

Green catalytic processing of native and organosolv lignins

B.N. Kuznetsov^{1,2}, N.V. Chesnokov¹, I.G. Sudakova¹,

N.V. Garyntseva¹, S.A. Kuznetsova^{1,2}, Yu. N. Malyar^{1,2}, V.A. Yakovlev³, L. Djakovitch⁴

¹*Institute of Chemistry and Chemical Technology SB RAS, FRC KSC SB RAS*

Krasnoyarsk, 660036, Akademgorodok, 50-24, Russia

*e-mail: bnk@icct.ru, Fax/Tel +7(391)249-48-94

²*Siberian Federal University, Krasnoyarsk, 660041, Svobodny prospect, 79, Russia*

³*Borekov Institute of Catalysis, SB RAS, Novosibirsk, 630090, pr. Ak. Lavrentieva, 5, Russia*

⁴*IRCELYON, 2 avenue Albert Einstein, F-69626 Villeurbanne Cedex, Lyon, France*

ABSTRACT

Two ways of catalytic depolymerization of native and isolated wood lignins are described: the peroxide delignification of hardwood (aspen, birch) and softwood (abies) in the medium of acetic acid – water over TiO₂ catalyst and the thermal dissolution of organosolv lignins (ethanol-lignin and acetone-lignin) in supercritical alcohols (ethanol and butanol) over solid Ni-containing catalysts.

The catalyst TiO₂ in rutile modification has the higher activity in wood peroxide delignification at 100°C as compared to TiO₂ in anatase modification. The results of kinetic studies and optimization of the processes of peroxide depolymerization of hardwood (aspen, birch) and softwood (abies) lignins in the medium of acetic acid – water over catalyst TiO₂ (rutile) at mild conditions (≤ 100°C, atmospheric pressure) are compared. The catalyst TiO₂ initiates the formation of OH[•] and OOH[•] radicals from H₂O₂ which promote the oxidative fragmentation of wood lignin. In this case, the peroxide depolymerization of softwood lignin, constructed from phenylpropane units of guaiacyl-type proceeds more difficult than the hardwood lignins, mainly containing syringyl-type units.

The solid and soluble products of peroxide catalytic delignification of wood under the optimized conditions were studied by FTIR, XRD, GC-MS and chemical methods. Regardless of the nature of wood the cellulosic products have a structure similar to microcrystalline cellulose. The soluble products mainly consist of monosaccharides and organic acids. Aromatic compounds are present only in a low amount which indicates the oxidative degradation of aromatic rings of lignin phenylpropane units under the used conditions of wood catalytic delignification.

The processes of thermal dissolution of acetone-lignin and ethanol-lignin from aspen-wood in supercritical ethanol and butanol over Ni-containing catalyst (NiCu/SiO₂,

NiCuMo/SiO₂) are compared. The composition, structure and thermal properties of organosolv lignins were studied with the use of FTIR, GPC, ¹H - ¹³C HSQC NMR, DTA and elemental analysis.

The influence of a composition of Ni-containing catalyst on the thermal conversion in supercritical butanol and ethanol of ethanol-lignin and acetone-lignin was established. The highest conversion of lignins (to 93% wt.) in supercritical alcohols and the highest yield of liquid products (to 90 % wt.) were achieved at 300 °C in the presence of catalyst NiCuMo/SiO₂.

Scheme of green biorefinery of wood based on the use of non-toxic and low-toxic reagents (H₂O₂, H₂O, acetic acid, ethanol, butanol) and solid catalysts (TiO₂, NiCuMo/SiO₂) is suggested.

Keywords: lignin, depolymerization, catalysts, bio-liquids.

1. Introduction

Wood biomass is constructed from polysaccharides and lignin [1]. The lignin content depends on the type of tree: about 28 % for softwood and 20 % for hardwood. The cellulose content is approximately 45 % in the wood of both types, while the hemicelluloses content is roughly 17 % in softwoods and 25 % in hardwoods. Lignin is a polymer of aromatic nature [2]. The principal monomer for softwood lignins is coniferyl alcohol. Hardwood lignins have two main monomers: coniferyl and sinapyl alcohols. The aromatic rings in lignins are presented by guaiacyl units with the one aryl-OCH₃ group, which derived from coniferyl alcohol, by syringyl units with the two aryl-OCH₃ groups, which derived from sinapyl alcohols and by p-hydroxyphenyl units without the OCH₃-groups, which derived from p-coumaryl alcohol.

The huge amounts of waste lignin are produced by pulp and hydrolysis plants. But the high-tech methods of lignin valorization are lacking to date. The variable composition and structure of native and technical lignins complicate the choice of their utilization strategy.

With its unique structure and chemical properties a wide variety of bulk and fine chemicals, particularly aromatic and phenolic compounds are potentially obtainable from lignin. At present the different processes are used for lignin conversion: pyrolysis, catalytic hydrogenation, catalytic oxidation, alkaline depolymerization in supercritical fluids [3-5].

The studies, directed on catalytic processing of biomass and lignin into biofuels and chemicals are intensified in the last decade [4-7]. Application of catalysts allows to speed up the reactions of lignin depolymerization and to increase the yield of liquid products [8-11].

Promising directions of lignocellulosic biomass processing are connected with the use of solid catalysts which have a number of technological advantages in comparison with the dissolved catalytic systems [12-14].

Catalysts based on noble metals (Pd, Ru, Pt) and on the less expensive metals (Ni, Mo, etc.) supported on Al₂O₃, SiO₂ and carbon carries are used in the different processes of lignin valorization [8, 15-16]. In particular, the catalyst Ni/C shows the comparable with catalysts Pt/C, Pd/C, Ru/C activity in organosolv lignin depolymerization in supercritical butanol with obtaining of acylated phenols [17]. In alcohol medium the catalyst Ni/C is active in the rupture of β-O-4 bonds between lignin structural fragments with the formation of monomeric phenols, mainly 4-propyl-4-propenyl-phenol [18].

Catalytic depolymerization of birch-wood organosolv lignin was studied in supercritical ethanol at 260 °C [19]. Different acid-basic materials, namely sepiolite, zeolite ZSM-5 supported on Al₂O₃ and Sibunit graphite-like mesoporous carbon, Ru-containing catalysts based on these supports were used in lignin depolymerization process. The catalyst Ru/Sibunit allows to avoid coke formation, increases the amount of aromatic monomers and the total yield of liquid products up to 76 %.

The promising catalytic processes in wood biorefinery include, as a key stage, biomass fractionation on polysaccharides and lignin and their subsequent transformation to various chemicals and liquid biofuels.

The known ways of lignocelluloses biomass fractionation can be united into two groups. In one of them the cellulose and hemicelluloses are removed and the lignin remains as a rest, another includes methods in which the lignin is removed.

Reductive catalytic fractionation is an effective way to separate lignocellulosic biomass into lignin-based soluble mono-, di- and oligomers while retaining most of the carbohydrates in the pulp [20–22].

Single-stage processes of wood fractionation on cellulose and soluble lignin, based on the oxidative depolymerization of lignin in "hydrogen peroxide-acetic acid-water" medium at 120–130 °C in the presence of different catalysts were suggested [23]. At optimum conditions of wood peroxide delignification in the presence of H₂SO₄ catalysts (2 wt%) and TiO₂ (0,5 wt%) the cellulosic products containing less than 1 wt% of residual lignin can be obtained with an acceptable yield (44–48 wt% on abs. dry wood) along with soluble products from lignin and hemicelluloses.

It was shown that the use of small particles of wood, high liquid to wood ratio (LWR) and the intensive mixing of the reaction solution allows to reduce the external diffusion

limitations and to provide a high rate of aspen wood peroxide delignification under mild conditions (70–100 °C, atmospheric pressure) in the presence of 2 % H₂SO₄ catalyst [24].

In this paper the two ways of catalytic depolymerization of native and isolated wood lignins are described: the peroxide delignification of hardwood (aspen, birch) and softwood (abies) over the catalyst TiO₂ in the medium of acetic acid – water at mild conditions (≤ 100 °C, atmospheric pressure) and the thermal dissolution of organosolv lignins (ethanol-lignin and acetone-lignin) in supercritical alcohols (ethanol and butanol) over solid Ni-containing catalysts.

2. Experimental

2.1. Catalyst preparation and characterization

Preparation of TiO₂

The synthesis of titanium dioxide was carried out by hydrolysis of ammonia solution of titanium tetrachloride with the subsequent calcination of a titanium (IV) hydroxide according to [25].

The necessary amount of TiCl₄ was slowly added to a chemical glass with distilled water and the mixture was boiled within 10 minutes. Then a solution was cooled up to the temperature of 70–80 °C and NH₄OH was added up to full sedimentation of Ti(OH)₄. Precipitate was filtered on Buchner funnel and washed out by hot water from chlorine ions. Obtained paste of titanium hydroxide (IV) was then transferred to Petri's dish and dried up in muffle at 110 °C up to the constant weight. The dried-up precipitate was placed to the porcelain boat and calcinated in the muffle furnace at various temperatures within one hour.

For obtaining TiO₂ samples in the rutile modifications, the dried-up precipitate was calcinated at 800 °C within one hour, then crushed in an agate mortar, washed out by water from chlorine ions and calcinated at 1000 °C within 1,5 hours.

Preparation of NiCuMo/SiO₂

Catalysts NiCuMo/SiO₂ were obtained from nickel (II) carbonate basic hydrate NiCO₃ · mNi(OH)₂ · nH₂O, copper(II) carbonate basic CuCO₃ · mCu(OH)₂, molybdenum(VI) oxide MoO₃, and an alcohol solution of ethyl silicate-32 in the presence of ammonia water (25%), using the sol-gel technique described in [26]. The resulting viscous paste was then dried at 100°C and calcined at 500°C. The samples were heated to 500°C in the H₂ (flow) in a quartz reactor, kept at this temperature for 1 h, and then cooled and passivated with a mixture of O₂(2%)/N₂ [27].

2.2. Initial wood materials

Air dry sawdust (fraction 0.5-2.0 mm) of birch-wood, aspen-wood and abies-wood were used in experiments. The contents of cellulose, lignin and hemicelluloses in wood were defined by analytical methods, common in wood chemistry [28]. The cellulose content in wood was defined by Kurschner method. The lignin content was determined by hydrolysis of the sample with 72 wt% of sulfuric acid at 20 °C for 2.5 h, followed by dilution of a solution with water and boiling for 4 h. The hemicelluloses content was defined by McKein and Shoorly method using the hydrolysis by 2 wt% HCl at 100 °C during 3 h.

The composition of wood samples is given in Table 1.

Table 1
Composition of wood samples.

Wood	Composition, wt%		
	Cellulose	Hemicelluloses	Lignin
Aspen-wood	46.3	24.5	21.9
Birch-wood	46.5	27.2	21.8
Abies-wood	45.7	17.7	25.3

Samples of acetone-lignin and ethanol-lignin were isolated from aspen-wood by methods described in [29, 30].

