

Thermal conversion of aspen wood in supercritical ethanol in the presence of high-silica zeolite catalysts

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ABSTRACT

The use of high-silica zeolite catalysts and the preliminary mechanical treatment of aspen wood increase the wood conversion in supercritical ethanol at temperatures 270 and 350 °C and rise the yield of resulting liquid products.

The suggested mechanism of aspen-wood conversion over solid catalysts includes the steps of thermal dissolution of native wood lignin in supercritical ethanol and its further catalytic conversions to liquid hydrocarbons.

At temperature 270 °C and pressure 6.4 MPa zeolite catalysts increase by 2.3–2.5 times the yield of liquid products with b.p. < 180 °C and the content of furan derivatives (mainly furfural and 5-HMF) in ethanol soluble products. The highest activity demonstrates the catalyst H-HSZ-30 with Si/Al=30, which has the most high concentration of acidic sites. The rise of a pressure from 6 to 17 MPa at 270 °C increases 2 times the yield of fraction with b.p. > 180 °C (to 63 wt.%) and reduces the yield of fraction with b.p. < 180 °C.

The increase a temperature of aspen wood catalytic conversion in supercritical ethanol to 350 °C decreases the yield of liquid products and initiates the secondary reactions of liquid components transformation to gaseous and char products.

Thus, the conversion of mechanically activated mixture of aspen wood and zeolite catalysts in supercritical ethanol at 270 °C allows to separate the biomass components on liquid products from hemicelluloses and solid lignocellulose. At temperature of wood catalytic conversion 350 °C mainly the liquids from polysaccharides and lignin are formed along with gaseous and char products.

Key words: wood, zeolites, ethanol, conversion, products, composition.

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1. Introduction

Lignocellulosic biomass is a promising renewable raw material, the use of which, unlike fossil fuels, does not lead to accumulation of carbon dioxide in the atmosphere [1].

To obtain chemicals and liquid biofuels from lignocellulosic biomass, it is necessary to depolymerize such macromolecules as cellulose, hemicelluloses and lignin. For this purpose thermal methods have traditionally been used [2–4]. Pyrolysis of wood in inert atmosphere at temperatures 500–700 °C leads to the formation of resins, gaseous products, carbon residue and water. Pyrolysis liquids contain a significant amount of polyphenols and polyaromatic hydrocarbons. Also they have a high viscosity and corrosive activity. When they are distilled under vacuum, not less than 50 wt.% of solid residue is formed [3,4]. All this complicates the use of liquids of lignocellulosic biomass pyrolysis as a raw material for the production of motor fuels and chemicals.

The high yield of low-boiling liquid products can be obtained by thermal transformations of biomass in supercritical organic solvents [5–11].

In the last decade, the considerable attention is paid to the study of the thermal conversion of lignocellulosic biomass in supercritical ethanol [6, 9–11]. The critical temperature of ethanol (243 °C) corresponds to the beginning of a intensive thermal depolymerization of lignocellulosic biomass [7]. In addition ethanol can stabilize the intermediate radical products of thermal degradation of biopolymers, preventing their repolymerization. Besides that, ethanol can react with acid components of the bio-oil with the formation of corresponding ethyl esters, which can be used as biodiesel [11].

The accomplished studies on biomass liquefaction in sub- and supercritical ethanol has shown that the yield of bio-oils depends to a great extent on the nature of lignocellulosic biomass and on the process temperature [6–15]. In supercritical ethanol at temperature of 300 °C, the yield of bio-oils from pine wood was varied from 31 wt.% [8] up to 63 wt.% [9], from the stalks of maize it was 19 wt.% [13], from rice husk 21 wt.% [14], from cane 54 wt.% [7], from microalgae *Spirulina* about 40 wt.% and from *Dunaliella tertiolecta* about 50 wt.% [15]. Bio-oils obtained in the ethanol medium have a complex composition and they contain various derivatives of phenol, furan, ethyl esters and other organic compounds.

It was proposed to use the solid catalysts for intensification of biomass conversion processes [16–19]. Zeolites received a wide application as acid type solid catalysts in the processes of biomass pyrolysis and in bio-oils refining [20–26].

Fast pyrolysis of wood, cellulose, hemicelluloses, lignin and a number of agricultural wastes was studied at temperature of 550 °C in the presence of commercial zeolites with a different silicate module: H-ferrierite with Si/Al = 20, H-mordenite with Si/Al = 20, HY with

Si/Al = 5,1, H-ZSM-5 with Si/Al = 23, 50, 280 and H-beta zeolite with Si/Al = 25, 38, 360 [21]. These catalysts reduced the content of oxygen-containing compounds in liquid products of biomass pyrolysis. The highest content of aromatic hydrocarbons in liquid products was obtained in the presence of catalyst H-ZSM-5 with Si/Al=50. In the series of zeolites H-ZSM-5 and H-beta, the decrease in the silicate module led to an increase in the yield of gaseous products and aromatics.

Zeolite catalysts H-ZSM-5 with a different silicate module increase the yield of light fractions of liquid products of Kraft lignin pyrolysis at 600 °C [22]. This effect was more pronounced for zeolites with a low Si/Al ratio. But zeolites with Si/Al ratio 50 and 80 were the most active in the reaction of removal of methoxyl groups and ether bonds breaking.

Fast pyrolysis of biomass in the presence of zeolite catalysts allows to obtain aromatics of the BTX type (benzene, toluene, xylenes), as well as heavier aromatic compounds [23]. The increase of acidity of the zeolites, typically rises the yield of aromatic hydrocarbons. The reduction of their silica module increases the yield of coke and gas.

Acidic high-silica zeolite catalysts with the ratio Si/Al=30 and 100 increase the conversion of alkaline lignin in supercritical ethanol at temperatures of 300, 350 and 400 °C [25]. The maximum conversion of lignin (71 wt.%) and the highest yield of the low-boiling fraction of liquid products (44 wt.%) are achieved at 350 °C in the presence of a zeolite catalyst with a silicate module 30, containing a high concentration of acid sites. At temperature of 400 °C, these catalysts reduce the phenol content in liquid products by 4–16 times [25].

