of CO_2 and hydrocarbon gases was carried out on a column with

Porapak Q in the mode: 1 min – 60 °C and then the temperature was increased to 180 °C at a rate of 10 °C/min. Total yield of gaseous products (α_4) was calculated according to Eq.5

$$\alpha_4 = \frac{m_g\ (g)}{m_w\ (g)} \times 100\%, \quad (5)$$

Where: m_g is the mass of the gaseous products (g).

Chemical analysis

The content of residual lignin in the cellulose product was determined in the modification of Komarov [39], by hydrolysis of 72% sulfuric acid hemicellulose – by hydrolysis of 2% hydrochloric acid according to [40]. The cellulose content was calculated by the difference between the mass of the solid residue and the contents of hemicelluloses and lignin. The conversion of hemicelluloses (χ_h), cellulose (χ_c) and lignin (χ_l) was calculated by the formulas 6–8:

$$\chi_h = \frac{m_{hw} - m_{hsr}}{m_{hw}} \cdot 100\% \quad (6)$$

$$\chi_l = \frac{m_{lw} - m_{lsr}}{m_{hw}} \cdot 100\% \quad (7)$$

$$\chi_c = \frac{m_{cw} - m_{csr}}{m_{cw}} \cdot 100\% \quad (8)$$

Where: m_{hw} and m_{hsr} are the mass of hemicelluloses in wood and in the solid residue after extraction with water, g; m_{lw} and m_{lsr} — mass of lignin in wood and in the solid residue after extraction with water, g; m_{cw} and m_{csr} are the mass of cellulose wood and in the solid residue after extraction with water.

The elemental composition of wood and the liquid products was determined using an HCNS-O EAFLAS HTM 1112 analyzer (Thermo Quest).

3. Results and discussion

3.1. Thermal depolymerization of aspen wood in supercritical ethanol medium

The impact of temperature and pressure of the process of aspen wood thermal depolymerization in supercritical ethanol on the wood conversion and on the yield of liquid, solid and gaseous products was studied. At the process temperatures 270 °C and 350 °C the conversion of wood significantly increases with the rise of pressure from 4.0 MPa to 20.8 MPa (Fig. 2).

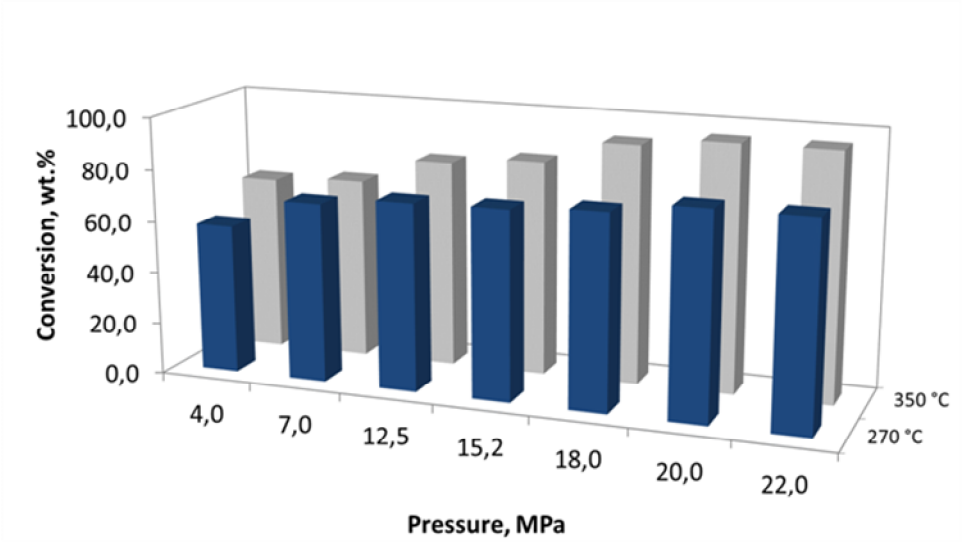

Fig. 2. Effect of pressure and temperature on the conversion of aspen wood (process time 3 h).

The most high conversion of aspen wood (95.5 wt%) is reached at the process temperature 350 °C and pressure 20.8 MPa. In subcritical conditions (pressure 4.0 MPa and process temperature 270 °C) the yield of ethanol-soluble products reaches 55.2 wt%. More than 60 % of these liquid products belong to the light fraction with b.p. ≤ 100 °C. The rise of a process pressure up to 22 MPa increases the yield of ethanol-soluble products to 76.2 wt% and reduces the yield of solid rest (Fig. 3).