For isolation of acetone-lignin the treatments of aspen-wood sawdust (fraction less 0.5 mm.) at first by water at 180 °C during 1 h and then by boiling acetone (high purity, EKOS-1, Russia) during 1 h were used. Yield of acetone-lignin was 29.5 wt% from content of Klason lignin in the wood.

Ethanol-lignin was isolated from aspen-wood (fraction less 0.5 mm) by treatment of 60 wt% ethanol-water mixture (high purity, EKOS-1, Russia) at 190 °C during 3 h. Yield of ethanol-lignin was 56 wt% from content of Klason lignin in the wood.

The elemental composition of organosolv lignins was determined using Thermo quest HCNS – O EA FLASH TM 1112 analyzer.

The elemental composition of lignins is given in Table 2.

Table 2
Elemental composition of organosolv lignins.

Lignin	Elemental composition, wt%			
	C	H	O	Ash
Acetone-lignin	64.6	6.8	26.7	0.5
Ethanol-lignin	67.2	6.7	25.1	0.4

2.3. Peroxide catalytic delignification of wood

Catalytic delignification of wood sawdust by H₂O₂ was carried out as in [31] using 250 cm³ glass reactor equipped with mechanical stirrer, reflux condenser and thermometer. Wood sawdust (10 g) was placed into glass reactor. Then, a mixture of glacial acetic acid (high purity, Ekos-1, Russia), hydrogen peroxide (high purity, Ekos-1, Russia), distilled water and TiO₂ was added. The reaction mixture was vigorously stirred (700 rpm) at selected temperature (70–100 °C) during 1–4 h. Composition of the of reaction mixture was varied in the following range: hydrogen peroxide 3–7 wt%, acetic acid 15–40 wt%, liquid/wood ratio (LWR) –10–15. Concentration of TiO₂ catalyst was 1 wt%. When the reaction was completed, the solid product was separated under vacuum using Buchner funnel, following by washing distilled water and drying at 105 °C until constant weight.

Such parameter as the residual lignin content in cellulosic product was used to evaluate the delignification activity of TiO₂ catalyst. The cellulosic product yield was estimated by gravimetric method and calculated as follows: $Y = (m/m_0) \times 100$, where Y – yield of cellulosic product, wt%; m – weight of abs. dry cellulosic product, g; m₀ – weight of abs. dry wood, g.

2.4. Conversion of organosolv lignin in supercritical alcohols

The thermal conversion of organosolv lignins in supercritical alcohols was carried out at 250–350 °C in a rotating autoclave (Autoclave Engineers, USA) of 300 cm³ volume as in [32].

A mixture 3 g lignin and 0.3 g catalyst crushed to the particles with the average size less 0.5 mm and 15 ml of ethanol or butanol (high purity, Ekos-1, Russia) was placed into autoclave. Air was removed from the sealed autoclave by purging it with argon through its stop valves. Thereafter, the autoclave was heated at a rate of 10 C/min to the desired temperature and was kept at this temperature for 1 h under vigorous mixing (850 rpm). Under the used supercritical conditions, the pressure in the autoclave was 5.0 MPa for butanol (critical pressure and temperature 4.6 MPa and 288°C) and 11.6 MPa for ethanol (critical pressure and temperature 6.4 MPa and 243 °C). Then the autoclave was cooled to room temperature and the products were quantitatively washed out of the autoclave. The condensed products were filtered through a filter paper (blue ribbon) in a vacuum using a Büchner funnel. The filtration residue was sequentially extracted with hexane, diethyl ether and acetone (all high purity, Ekos-1, Russia). The extract was dried to a constant weight under vacuum at room temperature. The yields of extracts and solid residues were determined by the gravimetric method after solvent removal.

2.5. Methods of analysis

The content of cellulose, hemicelluloses and lignin in the cellulosic products was defined by chemical methods generally accepted in wood chemistry [28].

Infrared spectroscopy analysis (FTIR) was carried out in transmission mode. Samples of cellulose (4 mg for each) were prepared in tablets with matrix KBr. The spectra were recorded with Bruker Tensor – 27 in the range of wavelength 4000–400 cm^{-1} . Spectral data were processed by the program OPUS/YR (version 2.2).

X-ray diffraction analysis was carried out on PANalytical X'Pert Pro diffractometer using Cu-K α source ($\lambda = 0,154 \text{ nm}$) in the 2θ range 5–70 ° and scanning step width of 0,01 °/scan. The cellulose samples were analyzed by the powder method in cuvette with 2,5 cm diameter.

Crystallinity index (CI) was calculated from the ratio of the height between the intensity of the crystalline peak and total intensity after subtraction of the background signal [33]: $CI = (I_{002} - I_{AM}) / (I_{002})$, where I_{002} – is the height of the 002 peak; I_{AM} – is the height of the minimum between the 002 and the 101 peaks.

The liquid products of wood peroxide delignification and of lignin conversion in supercritical alcohols were analyzed by GC-MS using Agilent 7890A chromatograph fitted with an Agilent 7000A Triple Quad mass-selective detector (Agilent, United States) by recording the total ion current. The products were separated in an HP-5MS capillary column (30 m in length, 0.25 mm in inner diameter) in the temperature programmed mode while raising the temperature from 40 to 250°C at a rate of 3°C/min.

Molecular weight and molecular-weight distribution of organosolv lignins were examined using a gel permeation chromatograph (“Agilent Technologies@ 1260Infinity, U.S.) with a refractive index detector, using an Agilent PLgel Mixed-C column. Chloroform was used as the eluent, with a flow rate of 1.0 ml/min at 40 °C. Typical sample volumes were 50 ml at a polymer concentration of 2 mg/ml. Narrow polydispersity polystyrene standards (Agilent, U.S.) were used to generate a universal calibration curve, from which molecular weights (weight average, M_w , and number average, M_n) and polydispersity were determined.

Thermal properties of lignin samples were studied using “Netzsch STA 449F1” instrument with a heating rate of 10 °C/min. For each experiment ~ 5 mg of lignin samples were employed. The samples were heated in the temperature range 30-800 °C.

NMR data were collected on a Bruker Avance III 600 spectrometer system (14.1 T, Bruker, Germany) at 295 K. Samples of 5-10 mg of lignin were placed into a 5 mm NMR tube and dissolved in 0.5 ml of DMSO- d_6 . The two-dimensional multiplicity edited ^1H - ^{13}C heteronuclear single quantum correlation (HSQC) spectra were recorded with four scans of 2048

data points, 256 increments and relaxation delay of 2.5 s. All spectra were acquired and processed using Top Spin 2 software supplied with the spectrometer.

The specific surface areas and pore volumes of the catalysts were measured using nitrogen adsorption at 77 K on a Micromeritics ASAP 2020 analyzer.

The electron images were obtained by scanning electron microscopy (SEM) TM-1000 HITACHI (Japan) with acceleration potential 15 kV. Samples were coated on carbon support.

3. Results and discussion

3.1. Peroxide delignification of hardwood and softwood over catalyst TiO₂

3.1.1. Influence of a state of TiO₂ on catalytic activity in aspen wood delignification

In plant biomass the cellulose, hemicelluloses and lignin are tightly bond with one another. Preliminary fractionation of biomass on polysaccharides and lignin opens new prospects for the production of bio-based products. The features of hardwood and softwood peroxide catalytic fractionation in the acetic acid – water medium over TiO₂ catalyst at mild conditions were compared in the present study.

Earlier [23] the activity of soluble and solid catalyst (H₂SO₄, H₂MoO₄, Na₂MoO₄, TiO₂) in peroxide delignification of hardwood and softwood was studied at the elevated temperature (120 – 130 °C) and pressure.

Recently it was shown that the decrease of wood particles sizes, the use of vigorous agitation of the reaction mixture and the high liquor to wood ratio (LWR) allow to reduce the diffusion limitations and to decrease the temperature of wood peroxide delignification up to 70-100 °C [24, 34].

Catalyst 2 wt% H₂SO₄ has a high activity in peroxide delignification of aspen-wood at temperatures 90-100 °C [24]. But disadvantages of this catalyst are its high toxicity and corrosive activity. Therefore, it was suggested by us to use for the abies wood peroxide delignification under mild conditions (≤ 100 °C, atmospheric pressure) the more technologically convenient TiO₂ catalyst [34].

Catalytic activity of TiO₂ in the peroxide delignification of wood is due to its ability to initiate the formation of radicals •OH and •OOH from H₂O₂ [35]. Being formed radicals participate in reactions of oxidative fragmentation of wood lignin [36].

It is known that catalytic properties of TiO₂-based catalysts are sensitive to the method of their preparation [37].

Catalysts TiO₂ prepared by titanium hydroxide treatment at 300 °C and 500 °C have a crystal modification of anatase. This conclusion is confirmed by data of X-ray diffraction analysis (Fig. 1)

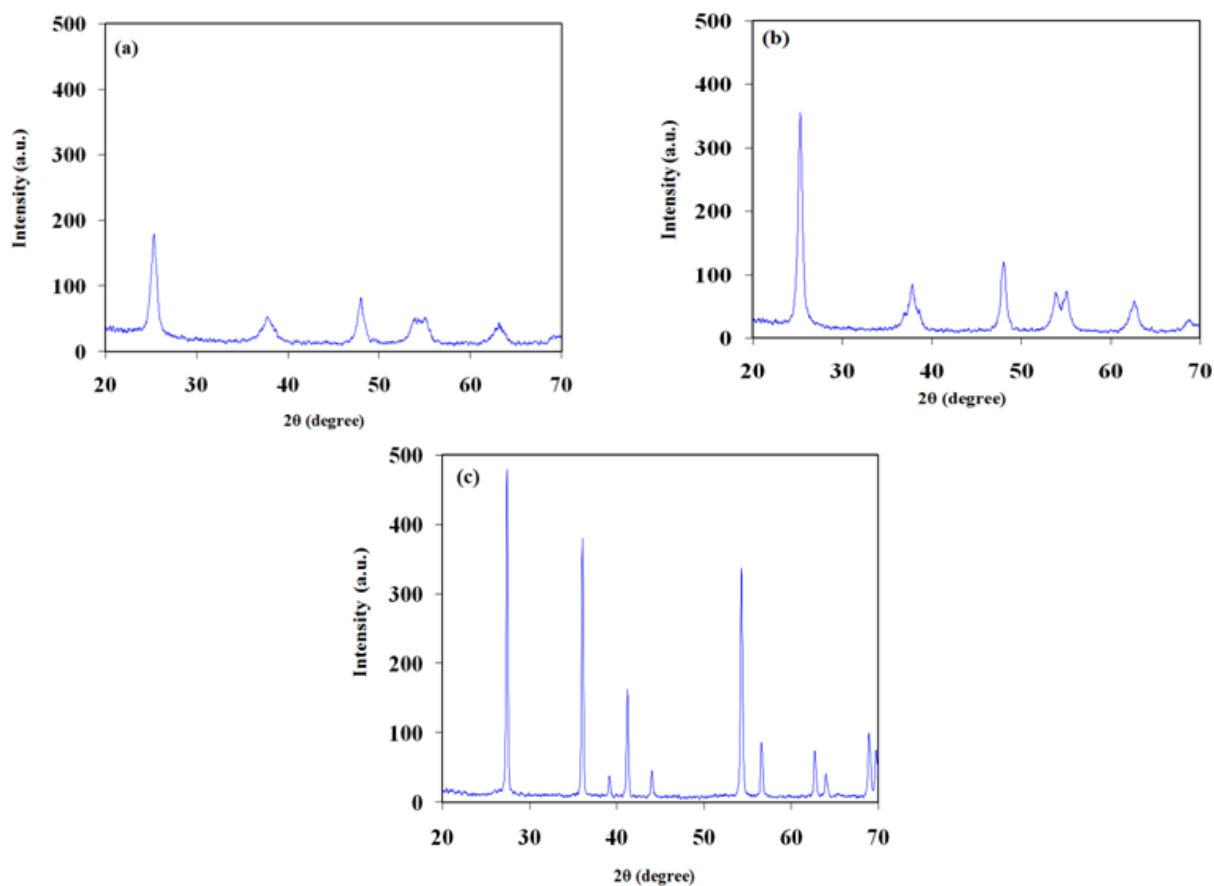


Fig. 1. X-ray diffraction pattern of TiO₂ samples treated at temperatures 300°C (a); 500 °C (b); 1000 °C (c).