The study of the conversion of pine sawdust at 300 °C in a supercritical ethanol showed that zeolites ZSM-5 (Si/Al=25), H-beta (Si/Al=25), HY(Si/Al=5), HY(Si/Al=80), K₂CO₃ and KOH, FeSO₄ only slightly increase the yield of bio-oils [8]. The authors associate this result with the poor contact of the zeolite catalyst particles with the wood, what hinders the diffusion of products of thermal conversion of wood to the active centers of catalyst.

Better contact between solid catalyst and biomass can be achieved by the mechanical treatment, which reduces the particle size and increases the homogeneity of catalyst distribution in reaction mixture [27, 28]. However, to date, there are only a few examples of the positive effect of mechanical activation of mixtures biomass – catalyst on the conversion of biomass into low-molecular products [29–31]. In particular, it has been found that the use of mechanical treatment of mixtures of cellulose and solid acid catalysts in a ball mill intensifies the conversion of cellulose into water-soluble products: levoglucosan, levoglucosenone, furfural and 5-hydroxymethylfurfural [29]. The highest conversion of cellulose (84 wt.%) was achieved with the use of kaolinite as a catalyst. In the presence of Y-zeolite, the degree of conversion of cellulose was only 20 wt.%.

The mechanical treatment of the mixtures of beech wood or ethanol-lignin with Na_2SO_4 in a planetary mill, intensified the depolymerization of cellulose, hemicelluloses and lignin [30].

Taking into account the data considered, it can be assumed that the use of mechanical activation of wood – zeolite catalysts mixtures will allow to intensify the processes of thermal depolymerization of wood polymers in a supercritical ethanol medium.

The expected mechanism of wood lignin depolymerization in supercritical ethanol at the temperature, which corresponds to the intensive degradation of lignin, initially includes the dissolution of lignin in the form of so-called ethanol-lignin. In the presence of zeolite catalysts the soluble ethanol-lignin undergoes further conversion to polyphenols, phenolic and aromatic compounds.

This paper describes the thermal conversion of mechanically activated mixtures of aspen wood – zeolite catalysts in a supercritical ethanol medium. The effect of the nature of zeolite catalyst and the conditions of depolymerization process on the yield and composition of the resulting liquid, gaseous and solid products was studied.

2. Materials and methods

2.1. Materials

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

High-silica zeolites in the H-form with a silicate module $\text{Si}/\text{Al} = 100$ (H-HSZ-100), $\text{Si}/\text{Al} = 60$ (H-HSZ-60) и $\text{Si}/\text{Al} = 30$ (H-HSZ-30) were obtained by hydrothermal crystallization of alkaline alumina-silicagels using hexamethylenediamine as a structure-forming additive. The procedure of zeolite catalysts preparation is described in [25]. The specific surface area of the catalysts was measured by the method of equilibrium adsorption of nitrogen at 77 K on the Sorbtometr-M (KATAKON, Russia). The acid properties of the catalysts were studied by the method of thermo-programmed desorption (TPD) of ammonia. The strength of the acid sites was evaluated from the temperature peaks on the thermal desorption curves. Their concentration was determined from the amount of ammonia desorbed from catalyst at the time of fixation of the desorption peaks.

2.2. Thermal conversion of aspen wood

The process of thermal conversion of wood sawdust in supercritical ethanol was carried out at 270 and 350°C in a rotating 0.25 liter stainless steel autoclave (Autoclave Engineers, USA). The temperatures of conversion were chosen based on the results of DTA study of the thermal

conversion of aspen wood. The used temperatures correspond to two maxima of mass loss on the TGA curve of aspen-wood at 270 and 353 °C.

A mixture of dried at 100°C sawdust (15g) and catalyst (1.5g) was mechanically activated in an energy-intensive ball-type activator (AGO-2) during 30 min at acceleration of grinding bodies 600 m/s².

The activated mixture of catalyst and wood (5.5g) and ethanol (15-120ml) was charged to the autoclave. The air was removed from the autoclave by purging it with argon. Then the autoclave was heated to the required temperature at a rate of 10°C/min. The duration of heat treatment at the final temperature was 1 hour. The operating pressure in the autoclave was varied in the range of 4.0-21.0 MPa.

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 (Kristall-2000m, Chromatech, Russia). Liquid and solid products were removed from the autoclave by washing with ethanol. The solid rest additionally was extracted with ethanol in a Soxhlet apparatus. The aliquot of liquid products was selected from ethanol extract to study their composition. Ethanol was distilled from the extracts under mild conditions, eliminating the boiling of the solvent, then the extracts were dried in vacuo at pressure 1.0 torr.

The yield of the fraction of liquid products boiling above 180°C ($\alpha 1$, wt.%) was calculated according to equation 1:

$$\alpha 1 = \frac{m_{\text{extr}}}{m_0 - \left(\frac{m_0 A_0}{100}\right)} \times 100, \quad (1)$$

Where m_0 and m_{extr} are the weight of wood and extract (g), respectively, A_0 - ash content of the initial wood (%).

After extraction, the solid residue was dried at 100°C to constant weight, and the total yield of gaseous and liquid products (X , wt.%) was determined according to equation 2:

$$X = \frac{\left(m_{\text{res}} + m_{\text{kt}} + \left(\frac{A_0 \times m_0}{100}\right)\right)}{m_0 - \left(\frac{A_0 \times m_0}{100}\right)} \times 100 \quad (2)$$

Where m_{res} is the weight of the solid residue (g) after extraction with ethanol, m_{kt} is the catalyst weight (g).