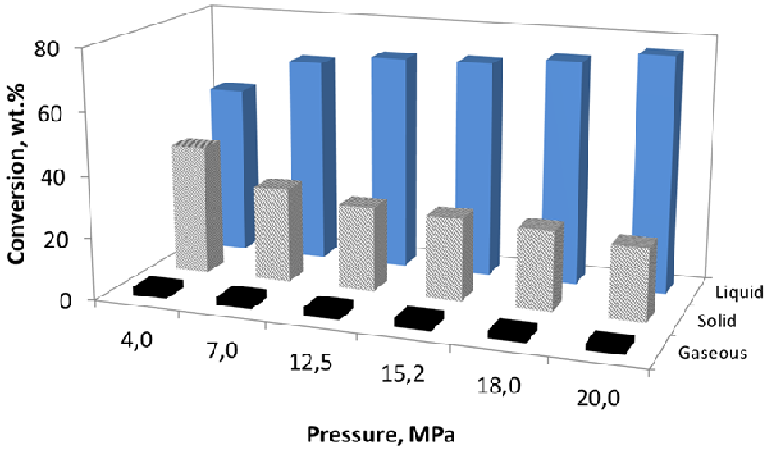

Fig. 3. Effect of pressure on the yield of products of aspen wood thermal depolymerization in ethanol at 270 °C (process time 3 h).

The influence of temperature and pressure on the conversion of main wood components (cellulose, hemicelluloses, lignin) was studied (Fig. 4). Hemicelluloses undergo the most intense depolymerization and their conversion reaches to 100 % already at pressure of 15.2 MPa. At the process pressure 20.0 MPa the conversion of lignin reaches 70 wt%. Cellulose is the most inert component of wood. The solid residue of aspen wood depolymerization in supercritical ethanol at 270 °C and pressure 20 MPa contains 71 wt% of cellulose (Fig. 4).

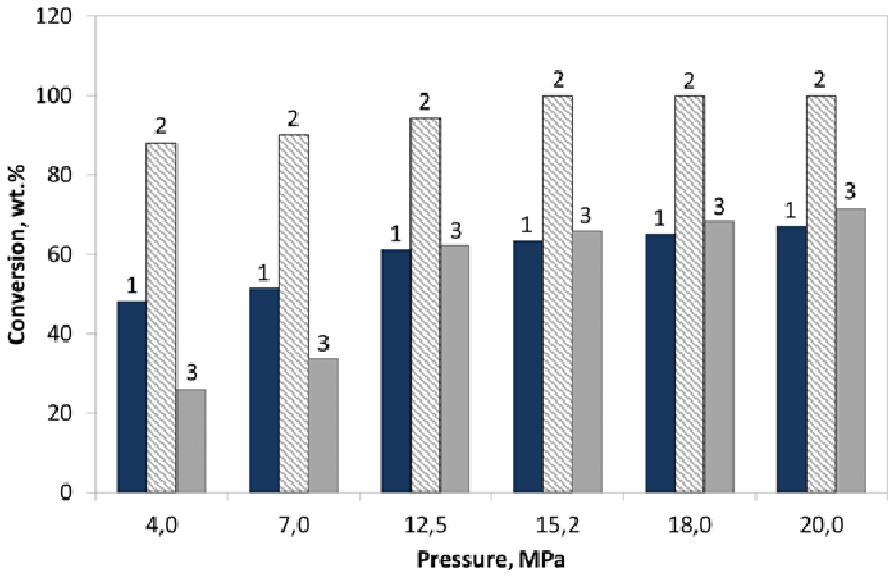

Fig. 4. Effect of pressure on the conversion of the main components of aspen wood in the process of thermal depolymerization in ethanol at 270 °C: 1 – cellulose, 2 – hemicelluloses, 3 – lignin (process time 3 h).

The rise of the temperature from 270 to 350 °C increases the yield of ethanol-soluble and gaseous products and reduces the yield of solid rest. At the temperature of 350 °C the rise of pressure from 4 to 20 MPa increases by 2 time the yield of ethanol-soluble product (up to 91 wt%) (Table 1).

Table 1
Effect of pressure on the yield of products of thermal depolymerization of aspen wood in ethanol (350 °C, 3 h).

Products	Solvent pressure, MPa					
	4.0*	7.0	12.5	15.2	18.0	20.0
	Yield, wt.%					
Ethanol soluble	46.8	49.8	64.1	73.5	86.1	91.0
Gaseous	21.3	20.4	16.2	9.7	6.21	4.1
Solid residue	31.9	29.5	19.7	16.8	7.7	4.5

* subcritical pressure of the solvent.

3.2. Catalytic hydrogenolysis of aspen wood in supercritical ethanol medium

Taking into account the results of the study of aspen wood thermal depolymerization in ethanol medium, the following conditions for catalytic hydrogenolysis of wood in supercritical ethanol were chosen: temperature 250 °C, pressure 9 MPa. At these conditions the catalytic properties of bifunctional catalysts Ru/C, Pt/ZrO_2 and $NiCuMo/SiO_2$ were compared (Fig. 5).