The increase of a temperature of TiO₂ treatment to 1000 °C promotes the transformation of its anatase form into rutile form. The high temperature treatment also reduces the specific surface area of titanium dioxide and increases the size of pores (Table 3).

According to SEM data the crystals of TiO₂ in a rutile modification have a spherical form (Fig. 2).

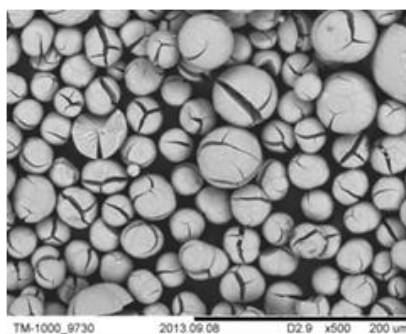


Fig. 2. SEM image of sample of titanium dioxide in rutile modification treated at 1000 °C.

The sizes of TiO₂ particles are varied between 10-50 μm.

IR-spectra of TiO₂ samples of anatase and rutile modifications were compared (Fig. 3). The absorption bands corresponding to deformation (1040-1140 cm⁻¹) and stretching (3200-3400 cm⁻¹) vibrations of Ti-O-H bonds are more intensive in the spectrum of TiO₂-anatase samples

indicating on the higher content of OH-groups as compared to TiO₂-rutile. The increase of temperature of TiO₂ treatment from 300 to 1000 °C considerably decreases the intensity of peaks of OH-groups (Fig.3).

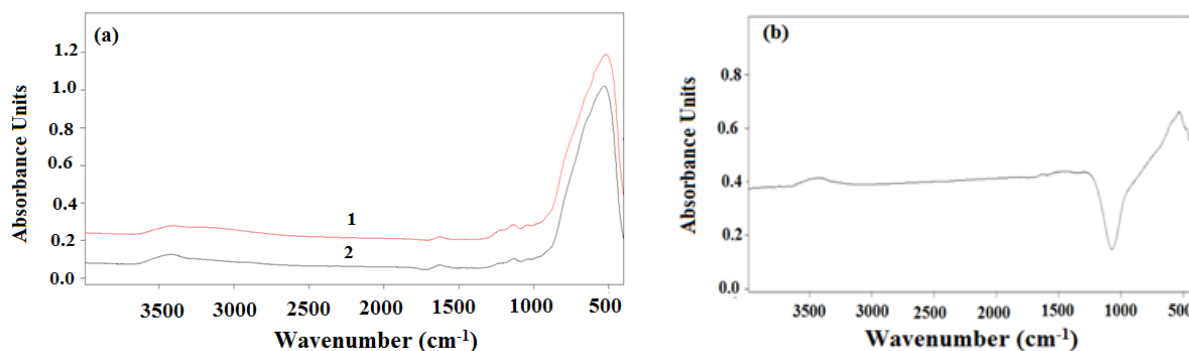


Fig. 3. IR spectra of samples of titanium dioxide in anatase modification (a), treated at 300 °C (1) and 500 °C (2) and in rutile modification (b) treated at 1000 °C.

Catalytic properties of TiO₂ samples in anatase and rutile modifications were compared in the process of aspen wood peroxide delignification at 100 °C (Table 3).

Table 3

Yield and composition of cellulosic products, obtained by aspen-wood peroxide delignification over TiO₂ catalysts in anatase and rutile modification (reaction conditions: 100 °C, H₂O₂ 5 wt% , CH₃COOH 25 wt%, TiO₂ 1wt % , LWR 15, time 4 h).

TiO ₂ modification	Temperature of TiO ₂ treatment, °C	Surface area m ² /g	Pore size, nm	Yield of cellulosic product, wt% *	Composition of cellulosic product, wt%**		
					Cellulose	Lignin	Hemicelluloses
Anatase	300	111	12.4	68.3	77.4	9.8	12.3
Anatase	500	89	13.1	66.1	86.1	7.8	5.6
Rutile	1000	2	17.9	50.7	91.6	1.6	6.3

* on abs.dry wood, ** on abs.dry cellulosic product

The obtained data show that at the same process conditions the use of titanium dioxide catalyst in rutile modification gives the cellulosic product with lower content of residual lignin and higher cellulose content, as compared to TiO₂ in anatase modification.

Samples of TiO₂ (anatase) which were obtained at temperatures 300 °C and 500 °C have a rather high surface area (111 m²/g and 89 m²/g). Their lower catalytic activity in wood peroxide delignification can be explained by the following reasons. Probably, the smaller size of pores in anatase samples (12.4-13.1 nm) as compared to rutile sample (17.9 nm) reduces their catalytic activity in wood delignification owing to strengthening of diffusion limitations inside pores. The treatment of titanium dioxide at 1000 °C, which promotes TiO₂ transformation to rutile modification, reduces its surface area and increases the size of pores. The latter results in

the reduction of diffusion limitation inside pore and increase the catalytic activity of TiO₂ rutile in oxidative depolymerization of wood lignin.

Besides that, a higher concentration of hydrogen groups on the surface of anatase modification of TiO₂, as compared to its rutile modification can prevent the formation from H₂O₂ the radical species ([•]OH and [•]OOH) active in lignin oxidative depolymerization.

3.1.2. Kinetic studies and optimization of wood peroxide delignification over TiO₂ catalyst

The kinetic regularities of peroxide fractionation of hardwood and softwood on cellulose and soluble products from hemicelluloses and lignin under mild conditions (≤ 100 °C, 1 MPa) over TiO₂ catalyst were compared. Rutile modification of catalyst TiO₂ was used in the experiments.

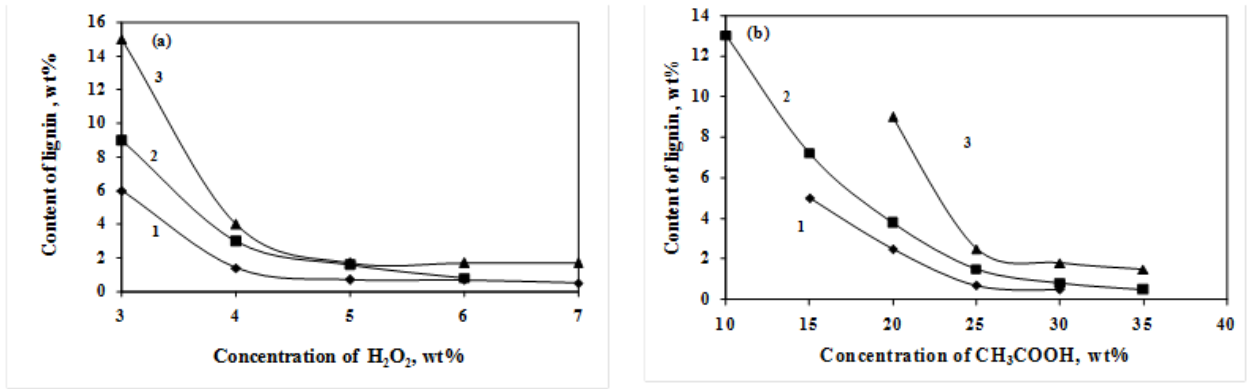
To optimize the processes of peroxide catalytic fractionation of different types of wood the influence of process conditions on the dynamics of lignin removal from wood was studied. It was found that the increase of temperature, concentrations of H₂O₂ and CH₃COOH in the reaction mixture reduces the yield of cellulosic product and the contents of residual lignin and hemicelluloses in this product (Table 4, Fig. 4). At the same time the content of cellulose in cellulosic products is increased.

Table 4

Influence of temperature of wood peroxide delignification over TiO₂ (1 wt%) catalyst on cellulosic products yield and composition.

Temperature, °C	Yield of cellulosic product, wt%*	Composition of product, wt% **		
		cellulose	lignin	hemicelluloses
Aspen-wood				
70	61.3	75.1	15.6	8.3
80	54.5	84.3	6.3	8.0
90	51.0	90.3	1.3	7.7
100	50.2	91.1	0.6	7.4
Birch-wood				
70	59.0	78.8	12.7	8.3
80	53.6	86.9	5.4	7.4
90	50.2	92.8	1.1	5.8
100	48.2	92.4	0.5	6.8
Abies-wood				
70	73.2	68.5	22.4	8.7
80	66.5	75.4	17.0	7.2
90	57.0	87.7	7.5	4.4
100	52.6	94.1	1.8	3.8

* on abs. dry wood, ** on abs. dry cellulosic product



1 – aspen-wood, 2 – birch-wood, 3 – abies-wood

Fig. 4. Influence of concentration of H₂O₂ (a) and CH₃COOH (b) on the content of residual lignin in cellulosic products obtained by peroxide delignification of different types of wood (100°C, LWR = 15, time 4 h, 1 wt% TiO₂).

At the same delignification conditions the softwood lignin (abies-wood) depolymerizes more difficult than hardwood lignin (aspen and birch woods).

Numerical optimization of wood peroxide delignification over TiO₂ catalyst was accomplished, according to the procedure described in [38]. As independent variables the following parameters were selected: X₁ – H₂O₂ concentration, %; X₂ – liquid to wood ratio (LWR). Next fixed parameters: temperature 100 °C, time 4 h, concentrations of CH₃COOH – 25 wt%, TiO₂ – 1 wt% were used. Parameters for optimization: Y₁ – yield of cellulosic product, wt%, Y₂ – content of cellulose in product, wt%, Y₃ – content of lignin in product, wt%, Y₄ – content of hemicelluloses in product, wt%.

Optimization was performed with the use of generalized parameter of optimization (W_a), which was calculated using the following equation:

$$W_a = \frac{\sum_{j=1}^p \delta_j d_j}{\sum_{j=1}^p \delta_j}$$

Where δ – the weight of the output parameter $0 \leq \delta_j \leq 1$; d_j – private utility function which was calculated using the following equation:

$$d_j = \frac{\Phi_0(x) - y_j^{(-)}}{y_j^{(+)} - y_j^{(-)}}$$

Where $\Phi_0(x)$ – the response of output parameter at the point X; $y_j^{(+)}$ and $y_j^{(-)}$ – the best and worst values of the output parameters within the studied region.