The yield of gaseous products ($\alpha 2$, wt%) was calculated from equation 3:

$$\alpha 2 = \frac{(m_{\text{CO}} + m_{\text{CO}_2} + m_{\text{CH}_4} + m_{\text{C}_2-4}) - (m'_{\text{CO}} + m'_{\text{CO}_2} + m'_{\text{CH}_4} + m'_{\text{C}_2-4})}{m_0 \left(1 - \frac{A_0}{100}\right)} \times 100 \quad (3)$$

Where m_{CO} , m_{CO_2} , m_{CH_4} and $m_{\text{C}_{2-4}}$ are respectively the weights of CO, CO₂, CH₄ and hydrocarbon gases C₂₋₄ obtained as a result of wood conversion in ethanol (g); m'_{CO} , m'_{CO_2} , m'_{CH_4} и $m'_{\text{C}_{2-4}}$ respectively, the weights of CO, CO₂, CH₄ and hydrocarbon gases obtained as a result of ethanol conversion under the same conditions (g).

The yield of liquid fraction of boiling below 180°C. (α , wt.%) was calculated according to equation 4:

$$\alpha = X - \alpha_1 - \alpha_2 \quad (4)$$

The data presented were calculated as the mean of two parallel experiments. If the difference between the values of the wood parallel conversion was more than 3 wt.% the additional experiment was conducted.

2.3. Analysis of wood and products of wood conversion

The content of cellulose, lignin and hemicelluloses in solid products was determined by the standard chemical methods described in [32].

The monosaccharide content was determined by GC using a gas chromatograph "VARIAN-450 GC" with a flame ionization detector. Separation of products was carried out on a capillary column VF-624ms (length – 30 m, internal diameter – 0.32 mm). Conditions for analysis: carrier gas – helium; the injector temperature is 250 °C; the initial temperature of the column thermostat was 50 °C under isothermal holding for 5 min, then the temperature was raised to 180 °C at the rate 10 °C/min and held at 180 °C for 37 min. Temperature of the detector was 280 °C. Before measurements the samples were derivatized to form the trimethylsilyl (TMS) esters according to the procedure described in [33]. Identification of peaks was carried out using retention times for each tautomeric form of monosaccharides. From the ratio of characteristic peaks area to standart peak area, the quantitative content of each monosaccharide in the sample was calculated.

Electronic images of the samples were obtained using a scanning electron microscope (SEM) TM3000 (Hitachi, Japan) with a built-in Quantax 70 microanalysis system (Bruker, EDS) in back-reflected electrons at accelerating voltage 15 kV.

Diffractograms of the sample were obtained using a DRON-3 X-ray diffractometer (LOMO, Russia) in the scanning mode in CuK α radiation (1.5418 nm), the scanning step was 0.02 degree, the accumulation time at the point 1 second and in the range of Bragg angles (2θ) from 5 to 70. For data processing the program "New-Profile" was used.

Liquid products soluble in ethanol, were analyzed by gas chromatography-mass spectrometry (GC-MS) method, using a chromatograph Agilent 7890A, equipped with a mass

selective detector Agilent 7000A Triple Quad (Agilent, USA) for registering the total ion current. The products were separated on a capillary column HP-5MS (length 30 m, internal diameter 0.25 mm) in a thermo-programmed mode with a temperature increase from 40 to 250°C at a rate of 3°C/min.

For thermal analysis of the samples, a synchronous thermal analyzer STA-449C Jupiter, combined with a mass spectrometer QMS 403C Aëolos (TG-DST type S) sensor with a platinum / platinum-rhodium-holder in combination with corundum (Al_2O_3) crucible with pierced lids was used. Samples with a mass of 8.5 ± 0.2 mg were heated from 40°C to 1000°C at a rate of 10°C/min in a flow of argon at a (40 ml/min).

3. Results and discussion

3.1. Mechanical activation of aspen wood

According to SEM data, the initial sample of aspen wood contains large, elongated particles with a size of more than 0.5 mm (Fig. 1A). The mechanical treatment of aspen wood–zeolite catalyst mixture in AGO-2 decreases the size of wood particles and changes their shape. In the mechanically treated wood, the destruction of such components as large vessels, fiber libris and tracheids was observed. In addition, this treatment contributes more homogenous distribution of catalyst particles in the mixture (Fig. 1B).

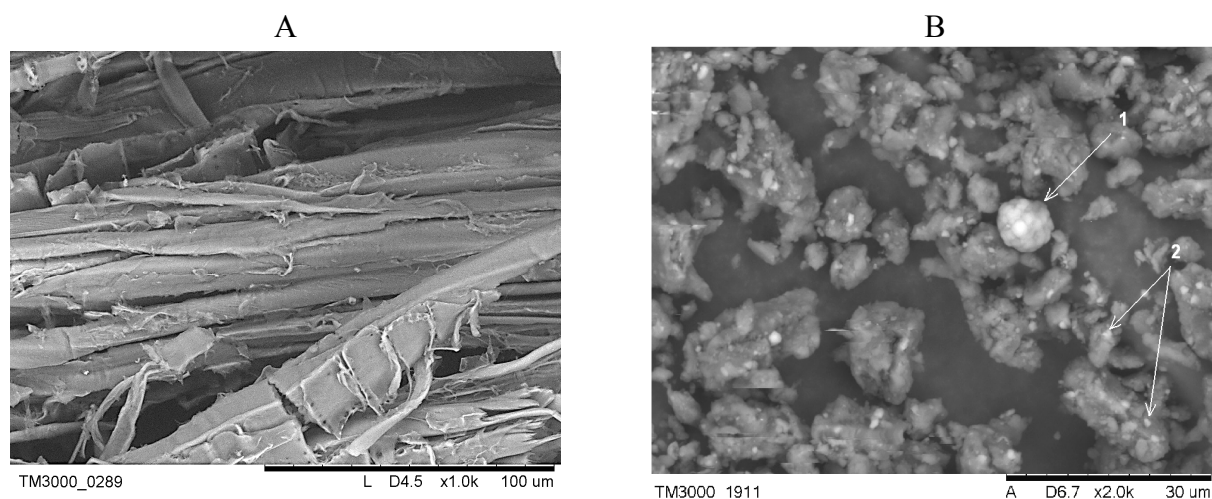


Fig. 1. SEM images of initial aspen wood sample (A) and the mixture of wood with zeolite H-HSZ-30 after activation in AGO-2 (1 – wood particles, 2 – catalyst particles).