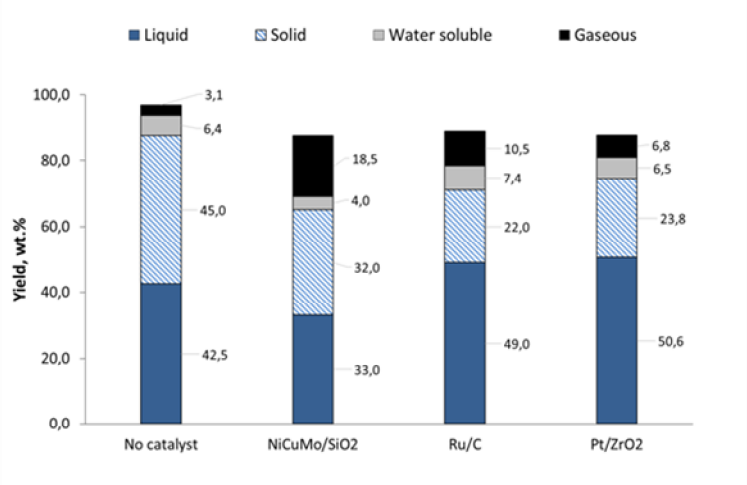

Fig. 5. Yield of products of aspen wood catalytic hydrogenolysis (250 °C, 9 MPa, 3 h).

The conversion of aspen wood in the process of non-catalytic hydrogenolysis at 250 °C is 55.0 wt% (Table 2), the yields of liquid and gaseous products are 42.5 wt% and 45 wt%, respectively (Fig. 5). All catalysts increase the conversion of wood and the yield of gaseous products compared to non-catalytic hydrogenolysis process. Catalysts reduce the yield of solid residue but have only little effect on the yield of liquid products (Table 2, Fig. 5). The most effective is the catalyst Ru/C, which provide the high conversion of wood (78 wt%), significant yield of liquid products (49 wt%) and low yield of solid residue (22 wt%). Catalyst Pt/ZrO_2 is somewhat inferior to ruthenium catalyst in its efficiency but superior to it in terms of low yield of gaseous products (6.8 wt% instead of 10.5 wt%).

Table 2
Conversion of aspen wood and its structural components in catalytic hydrogenolysis in supercritical ethanol (250 °C, 9 MPa, 3 h).

Catalyst	Conversion of wood, wt. %	Conversion of the structural components of wood, wt. %		
		Hemicelluloses	Lignin	Cellulose
No catalyst	55.0	95.0	36.7	43.0
$NiCuMo/SiO_2$	68.0	96.9	67.2	46.9
Ru/C	78.0	97.7	78.4	60.3
Pt/ZrO_2	76.2	98.0	81.5	57.7

The influence of hydrogenolysis conditions on the yield and composition of gaseous products is illustrated by Fig. 6. In gaseous products of non-catalytic hydrogenolysis of aspen wood dominates CO_2. In the composition of gaseous products of wood hydrogenolysis in the presence of catalysts $NiCuMo/SiO_2$ and Ru/C the main component is CO. Carbon oxides and methane are formed as a result of the reactions of decarbonylation, decarboxylation and cracking of the functional group of wood biomass.

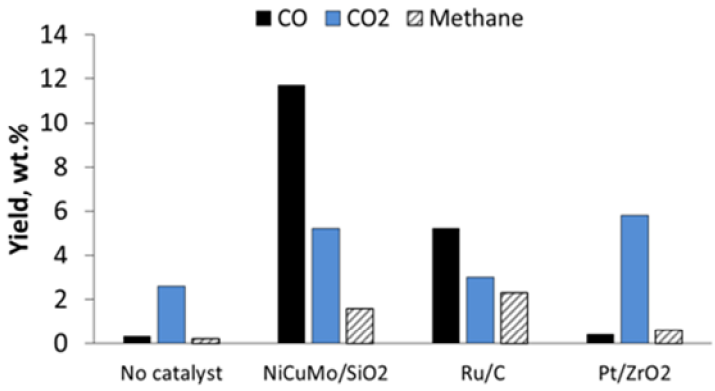

Fig. 6. Yield of gaseous products of aspen wood catalytic hydrogenolysis (250 °C, 9 MPa, 3 h).

According to chemical analysis date, the solid rest of non-catalytic hydrogenolysis of wood contains 68.6 wt% of cellulose and 28.7 wt% of lignin (Table 3). Catalysts increase the content of cellulose in solid rest to 76.8 wt% ($NiCuMo/SiO_2$) to 77.3 wt% (Ru/C) and to 82.2 wt% (Pt/ZrO_2). At the same time, the lignin content in the solid residue is decreased to a minimum value 15.9 wt% in the presence of catalyst Pt/ZrO_2 (Table 3). The content of hemicelluloses in solid residue does not exceed 2.7 wt%.

Table 3
Composition of solid products formed in the process of aspen wood catalytic hydrogenolysis (250 °C, 9 MPa, 3 h).