Analysis of variances showed that the effect of both factors X₁ and X₂ on the generalized parameter of optimization is statistically significant (P-Value less than 0.05 and the confidence level is above 95%).

As a result of mathematical processing the following regression equations were obtained:

for aspen-wood: $W_a = -1.3379 + 0.5373X_1 + 0.1332X_2 - 0.0380X_1^2 - 0.0137X_1X_2 - 0.0026X_2^2$
 for birch-wood: $W_a = -0.5829 + 0.2915X_1 + 0.0783X_2 - 0.0165X_1^2 - 0.0088X_1X_2 - 0.0008X_2^2$

for abies wood: $W_a = 0.5990 + 0.115X_1 + 0.1748X_2 - 0.0593X_1^2 + 0.0035X_1X_2 - 0.0468X_2^2$

Response surfaces of the generalized parameter of optimization of different types of wood are presented on Fig. 5.

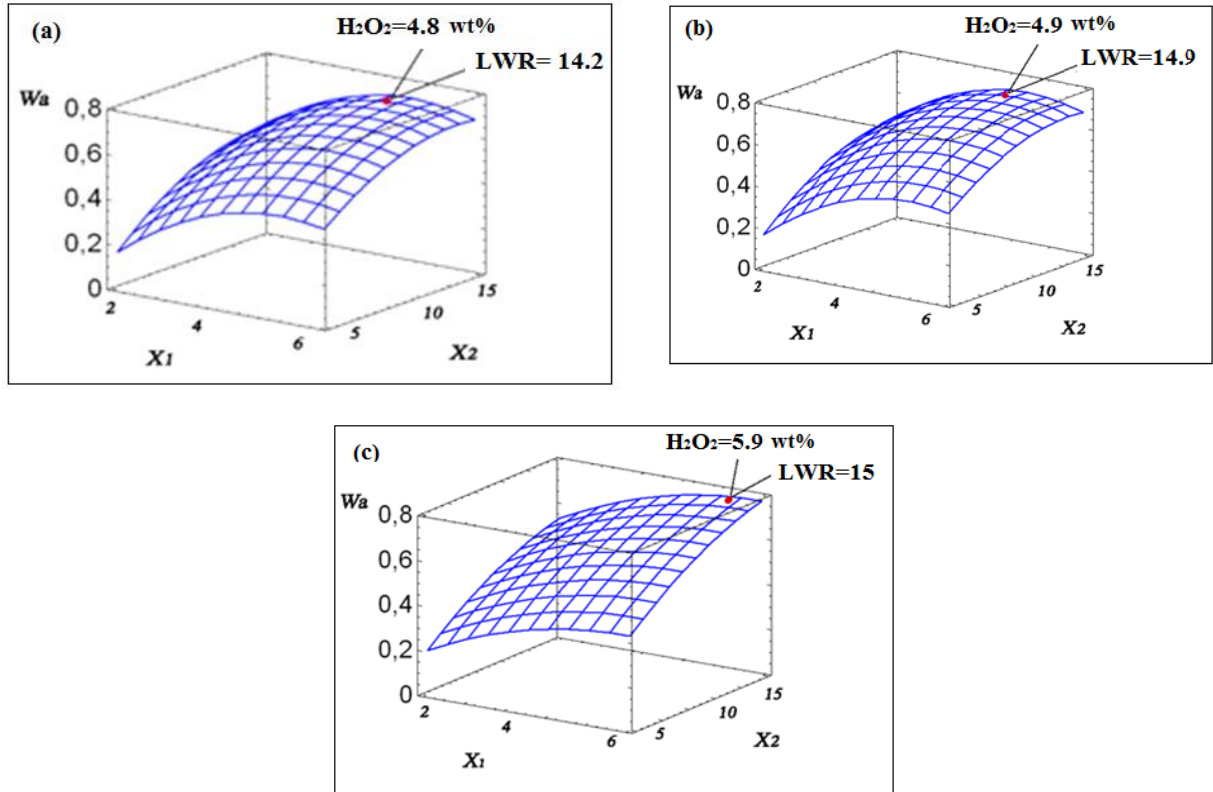


Fig. 5. The surfaces of generalized response of optimization parameters (W_a) of peroxide delignification of different types of wood over TiO_2 catalyst. (a) aspen-wood; (b) birch-wood; (c) abies-wood.

Calculated output parameters at optimal conditions have the following values:

Aspen-wood:

$X_1 = 4.8 \text{ wt\%}$; $X_2 = 14.2$; $Y_1 = 52.2 \text{ wt\%}$; $Y_2 = 91.3 \text{ wt\%}$; $Y_3 = 0.9 \text{ wt\%}$; $Y_4 = 6.6 \text{ wt\%}$.

Birch-wood:

$X_1 = 4.9 \text{ wt\%}$; $X_2 = 14.9$; $Y_1 = 51.0 \text{ wt\%}$; $Y_2 = 92.7 \text{ wt\%}$; $Y_3 = 0.5 \text{ wt\%}$; $Y_4 = 6.5 \text{ wt\%}$.

Abies-wood:

$X_1 = 5.9 \text{ wt\%}$; $X_2 = 15$; $Y_1 = 54.9 \text{ wt\%}$; $Y_2 = 90.3 \text{ wt\%}$; $Y_3 = 3.0 \text{ wt\%}$; $Y_4 = 7.0 \text{ wt\%}$.

The calculated optimized conditions of wood peroxide delignification coincide well with obtained experimental data (Table 5).

Table 5

Experimental data on optimized conditions of hardwood and softwood peroxide delignification at 100 °C over catalyst TiO₂ (1 wt%).

Wood nature	Optimized conditions	Yield of cellulosic product, wt% *	Composition of product, wt% **		
			Lignin	Cellulose	Hemicelluloses
Aspen wood	H ₂ O ₂ – 5 %, CH ₃ COOH – 25 %, LWR – 15	50.2	0.7	92.7	5.5
Birch wood	H ₂ O ₂ – 5 %, CH ₃ COOH – 25 %, LWR – 15	48.2	0.5	93.7	5.5
Abies wood	H ₂ O ₂ – 6 %, CH ₃ COOH – 30 %, LWR – 15	52.6	2.3	91.6	5.7

* on abs. dry wood; ** on abs. dry cellulosic product

The yields of cellulosic products obtained from different types of wood under optimized conditions are varied between 48.2–52.6 wt% (Table 5). Initial softwood contains more lignin, then hardwood, therefore the higher concentration of hydrogen peroxide (6 wt%) is needed for abies-wood delignification, as compared to aspen-wood and birch-wood.

3.1.3. Composition and structure of products of wood peroxide catalytic delignification

The structure of solid cellulosic products obtained by peroxide delignification of hardwood and softwood over TiO₂ (rutile) catalyst at optimized process conditions (Table 5) was studied by FTIR and XRD methods.

The FTIR spectra of cellulosic products from wood and the commercial sample of MCC Vivapur are very similar (Fig. 6). All samples have an absorption bands attributed to microcrystalline cellulose [39, 40]. The absence in the spectrum of cellulosic product from wood the peaks in the range 1509–1609 cm⁻¹, which would correspond to C=C aromatic skeletal vibrations, indicates the absence of residual lignin in the cellulosic product.

The absorption peak at 1430 cm⁻¹ corresponds to the CH₂ bending vibration that is attributed to the “crystallinity band” in the cellulose [41]. The band at 893 cm⁻¹ was attributed to the C–O–C stretching vibration of β-(1→4)-glycosidic linkages of cellulose, which was considered as an “amorphous band” in the cellulose [41].

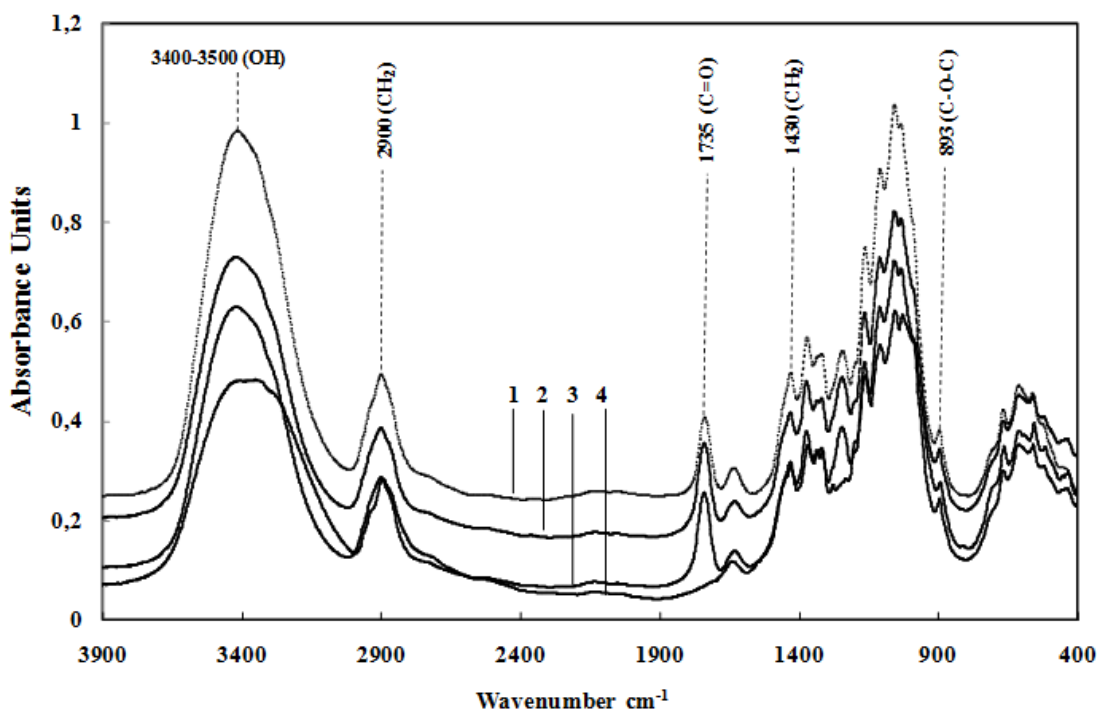


Fig. 6. Infrared spectra of cellulosic products obtained by peroxide delignification of different types of wood (1 – aspen; 2 – birch; 3 – abies) and of commercial microcrystalline cellulose Vivapur (4).

The absorption band, which corresponds to either the acetyl or uronic ester groups of hemicelluloses, normally appears in the region $1700\text{--}1740\text{ cm}^{-1}$ [42]. The presence of this band in the spectrum of cellulosic product from wood indicates that some part of hemicelluloses was not removed during wood delignification under the used conditions.

According to X-ray diffraction data (Fig. 7) the samples of cellulose obtained by peroxide delignification of aspen, birch and abies wood have the structure, similar to the commercial MCC. Diffractograms of all cellulosic samples contain two intensive peaks with maximum 2θ equal 22.6° (plane 002) and 16.2° (plane 110). A well crystallized and homogeneous on the lattice parameters of MCC gives narrow and high diffraction peaks. X-ray data (Fig.7) suggests that the crystal structure of MCC samples obtained from wood is the monoclinic cellulose I [43].