The diffractogram of non-activated aspen wood (Fig. 2, curve 1) has a classical form and has two main peaks with maxima at approximately 22.5° and 16°.

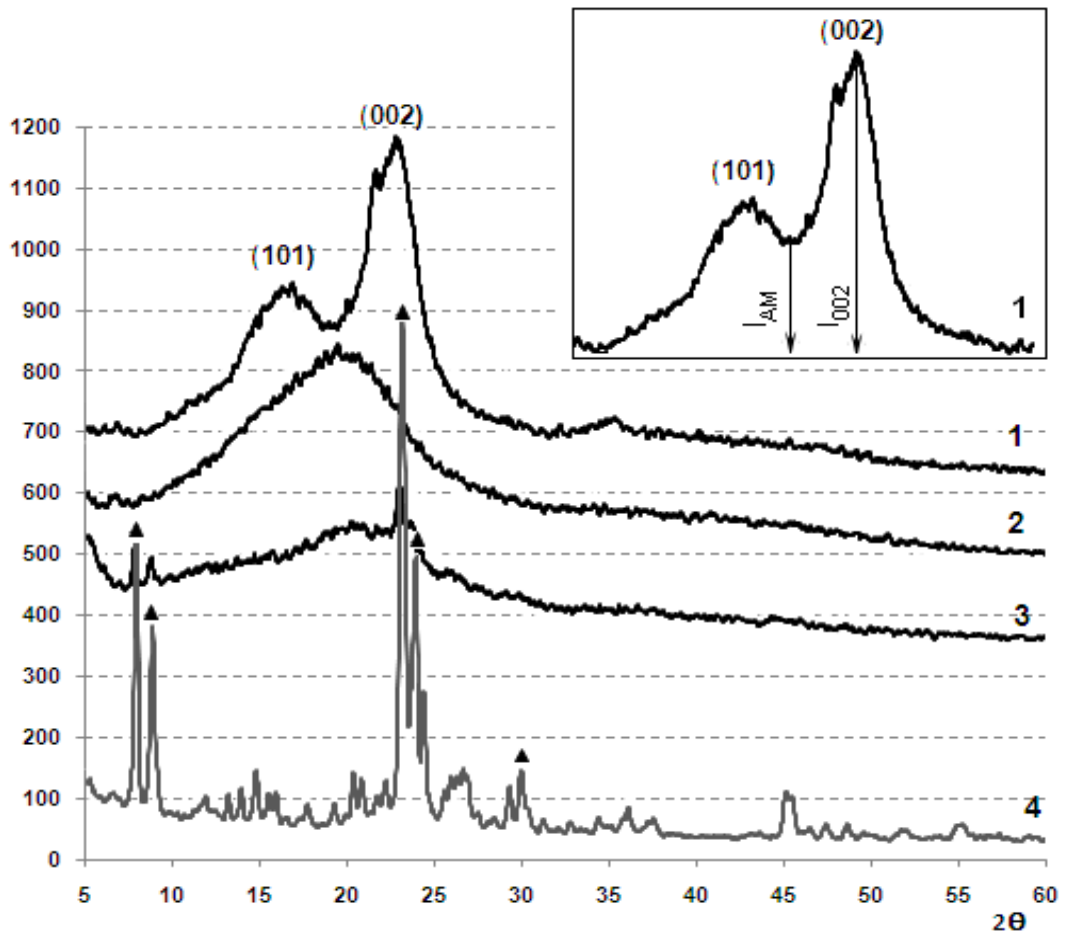


Fig. 2. Fragments of diffractograms of the initial aspen wood (1), aspen wood after treatment in AGO-2 (2), mixture of wood and H-HSZ-30 catalyst after treatment in AGO-2 (3), the initial H-HSZ-30 catalyst (4).

Legend: ▲ – reflexes corresponding to zeolite ZSM-5 (JCPDS, 37–359).

These peaks correspond to reflections of the atoms in planes of the crystal lattice of cellulose [34, 35]. The crystallinity index of wood was calculated as the ratio of the intensity of the crystalline peak ($I_{002} - I_{AM}$) to the total intensity (I_{002}) [34, 35]. The crystallinity index of the initial aspen wood is 0.5. On the diffractograms of the mechanically activated wood (Fig. 2, curve 2) and wood activated together with the H-HSZ-30 catalyst (Fig. 2, curve 3), there is only one broad peak at 20° , which agrees with the diffraction pattern of amorphous cotton cellulose [35]. It means that cellulose in aspen wood subjected to mechanical activation in an energy-intensive planetary-type ball mill AGO-2 has predominantly the amorphous state. All reflections corresponding to zeolite of ZSM-5 type (Fig. 2, curve 4) are present on diffractogram of mechanically activated mixture of woodzeolite catalyst. Thus, the crystal structure of the zeolite is retained during the mechanical treatment under the selected conditions.

3.2. Thermal conversion of aspen wood in supercritical ethanol over zeolite catalysts

Characteristics of zeolite catalysts used are listed in Table 1. High-silica zeolite catalysts have two types of acid sites, corresponding to the two maxima on the curve of thermo-programmed desorption (TPD). Desorption of ammonia from weak acid sites (type I) is observed at 100-320°C, and from strong acid sites (type II) at 320-600°C. From the results obtained, it follows that the highest concentration of both weak and strong acid sites has the catalyst H-HSZ -30 with Si/Al = 30.