Catalyst	The composition of solid products, wt. %		
	Cellulose	Lignin	Hemicelluloses
No catalyst	68.6	28.7	2.7
$NiCuMo/SiO_2$	76.8	20.9	2.3
Ru/C	77.3	20.1	2.6
Pt/ZrO_2	82.2	15.9	1.9

Results of elemental analysis of liquid products of wood hydrogenolysis are presented in Table 4. Catalysts promote the hydrodeoxygenation reactions, reducing the content of oxygen in liquid products from 31.6 wt% (non-catalytic hydrogenolysis) to 27.9 wt% (Ru/C).

Table 4
Elemental composition of aspen wood and liquid products obtained by hydrogenolysis of aspen wood (250 °C, 9 MPa, time 3 h).

Sample	C, wt%	H, wt%	O, wt%
Aspen Wood	49.9	6.1	44.0
Liquid products			
No catalyst	61.9	6.5	31.6
Catalyst $NiCuMo/SiO_2$	62.5	6.9	30.7
Catalyst Ru/C	63.9	8.2	27.9
Catalyst Pt/ZrO_2	63.3	7.1	29.6
Cellulose (calculation)	44.4	6.2	49.4

The analysis of liquid products of aspen wood hydrogenolysis was carried out by GC-MS method. Individual compounds identified in liquid products are given in Table 5.

Table 5
Effect of catalysts on the composition and relative yield of individual compounds formed in the process of aspen wood catalytic hydrogenolysis (250 °C, 9MPa, 3 h).

№ п/п	RT	Compound	Yield, wt%*			
			No/cat.	$NiCuMo/SiO_2$	Ru/C	Pt/ZrO_2
1	14.19	Phenol	1.0	0.5	0.7	1.5
2	18.13	Guaiacol	0.4	0.00	0.0	0.0
3	21.74	Methyl guaiacol	0.00	0.2	0.1	0.1
4	24.38	**Ethyl guaiacol**	**0.5**	**2.5**	**1.0**	**0.8**
5	26.45	Syringol	2.3	0.5	0.8	0.7
6	26.82	**Propyl guaiacol**	**0.3**	**2.3**	**13.3**	**13.9**
7	27.92	Propenyl guaiacol	0.8	0.0	0.2	0.3
8	28.97	Methyl siringol	0.00	0.5	0.00	0.0
9	30.93	**Ethyl syringol**	**0.7**	**4.1**	**2.1**	**1.8**
10	32.89	**Propyl syringol**	**0.7**	**7.0**	**21.3**	**20.5**
11	33.86	**Syring aldehyde**	**1.0**	**5.4**	**2.7**	**2.7**
12	34.98	Propenyl syringol	1.8	0.00	0.4	0.6
Total yield of compounds			**9.5**	**23.1**	**42.6**	**42.9**

*-on mass of lignin, %

It was found that alkyl derivatives of metoxyphenols predominate in the liquid products. In non-catalytic hydrogenolysis their total yield does not exceed 9.5 wt%. Bifunctional catalysts significantly increase the total yield of alkyl derivatives of methoxyphenols, which reaches to 42.6–42.9 % from mass of lignin in the wood in the presence of catalysts Ru/C and Pt/ZrO_2. The main monomeric compounds in liquid products are propyl syringol and propyl quaiacol. The yield of propyl syringol reaches to 20.5 % and 21.3 % on mass of lignin for catalysts Pt/ZrO_2 and Ru/C respectively. In the presence of these catalysts the yield of propyl quaiacol reaches to 13.3–13.9 % on mass of lignin.

The high yield of syringol and quaiacol derivatives indicates that bifunctional catalysts accelerate the cleavage of β-O-4 bonds in the native lignin and promote the reactions of C–C bonds breaking and C=C bonds hydrogenation [19, 37, 41]. At temperature 250 °C supercritical ethanol extracts from wood biomass and depolymerizes to oligomeric and monomeric products less than 37 % of lignin (Table 2). The conversion of native lignin increases more than 2 times in the presence of catalysts (Table 2). So, the used biofunctional catalysts not only increase the conversion of native lignin of aspen wood but raise the yield of monomeric compounds in liquid products form 9.5 wt% to 42.9 wt%.

3.3. Thermal depolymerization of aspen ethanol lignin in supercritical ethanol medium

The possible mechanism of catalytic hydrogenolysis of aspen wood in supercritical ethanol includes the isolation from wood the soluble ethanol lignin, which is subjected to reactions of thermal and catalytic depolymerization to liquid products.

The sample of ethanol lignin was isolated by treatment of aspen wood with supercritical ethanol at 190 °C during 3 hours as in [32]. Elemental composition of ethanol lignin is presented in Table 6. Aspen ethanol lignin is comparable in composition to aceton lignin, isolated from aspen wood [26].

Table 6
Elemental composition of aspen ethanol lignin.

The content of elements, wt.%			Atomic ratio		Ash content, wt%
C	H	O	H/C	O/C	
64.6	6.8	26.7	1.3	0.3	0.5

FTIR spectrum of aspen ethanol lignin contains absorption bands characteristic of phenylpropane structural units of the quaiacyl and syringyl type. According to thermogravimetric analysis, the thermal decomposition of ethanol lignin proceeds in two stages, which correspond peaks of mass loss at 300 °C and 390 °C.