According to the X-ray data, the crystallinity of MCC samples obtained from wood (67-74%) are close to the crystallinity of industrial MCC Vivapur and MCC Avicel PH 102 [44].

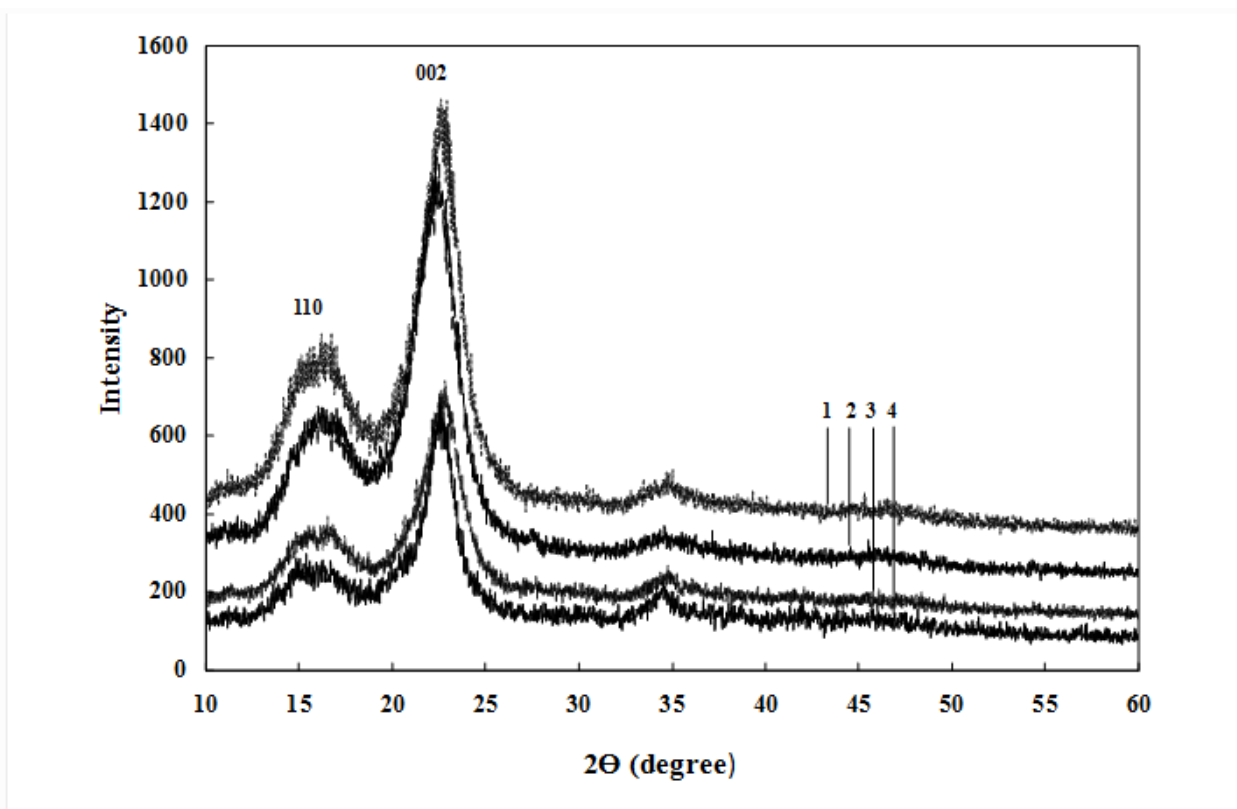


Fig. 7. Diffractograms of cellulosic products obtained by peroxide delignification of different types of wood (1 – aspen; 2–birch; 3 – abies) and of commercial microcrystalline cellulose Vivapur (4).

It is known, that hydrogen peroxide is also an effective oxidant for aromatic ring cleavage reactions and the complete oxidation of lignin by H_2O_2 leads to the formation of organic acids as end products [45]. The o-quinone structures are likely oxidized to muconic acids, while p-quinone structures may yield four-carbon acids (maleic acid, fumaric acid, malic acid, etc.) [5]. The transition- metal catalysts can accelerate the formation of reactive free-radical species from hydrogen peroxide which break the aromatic ring of lignin with the formation of organic acids.

The composition of soluble products obtained in the process of aspen wood peroxide delignification over catalyst TiO_2 (rutile) at $100^\circ C$ was studied using GC–MS method (Table 6).

Table 6

Results of GC-MS study the composition of benzene-soluble products obtained by peroxide delignification of aspen wood over catalyst TiO₂ (rutile) (reaction conditions: 100 °C, H₂O₂ 5 wt%, CH₃COOH 25 wt%, TiO₂ 1 wt%, LWR 15, time 4 h).

Retention time, min	Compound	Content, %*
9.29	Fumaric acid	3.18
12.44	Levulinic acid	1.43
16.48	Oxypropanoic acid	0.83
19.01	γ -hydroxybutanoic acid	0.77
21.38	Malic acid	3.16
24.45	Adipic acid	0.72
25.84	3,4-Hydroxyfuranone	0.02
28.24	p-hydroxybenzoic acid	6.24
29.97	2,3,4,5-tetrahydropentanoic acid 1.4 lactone	5.66
32.26	D-glucose	33.91
38.54	D -ribose	3.54
41.61	Glucofuranoside	6.91
46.95	Xylose	29.80
53.30	Azelaic acid	3.83

*from the sum of areas of all peaks

Obtained results show, that the benzene-soluble products of wood peroxide catalytic delignification over catalyst TiO₂ at 100°C mainly consist of monosaccharides and organic acids.

Aromatic compounds are present only in a low amounts which indicates oxidative degradation of aromatic units of lignin under the used conditions of wood catalytic delignification. The oxidation of benzene rings yields the fumaric, malic, oxypropanoic, γ – hydroxybutanoic acids and of a small amount (6.24 % rel.) of p-hydroxybenzoic acid (Table 6). The reactions of hydrolysis of hemicelluloses and amorphous cellulose give a significant amount of D-glucose (33.91 % rel.) and xylose (29.80 % rel.).

Thus, the results of the accomplished study demonstrate the possibility of efficient peroxide fractionation of hardwood and softwood at 100 °C over TiO₂ (rutile) catalyst into microcrystalline cellulose and low molecular mass products mainly presented by organic acids and C₆ and C₅ – monosaccharides.

3.2. Organosolv lignins depolymerization in supercritical alcohols

3.2.1. Characterization of the organosolv lignins

Organosolv lignins have the hydrophobic properties. They are not soluble in water, but have a good solubility in many organic solvents [46]. The organosolv lignins do not contain sulfur and have lower molecular mass as compared to conventional technical lignins. Therefore they are convenient objects for the use in the processes of catalytic depolymerization into liquid phenolic and aromatic hydrocarbons.

In this study acetone-lignin and ethanol-lignin isolated from aspen wood were characterized by FTIR, 2D NMR spectroscopy, gel permeation chromatography, elemental and thermogravimetric analysis.

IR spectra of acetone-lignin and ethanol-lignin contains adsorption bands characteristic for phenolic structural units of guaiacyl and syringyl types as well as aliphatic fragments and carboxylic groups (Fig. 8).

The broad intensive band at 3430 cm^{-1} belongs to the stretching vibrations of associated phenolic and aromatic hydroxyls. The intensive bands at 2935 cm^{-1} , 2851 cm^{-1} (C-H stretching vibrations in methyl and methylene groups) and at 1463 cm^{-1} (asymmetric deformation vibrations of these groups) indicates the presence of aliphatic fragments in lignins.

The groups of bands in the regions $1605\text{-}1593\text{ cm}^{-1}$, $1515\text{-}1505\text{ cm}^{-1}$, $1430\text{-}1422\text{ cm}^{-1}$ belong to the skeletal vibrations of aromatic ring. The bands at $1271\text{-}1266\text{ cm}^{-1}$ – skeletal vibrations of guaiacyl ring and stretching asymmetric vibrations of $\text{C}_{\text{ar}} - \text{O} - \text{C}$. The bands at $1230\text{-}1216\text{ cm}^{-1}$ - skeletal vibrations of syringyl ring and C – O stretching vibrations in phenols [47, 48].

The comparison of the intensity of bands at 1271 cm^{-1} and 1216 cm^{-1} suggests that organosolv lignins from aspen wood contain more syringyl units, than guaiacyl units.

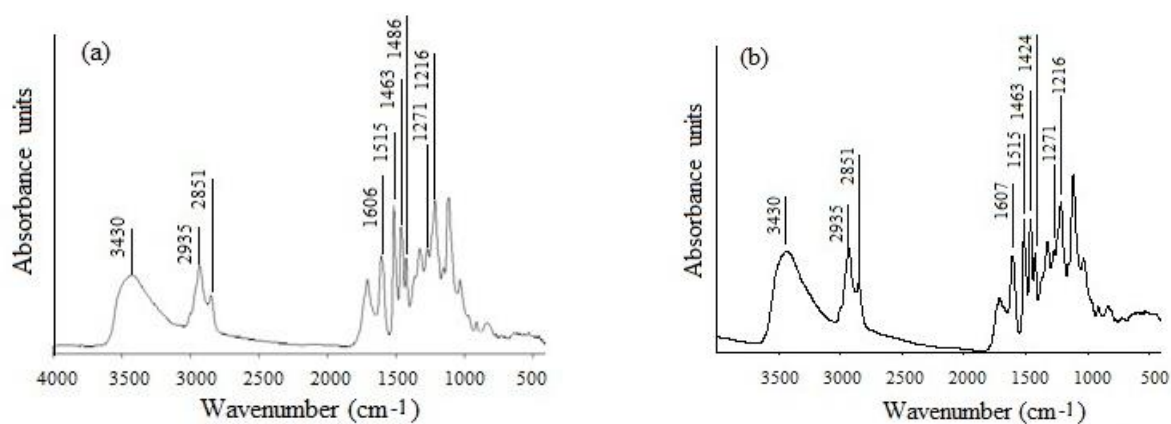


Fig. 8. FTIR spectra of acetone-lignin (a) and ethanol-lignin (b) obtained from aspen wood.