Table 1

Characteristics and acid properties of zeolite catalysts.

Catalyst	Specific surface area, m ² /g	Pore diameter, nm	Pore volume, cm ³ /g	T _{max} for acid sites, °C*		Concentration of acid sites, mmol/g**		
				T _I	T _{II}	C _I	C _{II}	C _S
H-HSZ -30	339	2,5	0,14	185	435	546	311	857
H-HSZ - 60	276	2,3	0,10	185	420	361	210	571
H-HSZ -100	352	2,1	0,14	180	410	273	187	460

* T_I и T_{II} – NH₃ desorption temperatures for acid centers of type I and II.

** C_I, C_{II}, и C_S – concentration of acid centers of type I and II and total concentration of acid sites, respectively.

Supercritical ethanol is not subjected to chemical conversions at temperature of 270°C. Its conversion at 350°C does not exceed 8 wt.%. Zeolite catalysts increased the conversion of ethanol to 28-31 wt.% already at a process temperature of 270°C and up to 80 wt.% at 350°C. Diethyl ether was a predominant product of ethanol conversion, which is consistent with the literature data [36].

Table 2 presents the data on the effect of zeolite catalysts on the thermal conversion of aspen wood in supercritical ethanol and on the yield of liquid products. Mechanical treatment of wood increases its conversion, the yield of liquid and gaseous products and reduces the yield of solid residue. Zeolite catalysts only slightly increase the conversion of the wood at 270 °C. But they rise 2.5 times a yield of light fraction of the liquid products, boiling below 180 °C. Also they reduce the yield of fraction with a boiling point > 180 °C and the yield of solid residue.

The increase in the temperature of wood conversion to 350 °C rises the yield of gaseous products and reduces the yield of liquid products with boiling point > 180 °C as a result of the intensification of cracking reactions by zeolite catalysts.

As follows from the data obtained, the highest yield of liquid products (83.5wt.%) is obtained in the presence of H-HSZ-30 catalyst at a wood conversion temperature 270 °C.

The effect of ethanol pressure on the conversion of wood and on the yield of liquid fractions in the presence of this catalyst was studied (Fig. 3).

Table 2

Effect of zeolite catalysts on the conversion of aspen wood in supercritical ethanol and the yield of liquid products.

Catalyst	Mechanical treatment	Conversion, wt.%	Yield of products, wt.%				
			Liquid		Total	Solid	Gaseous
			b.p. less 180 °C	b.p. more 180 °C			
270 °C (6,4–7,5 MIIa)							
Without catalyst	YES	73	24.8	46.3	71.1	27.3	1.6
Without catalyst	NO	58	21.6	35.0	56.6	42.0	1.1
H-HSZ-30	NO	67	42.3	23.2	65.5	33.0	1.5
H-HSZ-30	YES	86	62.7	20.8	83.5	13.9	2.5
H-HSZ-60	YES	81	58.9	19.6	78.5	18.8	2.4
H-HSZ-100	YES	82	55.8	24.1	79.9	18.1	2.1
350 °C (8,0–9,2 MIIa)							
Without catalyst	NO	69	23.7	35.0	58.7	30.6	9.9
Without catalyst	YES	86	27.7	46.6	74.3	14.2	11.5
H-HSZ-30	YES	89	54.4	16.0	70.4	10.9	18.7
H-HSZ-60	YES	87	55.5	15.6	71.1	13.0	15.9
H-HSZ-100	YES	88	53.9	17.4	70.3	12.0	16.7

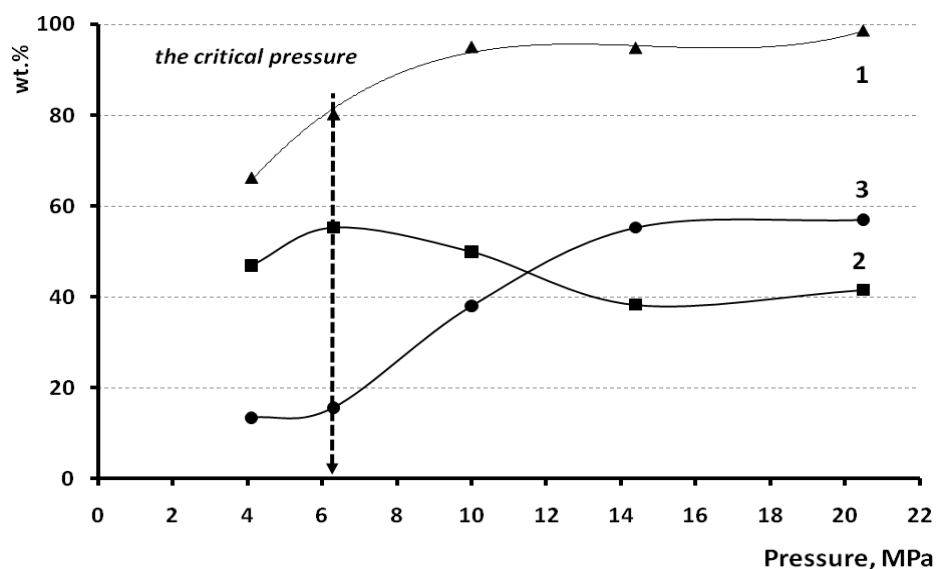


Fig. 3. Effect of the pressure on the conversion of aspen wood in supercritical ethanol (1) and on the yield of liquid fractions with b.p. < 180 °C (2) and b.p. > 180 °C (3) (temperature 270 °C, catalyst H-HSZ-30).

The dotted line in the figure corresponds to the critical pressure of ethanol. The rise of the pressure from 4 to 21 MPa increases the conversion of wood to 90 wt.%. The maximum yield of liquid fraction with boiling point <180 °C (54.3wt.%) was obtained at the pressure 6.4 MPa. The increase of the pressure to 21.0 MPa reduces significantly the yield of fraction with b.p. < 180 °C and increases by 2 times the yield of the fraction with b.p. >180 °C.