The influence of temperature of ethanol lignin thermal depolymerization in supercritical ethanol medium on the yield of liquid, solid and gaseous products was studied (Fig. 7). The most high yield of benzene-soluble liquid products (42 wt%) is reached at temperature 300 °C.

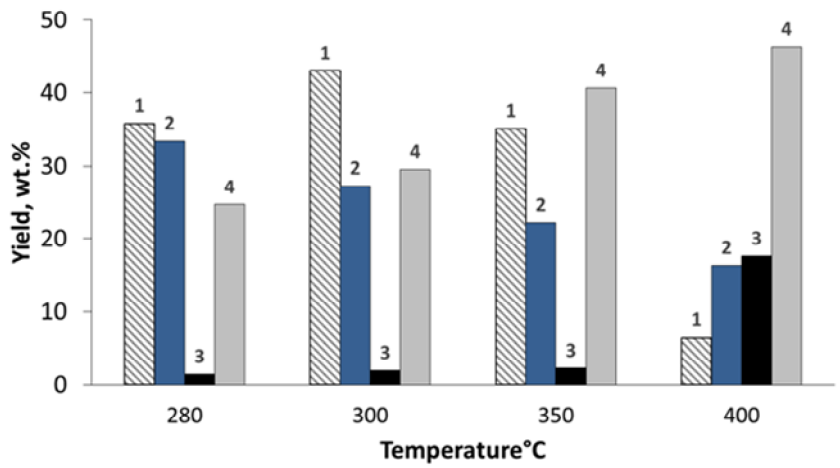

Fig. 7. Influence of the temperature of ethanol lignin depolymerization in supercritical ethanol on the yield of benzene-soluble (1), ethanol-soluble (2), gaseous (3) and solid (4) products (9,0 MPa, 3 h).

More than 80 individual compounds were identified by GC-MS methods in benzene-soluble products of ethanol lignin thermal depolymerization in supercritical ethanol. They contain derivatives of phenol and benzene and also ethyl esters. The presence of esters can be explained by reactions of ethanol with liquid products of lignin depolymerization [20, 21].

Group composition of benzene-soluble liquid products of ethanol lignin thermal depolymerization is given in Table 7. The rise of temperature of ethanol lignin thermal depolymerization from 280 to 300 °C increases significantly the relative content of methoxyphenols and methoxybenzenes in benzene-soluble products. The further increase in temperature does not lead to a noticeable changes in composition of these liquid products.

Table 7
Effect of the temperature of ethanol-lignin depolymerization in supercritical ethanol on the group composition of benzene-soluble products (GC-MS data)

Compounds	Content, %*		
	280 °C	300 °C	350 °C
Pnenols, i.e. methoxyphenols	37.4 27.9	55.9 44.7	56.9 45.9
Esters	43.8	18.5	18.1
Benzene derivatives, i.e. methoxybenzenes	7.5 7.5	17.8 17.4	18.4 17.9

* % on the sum of peak areas

3.4. Catalytic hydrogenolysis of aspen ethanol lignin in supercritical ethanol medium

The influence of bifunctional catalysts Ru/C, Pt/ZrO_2, $NiCuMo/SiO_2$ on the yield of products of aspen ethanol lignin hydrogenolysis in supercritical ethanol medium at 250 °C was studied (Fig. 8)

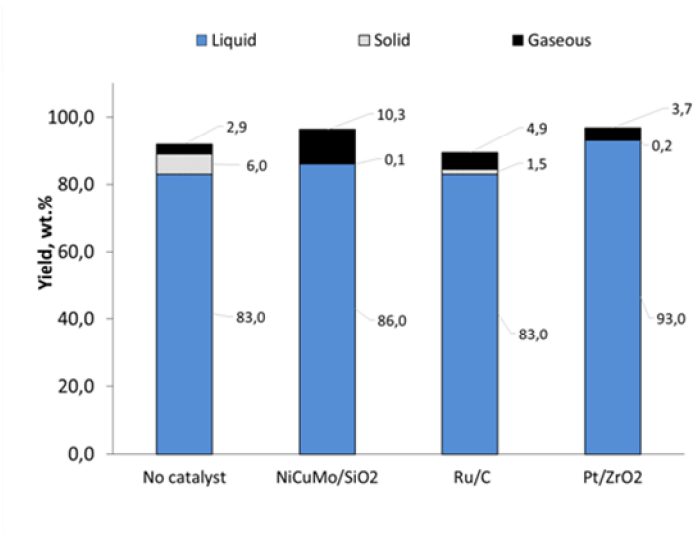

Fig. 8. Influence of catalyst nature on the yield of the products of aspen ethanol-lignin hydrogenolysis (250 ° C, 9 MPa, 3 h).