According to thermogravimetric data, the thermal decomposition of acetone-lignin and ethanol-lignin mainly proceeds in one stage. This is indicated by the appearance on the differential curve of the mass loss the peak of high intensity at $378\text{ }^{\circ}\text{C}$ for ethanol-lignin and $368\text{ }^{\circ}\text{C}$ for acetone-lignin (Fig. 9)

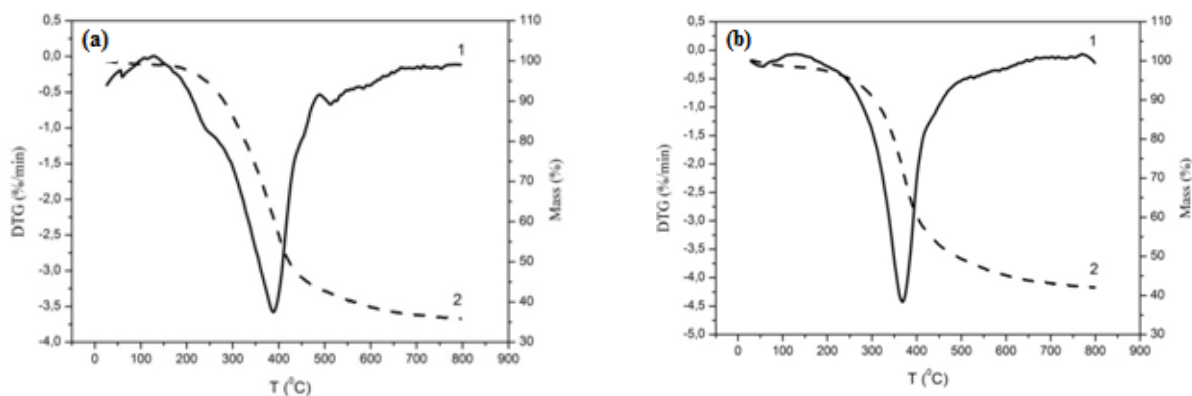


Fig. 9. Thermogravimetric DTG (1) and TGA (2) curves of ethanol-lignin (a) and acetone-lignin (b).

According to GPC data the samples of chloroform extracts of organosolv lignins are characterized by a wide distribution of molecular masses in the range 100-10000 Da. The peak on chromatograms with molecular weight less than 100 Da probably belongs to a low-molecular mass impurity. In general, the nature of the molecular weight distribution is similar for the samples of acetone-lignin and ethanol-lignin. Three peaks with MM \sim 250, \sim 600, \sim 900 with significant overlap can be singled out in chromatograms of ethanol-lignin sample (Fig. 10 a).

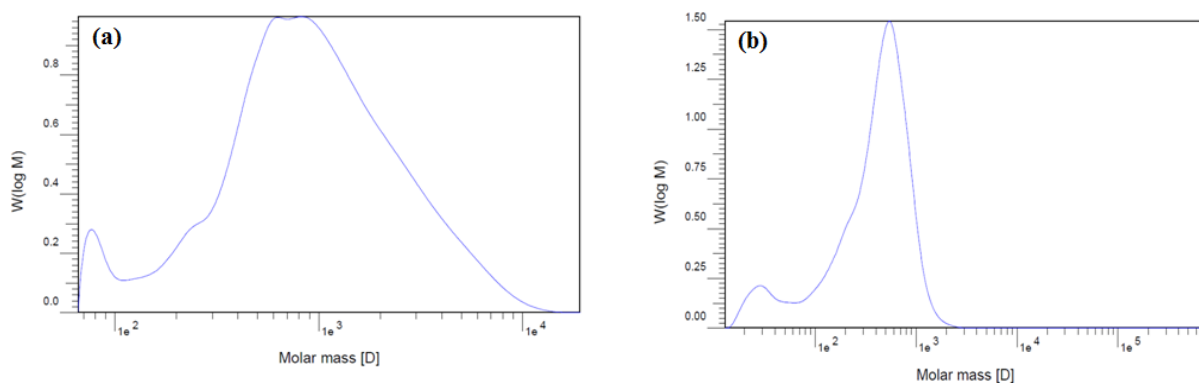


Fig. 10. Molecular weight distributions of chloroform extracts of ethanol-lignin (a) and acetone-lignin (b).

It should be noted that the solubility of acetone-lignin in chloroform is lower than ethanol-lignin. Due to the low solubility, the maximum molecular weight of acetone-lignin does not exceed 2kDa, and it characterizes by a single peak (\sim 700Da) with a low polydispersity index (\sim 1.5) (Fig. 10 b).

Lignin contours in the HSQC spectra (Fig. 11) were assigned with the use of the literature data [49-52]. Typically, three main regions in HSQC spectra of lignocellulosic samples are observed: the aromatic region of lignin ($\delta C/\delta H$ 160–102/8.0–6.0), the aliphatic region of lignin (main inter units ranged from $\delta C/\delta H$ 90–50/6.0–3.0), and the polysaccharide anomeric region ($\delta C/\delta H$ 110–60/6.0–3.0). In aspen organosolv lignins, the main linkages, such as β -O-4 aryl ethers, resinols, phenylcoumarans could be assigned (Fig. 11).

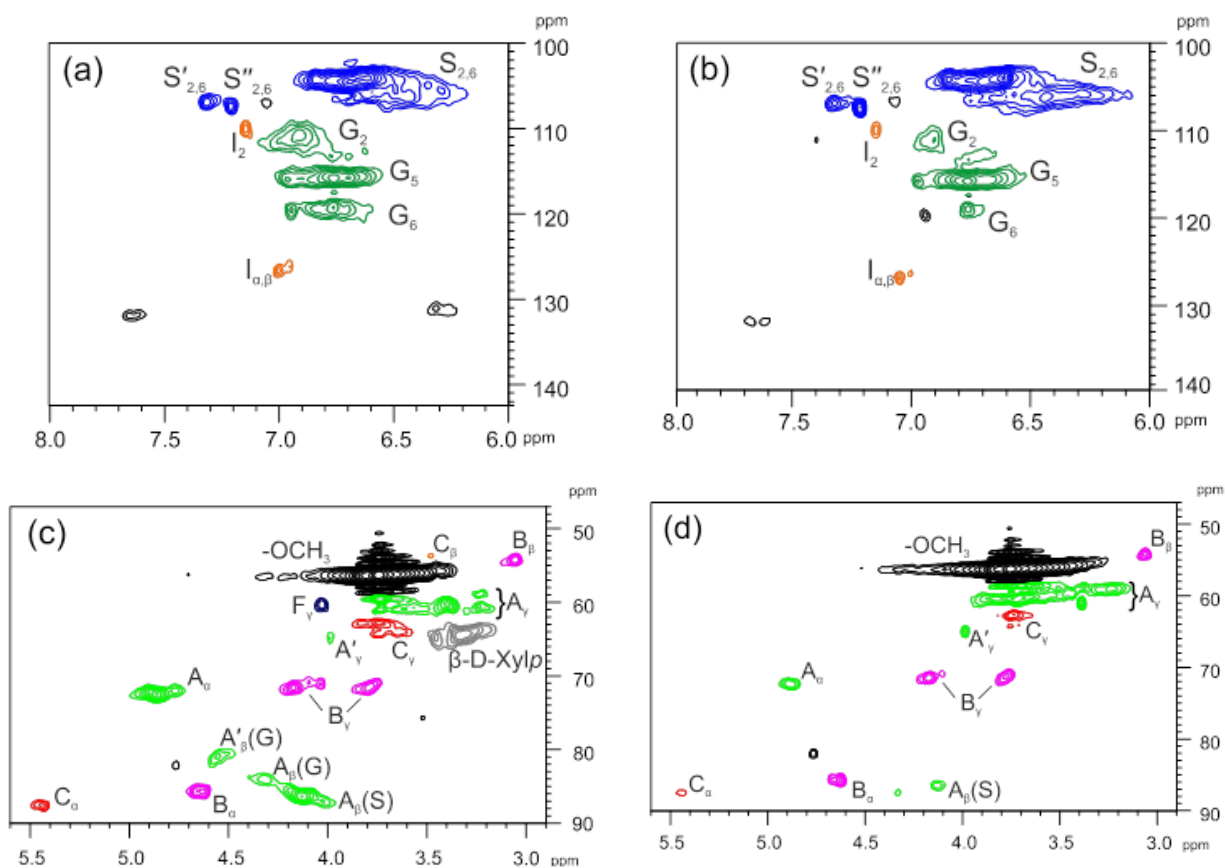


Fig. 11. ^1H - ^{13}C HSQC NMR spectra of aspen lignin samples: ethanol-lignin aromatic (a) and aliphatic (c) region; aceton-lignin aromatic (b) and aliphatic (d) region.

The assignment of main lignin ^{13}C - ^1H cross-signals in the HSQC spectra of aspen organosolv lignins is given in Table 7.

The comparison of ^1H - ^{13}C HSQC NMR spectra of the aspen organosolv lignin showed that in both lignins there are correlation peaks at $\delta\text{C}/\delta\text{H}$ 72.5/4.87 ppm (A_α) and $\delta\text{C}/\delta\text{H}$ 60.3–60.9/3.4–3.72 ppm (A_γ) assigned to β -O-4 aryl ether substructures. However, in acetone-lignin, in contrast to ethanol-lignin, the single correlation peak at $\delta\text{C}/\delta\text{H}$ 86.2/4.13 ppm is present. This peak assigned to the CH_2 -group in the β -position in syringyl substructures (A_β (S)).

For ethanol-lignin the peaks at $\delta\text{C}/\delta\text{H}$ 84.0/4.32 ppm are also observed. These peaks assigned to the CH_2 groups in the β -position of syringyl and guaiacyl units.

In the 2D-HSQC NMR spectra of ethanol-lignin the peak at $\delta\text{C}/\delta\text{H}$ 64.3/3.33 ppm, which was assigned to the C_5 of β -D-xylopyranoside fragments of the lignin-carbohydrate complex, was also detected. This peak is absent in the spectra of acetone-lignin.

Table 7

Assignment of main lignin ^{13}C - ^1H cross-signals in the HSQC spectra of the aspen organosolv lignins.

Label	$\delta\text{C}/\delta\text{H}$ (ppm)	Assignment
C_β	54.4/3.46	$\text{C}_\beta\text{-H}_\beta$ in phenylcoumarane substructures (C)
B_β	54.3/3.06	$\text{C}_\beta\text{-H}_\beta$ in resinol substructures (B)
$-\text{OCH}_3$	56.2/3.76	C-H in methoxyls
A_γ	60.3–60.9/3.4–3.72	$\text{C}_\gamma\text{-H}_\gamma$ in β -O-4substructures (A)
F_γ	61.9/4.09	$\text{C}_\gamma\text{-H}_\gamma$ in cinnamyl alcohol end-groups (F)
C_γ	62.8/3.74	$\text{C}_\gamma\text{-H}_\gamma$ in phenylcoumaran substructures (C)
$\beta\text{-D-}$ Xylp	64.3/3.33	$\beta\text{-D-Xylopyranoside}$
A'_γ	64.7/3.99	$\text{C}_\gamma\text{-H}_\gamma$ in γ -acetylated β -O-4' substructures (A') and others
B_γ	71.6/3.89 and 4.18	$\text{C}_\gamma\text{-H}_\gamma$ in resinol substructures (B)
A_α	72.5/4.87	$\text{C}_\alpha\text{-H}_\alpha$ in β -O-4substructures (A)
$\text{A}_\beta(\text{G})$	84.0/4.32	$\text{C}_\beta\text{-H}_\beta$ in β -O-4substructures linked to G units (A)
$\text{A}'_\beta(\text{G})$	80.7/4.55	$\text{C}_\beta\text{-H}_\beta$ in C_α -ethoxylation β -O-4 linkages
B_α	85.5/4.64	$\text{C}_\alpha\text{-H}_\alpha$ in resinol substructures (B)
$\text{A}_\beta(\text{S})$	86.2/4.13	$\text{C}_\beta\text{-H}_\beta$ in β -O-4' substructures linked to S units (A)
C_α	87.5/5.44	$\text{C}_\alpha\text{-H}_\alpha$ in phenylcoumaran substructures (C)
$\text{S}_{2,6}$	104.3/6.66	$\text{C}_{2,6}\text{-H}_{2,6}$ in etherified syringyl units (S)
$\text{S}'_{2,6}$	106.7/7.31	$\text{C}_{2,6}\text{-H}_{2,6}$ in oxidized ($\text{C}_\alpha=\text{O}$) syringyl units (S')
$\text{S}''_{2,6}$	107.0/7.21	$\text{C}_{2,6}\text{-H}_{2,6}$ in oxidized ($\text{C}_\alpha=\text{O}$) syringyl units (S'')
I_2	110.0/7.15	$\text{C}_2\text{-H}_2$ in stilbenes units (I)
G_2	111.0/6.90	$\text{C}_2\text{-H}_2$ in guaiacyl units (G)
G_5	115.6/6.76	$\text{C}_2\text{-H}_2$ in guaiacyl units (G)
G_6	119.2/6.76	$\text{C}_6\text{-H}_6$ in guaiacyl units (G)
$\text{I}_{\alpha,\beta}$	126.0/7.00	$\text{C}_{\alpha,\beta}\text{-H}_{\alpha,\beta}$ in stilbenes units (I)