3.3. Composition of products of catalytic conversion of aspen wood in supercritical ethanol

According to GC data, the gaseous products of non-catalytic conversion of aspen wood in ethanol at 270 °C contain mainly carbon oxides, methane and small amounts of gaseous hydrocarbons (ethane, ethylene, propane and propylene, and others). At this temperature no significant changes in the gas composition were observed in the presence of zeolite catalysts. But the yield of CO and hydrocarbon gases, especially methane (up to 8 wt.%), is significantly increased at a process temperature 350 °C, apparently due to the cracking of liquid products (Table.3).

Table 3

Effect of the temperature on the yield of gaseous products of aspen wood conversion in supercritical ethanol in the presence of zeolite catalysts.

Catalyst	Yield of gaseous products, wt.%			
	CO	CO ₂	CH ₄	Other hydrocarbon gases
270 °C (6,4-7,5 MPa)				
Without catalyst	n.d.*	0,4	1,2	n.d.*
H-HSZ-30	0,3	0,7	1,4	0,1
H-HSZ-60	0,3	0,5	1,6	> 0,1
H-HSZ-100	0,1	0,5	1,5	> 0,1
350 °C (8,0-9,2 MPa)				
Without catalyst	1,8	3,5	4,7	1,5
H-HSZ-30	5,1	2,7	8,0	2,9
H-HSZ-60	4,8	2,5	6,0	2,6
H-HSZ-100	4,8	2,8	6,4	2,7

*not detected

The solid residue of wood catalytic conversion in ethanol at temperature 270°C contains mainly cellulose and lignin. Hemicelluloses are almost completely absent in this solid product. The most thermally stable component of wood under these conditions is cellulose (Table 4). The solid residue of catalytic conversion of wood in supercritical ethanol at 350 °C does not contain any structural components of wood. On the TGA curve of this sample was recorded a maximum weight loss in the range of 250–580 °C, which is typical for condensed bio-oils products [37]. The formation of the carbon residue in the process of thermal conversion of pine wood sawdust in supercritical ethanol was also observed in [9].

Table 4

Conversion of the main components of aspen wood during its thermal transformation in supercritical ethanol at 270°C (pressure varies between 6.4–7.5 MPa).

Component	Conversion, mas. %			
	Without catalyst	H-HSZ-30	H-HSZ-60	H-HSZ-100
Cellulose	62	75	74	71
Hemicelluloses	84	98	99	98
Lignin	69	86	82	80

According to GC-MS data, the ethanol soluble products of wood conversion in supercritical ethanol at 270°C are a complex mixture of oxygen-containing organic compounds (Table 5).

Table 5

Composition of the liquid products of aspen wood conversion in supercritical ethanol in the presence of zeolite-containing catalysts at 270 °C (pressure varies between 6.4–7.5 MPa).

№	RT*	Product	Content, %**			
			Without catalyst	H-HSZ-30	H-HSZ-60	H-HSZ-100
1	6,49	Propanoic acid, 2-hydroxy-, ethyl ester	10,4	12,1	13,1	13,0
2	7,08	Furfural	5,2	17,5	14,3	12,4
3	9,89	Furfuryl formate	14,5	0,2	0,2	0,3
4	10,08	Butanoic acid, 2-hydroxy-, ethyl ester	3,0	1,9	2,3	1,9
5	10,47	Acetic acid, ethoxy-, ethyl ester	0,5	1,1	1,5	2,2
6	10,91	3-Hexene, 1-(1-ethoxyethoxy)	0,7	1,1	1,1	2,0
7	12,65	Furfural, 5-methyl-	3,1	3,3	3,1	3,6
8	13,75	Phenol	4,8	2,5	2,5	3,0
9	14,42	Hexanoic acid, ethyl ester	1,3	0,9	1,1	1,3
10	15,50	2-Cyclopenten-1-one, 2-hydroxy-3-methyl	2,0	1,7	2,1	1,7
11	16,64	2-Furancarboxylic acid, ethyl ester	2,1	2,1	2,6	3,3
12	17,05	Pentanoic acid, 4-oxo-, ethyl ester (levulinic acid, ethyl ester)	6,4	12,9	19,1	21,0
13	17,64	2-Furaldehyde diethyl acetal	6,1	6,1	5,2	2,8
14	17,98	Phenol, 2-methoxy	1,2	0,4	0,4	1,4
15	21,22	Butanedioic acid, diethyl ester	9,0	1,5	1,7	2,8
16	22,65	5-Hydroxymethylfurfural	1,1	13,4	12,2	10,8
17	26,23	Phenol, 2,6-dimethoxy-	4,6	1,3	1,4	1,5
18	26,67	Phenol, 2-methoxy-4-propyl-	1,4	0,6	0,9	0,8
19	28,76	1,2,4-Trimethoxybenzene	1,6	1,0	0,7	2,6
20	30,73	5-tert-Butylpyrogallol	2,5	1,5	1,6	2,3
21	32,71	3,5-dimethoxy-4-hydroxyphenyl acetaldehyde (S-homosyringaldehyde)	4,0	0,6	0,8	1,3
22	34,40	12-Oxododecanoic acid, ethyl ester	1,7	1,0	1,1	1,5

* retention time

** % from the sum of the areas of all detectable compounds.

Zeolite catalysts significantly increase in liquid products the content of furan derivatives formed from wood carbohydrates at a conversion temperature of 270 °C. In the presence of the

catalyst H-HSZ-30, which has the highest concentration of acid sites, the content of 5-HMF in liquid products increases 12 times, furfural - 3 times, ethyl ester of levulinic acid 2 times. Simultaneously the zeolite catalysts reduce the content of methoxyphenols which are formed by depolymerization of lignin. In particular, the content of 2,6-dimethoxyphenol is reduced 3.5 times, homosilene aldehyde more than 6 times, 2-methoxy-4-propylphenol more than 2 times.