The catalyst Pt/ZrO_2 increases the yield of liquid products up to 93 wt%, while the catalysts Ru/C and $NiCuMo/SiO_2$ have little effect on liquid products yield. All catalysts reduce the yield of solid rest, which is formed by repolymerization of lignin-based reactive intermediates [16, 42]. In the presence of hydrogen, the metal active centers of bifunctional catalyst prevent condensation reactions of intermediates resulting in lower yield of solid rest. In the presence of catalyst $NiCuMo/SiO_2$ the significant increase in the yield of gaseous products was observed (Fig. 9).

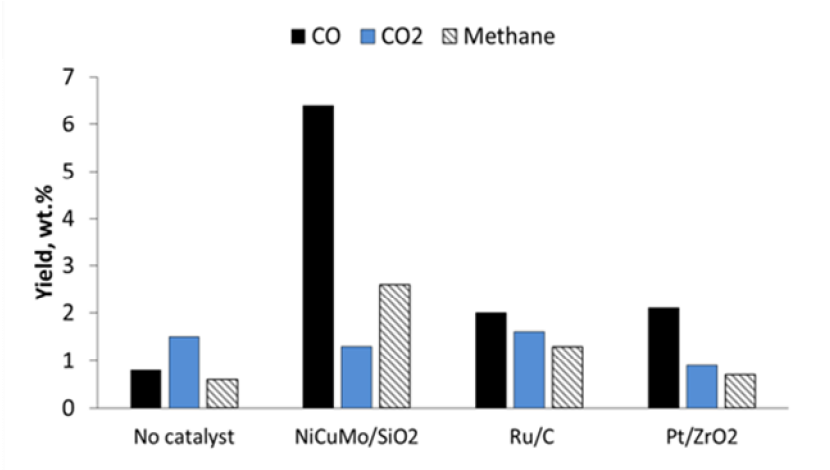

Fig. 9. Yield of gaseous products of aspen ethanol lignin catalytic hydrogenolysis (250 °C, 9 MPa, 3 h).

This catalyst promotes the formation of carbon monoxide and methane while carbon dioxide prevails in gaseous products of non-catalytic hydrogenolysis process. The increased yield of gaseous products in the presence of bifunctional catalyst can be explained by following reasons. Acid centers of the catalyst intensify the reactions of ester bonds hydrolysis in lignin and subsequent decarbonylation of the resulting acid groups with the release of CO_2. Metal centers of catalyst promote the reaction of decarbonylation of Hibbert ketones formed by acid-catalyzed depolymerization of lignin [8], and hydrocracking of methoxyphenols and phenols [43, 44] with CO and methane release.

The individual compounds formed in the processes of abies ethanol lignin catalytic hydrogenolysis were identified by GC-MS methods (Table 8). They are mainly represented by alkyl derivatives of methoxyphenols like liquid products of aspen wood hydrogenolysis.

In the process of non-catalytic hydrogenolysis of ethanol lignin the yield of phenol derivatives is 5.5 wt%, including 4.5 wt% of alkyl derivatives of methoxyphenols. The bufunctional catalysts increase the yield of alkyl derivatives of methoxyphenols, but to a lesser extent than was observed in the case of catalytic hydrogenation of aspen wood.

Table 8
Effect of catalysts on the yield of individual phenolic compounds formed in the process of aspen ethanol lignin hydrogenolysis (250 °C, 9 MPa, 3 h).

RT	Monomers	Yield, wt%*			
		No/cat.	$NiCuMo/SiO_2$	Ru/C	Pt/ZrO_2
14.19	Phenol	0.19	0.32	0.28	0.30
18.13	Guaiacol	0.18	0.23	0.24	0.11
21.74	Methyl guaiacol	0.36	0.00	0.08	0.23
24.38	Ethyl guaiacol	**0.28**	**0.41**	**0.50**	**0.29**
26.45	Syringol	**0.39**	**0.54**	**0.40**	**0.22**
26.82	Propyl syringol	**0.69**	**1.11**	**1.50**	**2.03**
28.97	Methyl syringol	**0.85**	**0.99**	**0.30**	**0.26**
29.03	Propenyl guaiacol	0.02	0.05	0.05	0.03
30.05	Acetoguaiacone (Acetovanillone)	0.04	0.04	0.04	0.02
30.93	Ethyl syringol	**0.60**	**0.71**	**0.60**	**0.32**
31.22	Homovanillyl alcohol		0.64	0.60	0.73
32.38	Ethyl vanillate	0.03	0.01	0.01	0.04
32.88	Propyl syringol	**1.75**	**2.32**	**2.10**	**4.16**
33.70	Ethylhomovanillate	0.04	0.04	0.04	
34.25	Propenyl syringol	0.08	0.14	0.19	0.09
35.77	Acetosyringone	0.12	0.04	0.04	0.01
35.99	Ethyl-β-(4-hydroxy-phenyl)-propionate	0.01	0.01	0.01	0.01
	Total yield	**5.63**	**7. 6**	**6.98**	**8.85**

*on mass of lignin, %

The sharp decrease in the yield of monomeric products from ethanol lignin compared to wood is probably due to reduced content of ether β-O-4 bonds in the structure of ethanol lignin in comparison with native lignin of aspen wood. Obviously, in the process of ethanol lignin isolation from aspen wood the reactions of condensation take place [18]. They reduce the content of reactive ether bonds and increase the content of low-reactive C–C bonds in ethanol lignin compared to native lignin. As a result, the content of monomeric derivatives of phenol in liquid products obtained by ethanol lignin hydrogenolysis is less than in the case of wood hydrogenolysis (Table 9).