3.2.2. Organosolv lignin conversion in supercritical alcohols

The effective depolymerization of lignin proceeds in supercritical lower alcohols (often ethanol and butanol) [4, 6, 7]. The choice of these alcohols is due to the fact that the values of their critical temperatures (243 °C for ethanol and 288 °C for butanol) are close to the temperature region of intensive thermal degradation of lignins. Besides, lignin is a waste of ethanol and butanol obtaining from wood and that allows its one-site valorization without the use of additional reagents and transport costs. Alcohols not only extract the products of thermal

fragmentation of lignin but also they are able to alkylate them, preventing the secondary reactions of their condensation [7, 32].

The catalytic properties of Ni-containing catalysts were studied in conversions of ethanol-lignin in supercritical ethanol and butanol. Table 8 shows the composition of the catalyst samples.

Table 8
Characteristics of the studied Ni-containing catalysts.

Catalyst	Catalyst composition, wt %	Specific surface area, m^2/g	Pore volume, cm^3/g
NiCu/SiO ₂ (400)	Ni-56; Cu-8.2; Si-18.2 (red. 400°C)	244	0.27
NiCu/SiO ₂ (500)	Ni-56; Cu-8.2; Si-18.2 (red. 500°C)	175	0.21
NiCuMo/SiO ₂ 20	Ni - 46; Cu - 6.7; Mo - 11.7; Si - 15 Mo \times 100/(Mo + Ni) = 20		
NiCuMo/SiO ₂ 30	Ni - 41; Cu - 6; Mo - 17.8; Si - 13.3 Mo \times 100/(Mo + Ni) = 30	104	0.22

In the absence of catalysts the conversion of supercritical ethanol and butanol is not observed to a temperature of 300 °C [53]. However, at these conditions the Ni-containing catalysts intensify the conversion of butanol, ethanol and organosolv lignins.

In conversion of acetone-lignin in supercritical butanol at temperature 300°C the maximum total yield of liquid products isolated by hexane, acetone and diethyl ether (90 wt%) is observed for catalyst NiCuMo/SiO₂ (30) (Fig. 12)

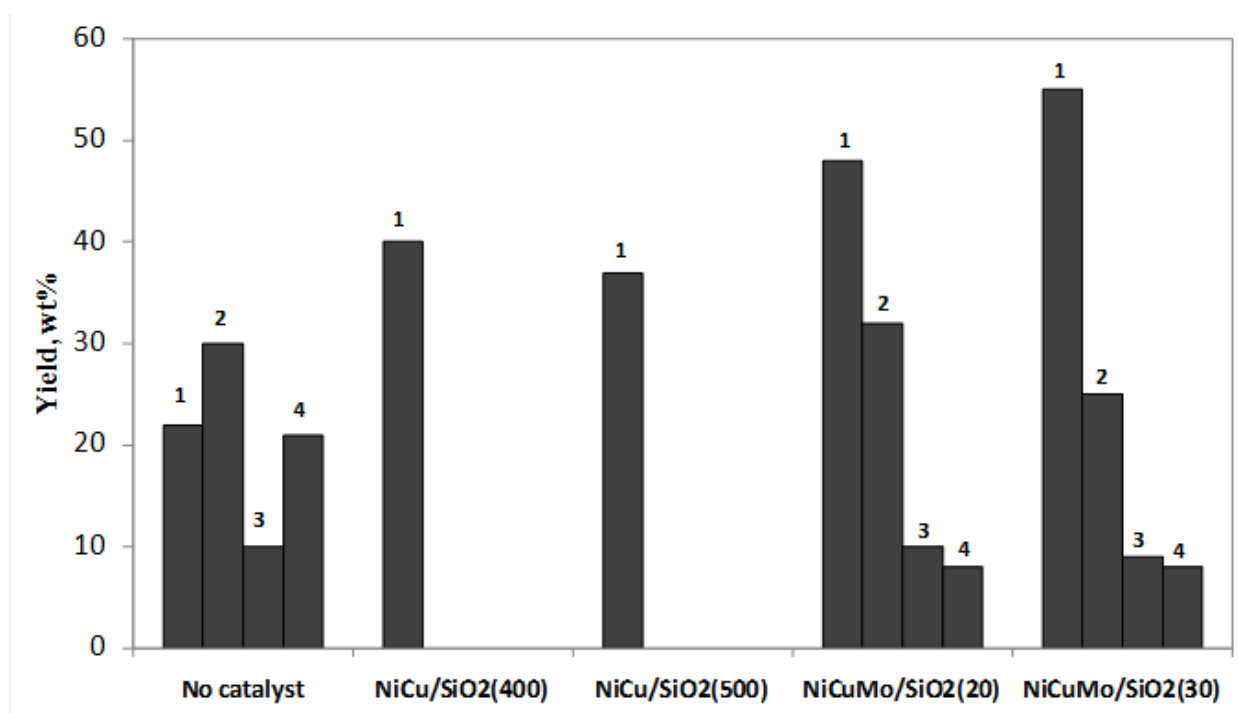


Fig. 12. Yield of products obtained by acetone-lignin conversions over Ni-containing catalysts in supercritical butanol at 300°C and 5.0 MPa (wt. ratio wood/catalyst 10:1)
1 – products soluble in hexane; 2 – in acetone; 3 – in diethyl ether; 4 – solid product.

This catalyst was used to study the thermal conversion of ethanol-lignin in supercritical ethanol (Fig. 13). The catalyst NiCuMo/SiO₂ increases both the conversion of ethanol-lignin and the yield of liquid products soluble in benzene (Fig. 13).

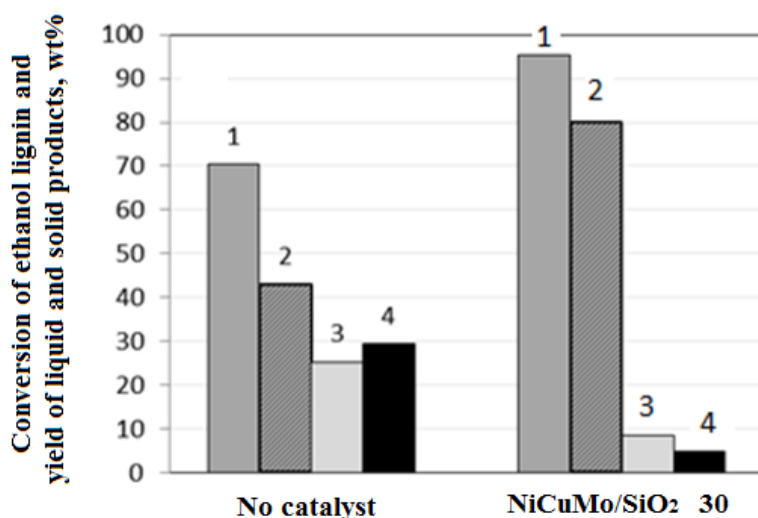


Fig. 13. Influence of catalyst NiCuMo/SiO₂ on the conversion of ethanol-lignin in supercritical ethanol and on the yield of liquid and solid products at 300 °C, 11.6 MPa: 1 – conversion; 2 – products soluble in benzene; 3 – products soluble in ethanol; 4 – solid product.

The total yield of liquid products of acetone-lignin conversion in supercritical butanol and of ethanol-lignin conversion in supercritical ethanol reaches to 90 wt%. Catalyst NiCuMo/SiO₂ influences significantly on the composition of liquid products obtained by lignin conversion in supercritical alcohols at 300 °C. It reduces the content of phenol and benzene derivatives and increases the content of esters, aldehydes and ketons in hexane-soluble products.

3.2.3. Green catalytic biorefinery of wood

Presented examples demonstrate the feasibility of obtaining the valuable chemicals with rather high yields by catalytic depolymerization of the native and organosolv lignins with solid catalysts and green reagents.

Solid catalysts (TiO₂, NiCuMo/SiO₂), low-toxic reagents (H₂O₂, acetic acid, ethanol, butanol) and the optimum processes conditions were selected for conversions of wood lignins to water-soluble organic products and liquid hydrocarbons.

The separate processes of wood oxidative catalytic fractionation into MCC and water-soluble products from hemicelluloses and lignin, catalytic depolymerization of lignin in supercritical alcohols to liquid hydrocarbons can be employed for the green biorefinery of wood.

The scheme of green biorefinery of wood with obtaining MCC, organic acids, alcohols and liquid hydrocarbons, based on the use of low-toxic reagents and solid catalysts is suggested (Fig. 14).