The increase of the temperature of catalytic conversion of wood in supercritical ethanol to 350 °C significantly influences on the composition of the resulting liquid products. In particular, the content of furfural is decreased 10 times and the 5-HMF is completely absent in liquid products. At this temperature the zeolite catalysts increase the relative content of ethyl esters of organic acids and reduce the content of methoxyphenols in liquid products (Table 6).

Table 6

Composition of ethanol soluble products of aspen wood conversion in supercritical ethanol at 350 °C in the presence of zeolite catalysts (pressure varies between 8.0–9.2 MPa).

RT*	Product	Content, %**		
		Without catalyst	H-HSZ -30	H-HSZ -100
5.90	Butanoic acid, - ethyl ester	1.5	5.3	2.7
6.49	Propanoic acid, 2-hydroxy-, ethyl ester	2.7	7.2	4.8
7.09	Furfural	1.0	3.7	3.8
7.56	2-Butenoic acid, - ethyl ester	0.9	0.9	1.4
10.01	2-Cyclopenten-1-one, 2-methyl-	3.6	4.7	3.2
10.11	Butanoic acid, 2-hydroxy-, ethyl ester	1.5	0.8	0.9
10.47	Acetic acid, ethoxy-, ethyl ester	1.3	3.7	3.3
10.90	3-Hexene, 1-(1-ethoxyethoxy)	3.1	6.2	3.7
12.65	Furfural, 5-methyl-	0.5	2.5	2.5
13.75	Phenol	4.3	5.7	5.1
14.25	2,3- dimethyl-2-cyclopenten-1-one	1.3	3.5	1.6
14.42	Hexanoic acid, ethyl ester	3.5	1.4	1.8
15.90	2,4- dimethyl-2-cyclopenten-1-one	1.1	1.4	1.2
16.64	2-Furancarboxylic acid, ethyl ester	1.3	2.3	2.3
16.80	Phenol, 3-methyl-	1.1	1.0	0.5
17.05	Pentanoic acid, 4-oxo-, ethyl ester (levulinic acid, ethyl ester) *	3.7	15.3	17.0
17.66	Propanoic acid, 2- methyl,-anhydride	6.1	3.0	2.7
17.98	Phenol, 2-methoxy*	5.2	3.9	3.8
21.22	Butanedioic acid, diethyl ester	4.4	3.9	3.3
21.50	Phenol, 2-methoxy-4-methyl-	4.2	3.4	3.4
21.70	Octanoic acid, - ethyl ester	0.5	-	0.5
22.10	Butanedioic acid, methyl-, diethyl ester	2.0	0.8	1.1
24.20	Phenol, 2-methoxy-4-ethyl-	2.8	1.4	1.6
24.26	Pentanedioic acid, - diethyl ester	3.2	1.5	1.2
26.23	Phenol, 2,6-dimethoxy-	7.4	3.1	4.0

26.60	Phenol, 2-methoxy-4-propyl-	4.7	1.0	1.3
28.76	1,2,4-Trimethoxybenzene	6.4	3.4	4.2
30.73	5-tert-Butylpyrogallol	2.0	2.0	2.0
32.71	3,5-dimethoxy-4-hydrophenyl acetaldehyde (S-homosyringaldehyde)	5.3	0.9	1.7
34.40	12-Oxododecanoic acid, ethyl ester	1.4	2.4	2.0
40.87	Hexadecanoic acid, ethyl ester	4.6	1.8	1.3

* retention time

** from the sum of the areas of all detected peaks.

The increase of the pressure of catalytic conversion of wood in supercritical ethanol at 270 °C from 7.1 MPa to 21.0 MPa has a little effect on the content of furfural and 5-HMF in liquid products (Table 7), but promotes the formation from wood polysaccharides of 3-furaldehyde, furfuryl formate, ethyl- β -D-riboside, α -D-glucopyranose 4-O- β -D-galactopyranosyl, galactopyranosyl and 1,6-anhydro- β -D-glucopyranose (levoglucosan).

Table 7

The effect of the pressure of aspen wood conversion process in supercritical ethanol at 270 °C in the presence of H-HSZ-30 catalyst on the composition of resulting liquid products.

	RT*	Products	Content, %*	
			7.1 MPa	21.0 MPa
1	6.49	Propanoic acid, 2-hydroxy-, ethyl ester	12.1	15.9
2	7.08	Furfural	17.5	12.9
3	9.07	3-Furaldehyde	<0.1	1.9
4	9.89	Furfuryl formate	0.2	2.6
5	10.08	Butanoic acid, 2-hydroxy-, ethyl ester	1.9	<0.1
6	10.47	Acetic acid, ethoxy-, ethyl ester	1.1	<0.1
7	10.91	3-Hexene, 1-(1-ethoxyethoxy)	1.1	2.0
8	12.65	Furfural, 5-methyl-	3.3	1.4
9	15.50	2-Cyclopenten-1-one, 2-hydroxy-3-methyl-	1.7	1.0
10	16.64	2-Furancarboxylic acid, ethyl ester	2.1	0.9
11	17.05	Pentanoic acid, 4-oxo-, ethyl ester (levulinic acid, ethyl ester)	12.9	11.0
12	17.64	2-Furaldehyde diethyl acetal	6.1	5.3
13	17.98	Phenol, 2-methoxy	0.4	<0.1
14	21.22	Butanedioic acid, diethyl ester	1.5	0.5
15	22.65	5-Hydroxymethylfurfural	13.4	10.1
16	25.97	Ethyl β -d-riboside	<0.1	5.5
17	26.23	Phenol, 2,6-dimethoxy-	1.3	<0.1
18	26.97	α -D-Glucopyranose 4-O- β -D-galactopyranosyl	<0.1	1.2
19	28.76	1,2,4-Trimethoxybenzene	1.0	2.7
20	29.62	1,6-Anhydro- β -d-glucopyranose (levoglucosan)	<0.1	10.2
21	30.73	5-tert-Butylpyrogallol	1.5	0.8
22	34.76	Phenol, 2,6-dimethoxy-4-(2-propenyl)	<0.1	4.4

* retention time

** from the sum of the areas of all detected peaks.

It is known that supercritical ethanol can extract the products of thermal depolymerization of polysaccharides and lignin [38], preventing their condensation reactions into high-molecular substances and coke. In the presence of catalysts, the primary products of thermal conversion of wood undergo further catalytic transformations.