Table 9
Effect of catalysts on the yield of monomeric phenol derivatives in the process of aspen ethanol lignin hydrogenolysis (250 °C, 9 MPa, 3 h).

Monomers	Yield, wt%*			
	No/cat.	$NiCuMo/SiO_2$	Ru/C	Pt/ZrO_2
Ethyl guaiacol	0.28	0.29	0.50	0.41
Propyl guaiacol	0.69	2.03	1.50	1.11
Ethyl syringol	0.60	0.32	0.60	0.71
Propyl syringol	1.75	4.16	2.10	2.32
Syringol	0.39	0.22	0.40	0.54
Methyl syringol	0.85	0.26	0.30	0.99
Total yield	**4.56**	**7.28**	**5.5**	**6.08**

*on mass of lignin, %

The influence of catalyst nature on the molecular mass distribution (MMD) of liquid products of aspen wood and ethanol lignin hydrogenolysis was studied by GPC method. All bifunctional catalysts shift the MMD of liquid products to the region of lower molecular mass (Fig. 10, Table 10).

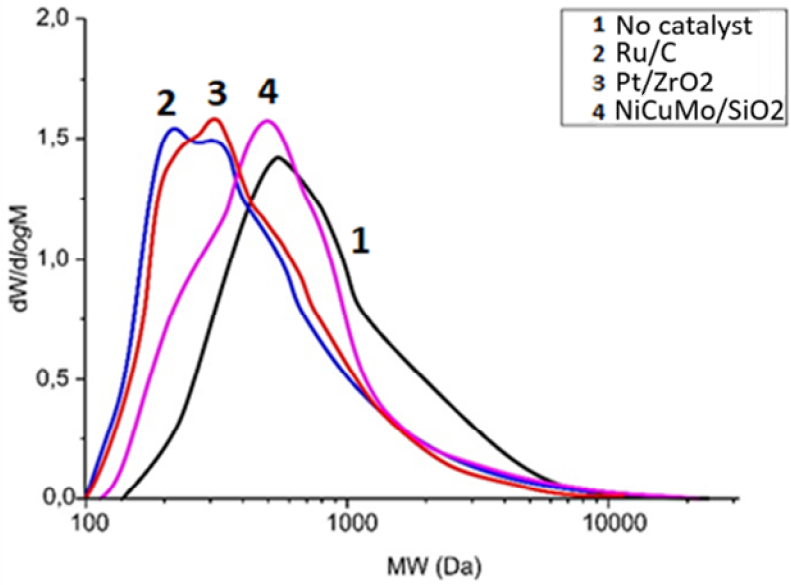

Fig. 10. Molecular mass distribution curves of liquid products of aspen wood hydrogenolysis (250 °C, 9 MPa, 3 h.

Table 10
Molecular mass characteristics of liquid products of aspen wood hydrogenolysis (250 °C, 9 MPa, 3 h).

Catalyst	Mn (Da)	Mw(Da)	D
No catalyst	643	1155	1.80
$NiCuMo/SiO_2$	572	906	1.58
Ru/C	398	731	1.84
Pt/ZrO_2	376	727	1.93

The most significant shift is observed for catalyst Ru/C and the least – in the case of catalyst $NiCuMo/SiO_2$. All catalysts change the profile of MMD curve. When the catalyst $NiCuMo/SiO_2$ is used the region higher 1000 Da practically disappears and the intensity of peak with MM 400–600 Da increases. Catalysts Pt/ZrO_2 and Ru/C increase the content of monomeric compounds in liquid products and reduce the content of oligomers with MM 400–600 Da.

Liquid products of ethanol lignin hydrogenolysis have a more broad range of MMD than that obtained by hydrogenolysis of aspen wood (Fig. 11, Table 11).

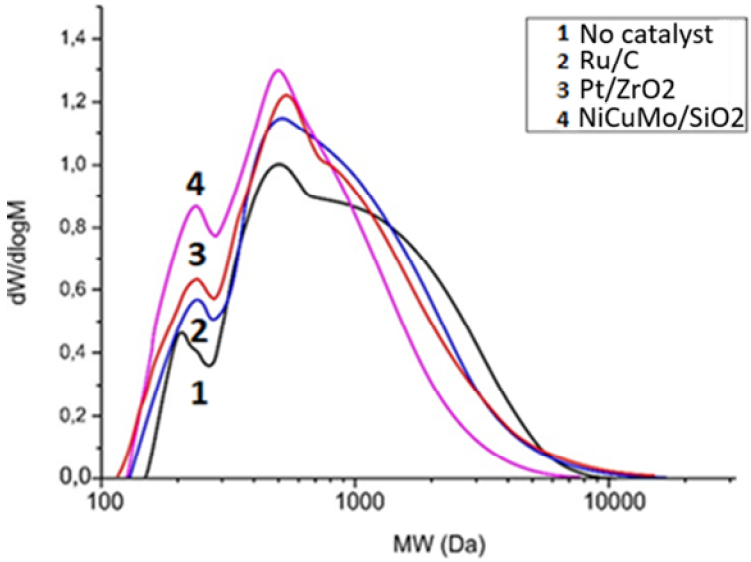

Fig. 11. Molecular mass distribution curves of liquid products of aspen ethanol lignin hydrogenolysis (250 °C, 9 MPa, 3 h).

Table 11
Molecular mass characteristics of the liquid products of aspen ethanol lignin hydrogenolysis (250 °C, 9 MPa, 3 h).

Catalyst	Mn (Da)	Mw(Da)	D
No catalyst	647	1301	2.01
$NiCuMo/SiO_2$	468	771	1.64
Ru/C	636	1147	1.80
Pt/ZrO_2	567	1112	1.96

They contain mainly the fragments of lignin depolymerization with MM from 1000 to 10000Da and oligomers (mainly dimers) with MM 400–600 Da. The low content of monomeric compounds in liquid products of ethanol lignin hydrogenolysis can be explained by the increased contribution of repolymerization reactions with the participation of lignin-based intermediates. The average molecular weight (M_w) of aspen ethanol lignin is 2230 Da. For liquid products of non-catalytic hydrogenolysis of ethanol lignin M_w decreases to 1301 Da (Table 11). The catalysts shift the MMD curve of liquid products of ethanol lignin hydrogenolysis to the region of lower molecular mass and change its profile. The intensity of peak with MM ~200 Da increases in the presence of catalysts, which indicates an increase in the content of monomeric compounds in liquid products of ethanol lignin catalytic hydrogenolysis.

The results of the study show that the native lignin of aspen wood is easier depolymerized to monomeric compounds in the process of catalytic hydrogenolysis compared to ethanol lignin isolated from aspen wood.

Conclusion

Catalytic properties of bifuctional catalysts Ru/C, Pt/ZrO_2, $NiCuMo/SiO_2$, containing nanosized metal particles on acidic supports were compared in the processes of aspen wood and ethanol lignin hydrogenolysis in supercritical ethanol at 250 °C and 9 MPa.

In non-catalytic hydrogenolysis of aspen wood at 250 °C the conversion of wood is 55 wt%, yield of liquid products 42 wt% and yield of solid rest 45 wt%. All studied catalysts increase the conversion of wood and yield of gaseous products and reduce the yield of solid residue. They weakly affect on the yield of liquid products, but increase significantly the content of monomeric lignin-based compounds. The most effective catalysts Ru/C and Pt/ZrO_2 provide high conversion of wood (78.0 wt% and 76.2 wt%), considerable yield of liquid products (49.0 wt% and 50.6 wt%) and low yield of solid residue (22.0 wt% and 23.8 wt%). The catalysts also promote the hydrodeoxygenation reactions, reducing the content of oxygen in liquid products compared to non-catalytic hydrogenolysis. According to GPC data, the catalysts shift the molecular mass distribution of liquid products to the region of lower molecular mass.

In contrast to acid catalysts based on high silica zeolites, which promote at 270 °C the conversion of polysaccharides in supercritical ethanol medium without hydrogen [12], bifunctional catalysts Ru/C, Pt/ZrO_2, $NiCuMo/SiO_2$ significantly increase the yield of alkyl derivatives of methoxyphenols (mainly propyl siringol and propyl quaiacol) in the presence of H_2.

Solid products of aspen wood catalytic hydrogenolysis contain up to 82.2 wt% of cellulose. Therefore, it is possible to fractionate the aspen wood biomass on cellulose and liquid product enriched with propyl syringol and propyl quaiacol using wood hydrogenolysis in supercritical ethanol at 250 °C in the presence of bifunctional catalysts Ru/C and Pt/ZrO_2.

In the process of aspen wood hydrogenolysis the bifunctional catalysts increase the yield of alkyl derivatives of methoxyphenols to a higher extent that in the case of catalytic hydrogenation of ethanol lignin. Obviously, in the process of ethanol lignin isolation from wood the condensation reactions take place, which reduce the content of reactive ether bonds and increase the content of less reactive C–C bonds compared to native lignin. Monomeric products of catalytic hydrogenolysis of native lignin of aspen wood have prospects to use for the production of fuel additives and components of motor fuels.

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