A distinctive feature of the conversion of mechanically activated mixtures of wood and zeolite catalysts in supercritical ethanol at 270 °C is the higher formation of such valuable compounds as furfural, 5-HMF, levulinic acid ethyl ester and methoxyphenols (Table 5) as compared to pyrolysis processes. According to the known schemes of wood components pyrolysis [39,40] and taking into account the experimental data obtained, it can be concluded that the acid high-silica zeolite catalysts promote the formation of 5-HMF from hexoses and its subsequent conversion to levulinic acid, as well as the reactions of pentoses conversion to furfural and 2-hydroxypropanoic acid.

Currently, 5-HMF is considered as a promising platform product for various application areas [41]. It can be used for the production of polymers, in the food industry and pharmaceuticals, for the production of additives for motor fuels, for fine organic synthesis, *etc.* Many chemicals obtained from 5-HMF have a high consumer potential. Examples of such products are 2,5-bis(hydroxymethyl) furan, 5-hydroxymethyl-2-furancarboxylic acid, 2,5-furan-dicarboxylic acid, which are used for the production of furan polyethers.

Furfural is also a key chemical product for the production of furan and tetrahydrofuran. The ethyl ester of levulinic acid is used in the food and perfume industries [42, 43]. In addition, it is considered as a promising additive to diesel and biodiesel fuels [44,45].

The phenol derivatives obtained by the catalytic depolymerization of lignins [46,47] can be used to prepare polymers [48] and new materials such as airogels, cryogels, catalyst carriers [49]. Alkyl benzene derivatives considered as high-octane components of automotive fuels [50] can be obtained by deoxygenation of phenols.

4. Conclusion

As a results of the performed studies a significant effect of preliminary mechanical treatment and the use of acid high-silica zeolite catalyst on the aspen wood conversion at 270 °C and 350 °C and on the yield of liquid products was established.

The mechanical treatment of the mixture of aspen wood and high-silica zeolite catalysts in a planetary activator mill decreases the size and shape of wood particles and the degree of cellulose crystallinity. In addition, this treatment contributes more homogeneous distribution of zeolite catalyst in the reaction mixture. In the mechanically treated wood the destruction of such components as large vessels fiber librins and tracheids takes place. All of the above factors increase

the reactivity of activated aspen wood in the process of its thermal dissolution in supercritical ethanol.

The suggested mechanism of wood lignin depolymerization in supercritical ethanol over solid catalysts at the temperature which corresponds to intensive degradation of lignin, at first includes the dissolution of native wood lignin with the formation of soluble ethanol-lignin. In the presence of zeolite catalysts the soluble ethanol-lignin undergoes further catalytic conversions to polyphenols, phenols and aromatic compounds. So, the used approach makes possible to combine the steps of ethanol-lignin extraction from wood by supercritical ethanol and further catalytic depolymerization of soluble ethanol-lignin to liquid products.

The mechanical treatment of wood increases its conversion in supercritical ethanol and the yield of liquid and gaseous products. Zeolite catalysts act in a similar manner.

The influence of conditions of wood–zeolite catalyst mixtures conversion in subcritical and supercritical ethanol on the yield and composition of the resulting products was established.

At temperature of 270 °C and a pressure of 6.4–7.5 MPa, zeolite catalysts increase 2.3–2.5 times the yield of liquid fraction with b.p. less 180 °C and the content of furan derivatives in the ethanol soluble products. Along with this the furfural content is increased up to 3.5 times, and 5-HMF - up to 12 times. The most active is the catalyst H-HSZ-30 with the ratio Si/Al=30, containing the highest concentration of acid sites. In the presence of this catalyst, the conversion of aspen wood in supercritical ethanol at 270 °C reaches to 86 wt.% at ethanol pressure of 6.4 MPa and to 90 wt.% at 21 MPa. The yield of the light liquid fraction with a b.p. less 180 °C reaches 62.7 wt.%. The rise of ethanol pressure from 6.4 MPa to 21 MPa significantly reduces the yield of this fraction, but increases while increasing the yield of the heavy fraction with b.p. more 180 °C. Liquid products obtained at 270 °C, mainly contain the compounds, formed from wood polysaccharides: 5-HMF, furfural, levulinic acid, ethyl ester, propanoic ester, 2-hydroxy-ethyl ester. The solid residue of aspen wood catalytic conversion in ethanol at 270°C contains mainly cellulose and lignin.

At the temperature of wood conversion 350 °C the zeolite catalysts only weakly affect on the conversion of aspen wood in supercritical ethanol and on the total yield of liquid products. But they increase the yields of liquid fraction with b.p. less 180 °C and gaseous products, while decreasing the yields of fraction with b.p. more 180 °C and solid residue. High temperature (350 °C) promotes lignin depolymerisation in supercritical ethanol with the formation of phenol derivatives and initiates the secondary reactions of their conversion into gas and coke.

Thus in the presence of high-silica zeolite catalysts, it is possible to fractionate the mechanically activated aspen wood biomass in supercritical ethanol at 270 °C on liquid products from hemicellulosic and solid lignocellulosic product. At temperature of wood catalytic

conversion 350 °C mainly liquids from polysaccharides and lignin are formed along with gaseous and char products.

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