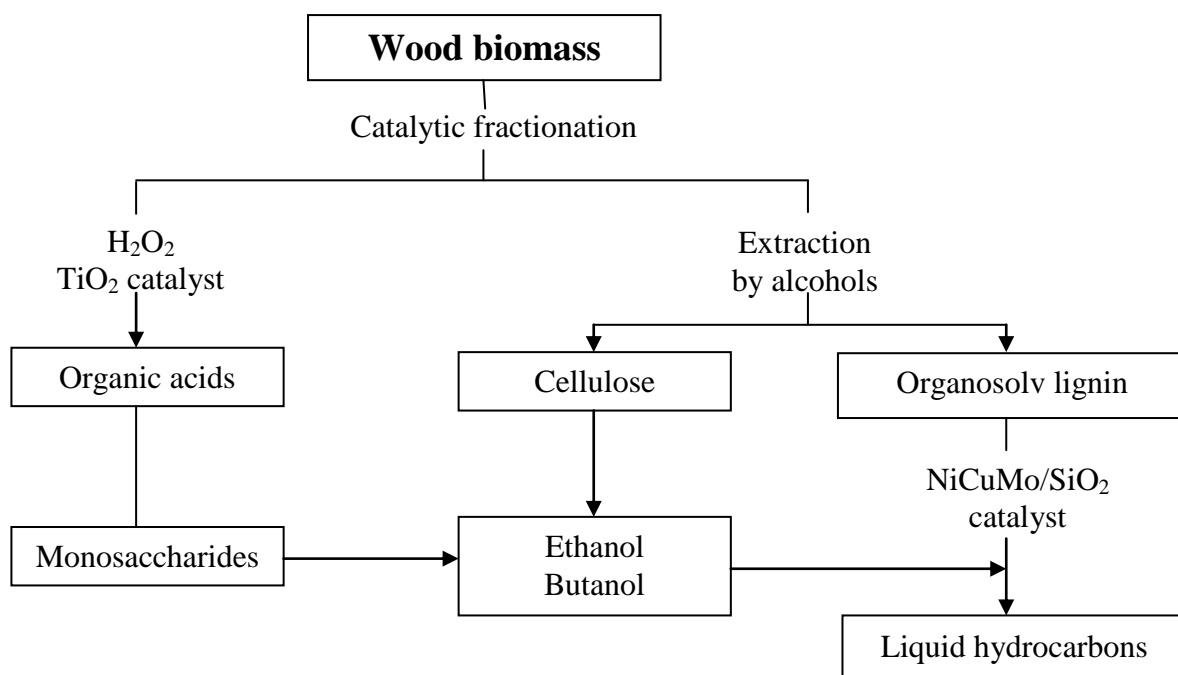


Fig. 14. Scheme of green biorefinery of wood biomass based on the use of low-toxic reagents and solid catalysts.

The integration of studied catalytic processes ensures the environmentally friendly biorefinery of different types of wood sawdust to produce microcrystalline cellulose and a wide range of fine chemicals from lignin and hemicelluloses.

The optimal conditions were found for the processes of peroxide fractionations of hardwood and softwood on MCC and on soluble products from lignin and hemicelluloses in acetic acid – water medium over catalyst $\text{TiO}_2(\text{rutile})$ at temperatures $\leq 100\text{ }^\circ\text{C}$ and for organosolv lignins conversion to liquid hydrocarbons over NiCuMo/SiO_2 catalyst in supercritical ethanol or butanol at temperature $300\text{ }^\circ\text{C}$.

The further development of suggested scheme of wood biorefinery should include the use of additional processes of cellulosic product transformation to platform chemicals (5 – HMF, levulinic acid, etc.) and the optimization of composition of soluble organic products for their rational use as fine chemicals and fuel additives.

The more deep study of properties of selected solid catalysts (TiO_2 , NiCuMo/SiO_2) is needed to demonstrate the possibility of their practical application. The effective solid catalysts for wood biomass oxidative fractionation should be resistant to water and its surface should have optimum hydrophilic-hydrophobic properties. For depolymerization of lignins in hydrocarbon media the solid acidic, metallic and bifunctional catalysts, employed in petrochemical processes can be adapted.

4. Conclusion

The following catalytic processes of native and isolated wood lignins depolymerization are described: the peroxide delignification of hardwood and softwood in the medium of acetic acid – water over TiO₂ catalyst and the thermal dissolution of organosolv lignins in supercritical alcohols over solid Ni-containing catalysts.

Catalytic properties of TiO₂ samples in anatase and rutile modifications were compared in the processes of aspen wood peroxide delignification at 100 °C. At the same process conditions the use of titanium dioxide catalyst in rutile modification with low surface area (2 m²/g) gives the cellulosic product with lower content of residual lignin and higher cellulose content, as compared to TiO₂ in anatase modification with higher surface area (89–111 m²/g). The reduced catalytic activity of TiO₂ anatase can be explained by the following reasons. Probably, the smaller size of pores in anatase samples (12.4–13.1 nm) as compared to rutile sample (17.9 nm) reduces their catalytic activity in wood delignification owing to strengthening of diffusion limitations inside pores. Besides that, a higher concentration of hydrogen groups on the surface of anatase modification of TiO₂, as compared to its rutile modification can prevent the formation from H₂O₂ the radical species ([•]OH and [•]OOH) active in lignin oxidative depolymerization.

The results of kinetic studies and optimization of the processes of peroxide depolymerization of hardwood (aspen, birch) and softwood (abies) lignins in the medium of acetic acid – water over solid TiO₂ catalyst at mild conditions (≤ 100°C, 1 MPa) are compared. It was found that the increase of temperature, concentrations of H₂O₂ and CH₃COOH in the reaction mixture reduces the yield of cellulosic product and the contents of residual lignin and hemicelluloses in this product.

The catalyst TiO₂ initiates the formation of OH[•] and OOH[•] radicals from H₂O₂ which promote the oxidative fragmentation of wood lignin. In this case, the peroxide depolymerization of softwood lignin, constructed from phenylpropane units of guaiacyl-type proceeds more difficult than the hardwood lignins, mainly containing syring-type units.

The yields of cellulosic products obtained from different types of wood under optimized conditions are varied between 48.2–52.6 wt%. Initial softwood contains more lignin, then hardwood, therefore the higher concentration of hydrogen peroxide (6 wt%) is needed for abies-wood delignification, as compared to aspen-wood and birch-wood.

The solid and soluble products of wood oxidative delignification over TiO₂ (rutile) catalyst at optimized conditions were studied by FTIR, XRD, GC-MS and chemical methods.

The FTIR spectra of cellulosic products from wood and the commercial sample of MCC Vivapur are very similar. All samples have an absorption bands attributed to microcrystalline cellulose.

According to XRD data the samples of cellulose obtained by peroxide delignification of aspen, birch and abies wood have the structure similar to the commercial MCC. The crystallinity of MCC samples obtained from wood (67–74%) are close to the crystallinity of industrial MCC.

According to GC-MS data the soluble products of wood peroxide catalytic delignification mainly consist of monosaccharides and of organic acids. Aromatic compounds are present in a low amounts which indicates oxidative degradation of aromatic units of lignin under the used conditions of wood catalytic delignification. The oxidation of benzene rings yields the fumaric, malic, oxypropanoic, γ -hydroxybutanoic acids and of a small amount (6.24 % rel.) of p-hydroxybenzoic acid. The reactions of hydrolysis of hemicelluloses and amorphous cellulose give a significant amount of D-glucose (33.91 % rel.) and Xylose (29.80 % rel.).

The results of the accomplished study demonstrate the possibility of efficient peroxide fractionation of hardwood and softwood at 100 °V over TiO₂ (rutile) catalyst into microcrystalline cellulose and low molecular mass products mainly presented by organic acids and C₆ and C₅ – monosaccharides.

The results of the study of thermal dissolution of organosolv lignins obtained from aspen-wood (ethanol-lignin and acetone-lignin) in supercritical alcohols (ethanol and butanol) over Ni-containing catalyst (NiCu/SiO₂, NiCuMo/SiO₂) are compared.

Data on composition, structure and thermal properties of organosolv lignins were obtained with the use of FTIR, GPC, ¹H - ¹³C HSQC NMR, DTA methods and elemental analysis. According to GPC data the samples of organosolv lignins are characterized by a wide distribution of molecular masses in the range 100–10 000 Da. In contrast to ethanol-lignin samples, the acetone-lignin characterized by a single peak (~ 700 Da) with a low polydispersity index (~ 1.5). The comparison of ¹H - ¹³C HSQC NMR spectra of the organosolv lignins shows that the structure of acetone-lignin is more condensed than that of ethanol-lignin.

The influence of a composition of Ni-containing catalyst on the thermal conversion of ethanol-lignin and acetone-lignin in supercritical butanol and ethanol and on the yield of liquid products was established. The highest conversion of lignins in supercritical alcohols (to 93 wt%) and the highest yield of liquid products (to 90 wt%) were achieved at 300 °C in the presence of catalyst NiCuMo/SiO₂ 30. This catalyst reduces the content of phenol and benzene derivatives and increases the content of esters, aldehydes and ketons in hexane-soluble products obtained from organosolv lignins.

The separate processes of wood oxidative catalytic fractionation into MCC and water-soluble products and catalytic depolymerization of lignin in supercritical alcohols to liquid hydrocarbons can be employed for the green biorefinery of wood.

The scheme of green biorefinery of wood with obtaining MCC, organic acids, alcohols and liquid hydrocarbons, based on the use of low-toxic reagents and solid catalysts is suggested.

The integration of studied catalytic processes ensures the environmentally friendly biorefinery of different types of wood sawdust to produce microcrystalline cellulose and a wide range of fine chemicals from lignin and hemicelluloses.

Acknowledgements

The reported study was supported by Russian Science Foundation, grant № 16-13-10326.

This work is a part of GDRI “Biomass” between France and Russia.

Reference

- [1] Von D. Fengel, G. Wegener, Wood. Chemistry, Ultrastructure, Reactions, Berlin 1984.
- [2] C. Heitner, D. R. Dimmel, J. A. Schmidt, Lignin and ligans. Advances in Chemistry, CRC Press: Teylor &Francis Group, 2010.
- [3] P. Azadi, O.R. Inderwildi, R. Farnood , D.A. King, Renewable and Sustainable Energy Reviews. 21 (2013) 506–523.
- [4] J. Zakzeski, P.C.A. Bruijninx, A.L. Jongerius, B.M. Weckhuysen, Chem. Rev. 110 (2010) 3552-3599.
- [5] R. Ma, Y.Xu, X. Zang, ChemSusChem. 8 (2015) 24-51.
- [6] M. Kleinert, T. Barth , Chem. Eng. Technol. 31 (2008) 736-745.
- [7] M. Kleinert, T. Barth , Energy-Fuels. 22 (2008). 1371-1379.
- [8] X. Huang, T.I. Koranyi, M.D. Boot, E.J.M. Hensen, Chem. Sus. Chem. 7 (8) (2014) 2276–2288.
- [9] T. Ennaert , J. Van Aelst, J. Dijkmans, R. De Clercq, W. Schutyser, M. Dusselier, D. Verboekend, B.F. Sels, Chem. Soc. Rev. 45 (2016) 584-611.
- [10] B. Güvenatam, E.H.J. Heeres, E.A. Pidko, E.J.M. Hensen, Catal. Today 259 (2016) 460-466.
- [11] H. Wang, M. Tucker, Y. Ji , J. of Appl. Chem. 2013 (2013) 9.
- [12] S. Van de Vyver, J. Geboers, P.A. Jacobs, B.F. Sels, Chem.Cat.Chem. 3 (2011) 2-99.
- [13] P. Maki-Arvela, B. Holbom, T. Salmi, D. Yu. Murzin, Catal. Rev. 49 (2007) 197-340.
- [14] S.N. Raveendran, V. Guliants, Appl. Catal., A. 356 (2009) 1–17.
- [15] J.Y. Kim, J. Park, H. Hwang, J.K. Kim, K. Song, J.W. Choi, J. Anal. Appl. Pyrolysis. 113 (2015) 99–106.
- [16] J. Y. Kim, J. Park, U. J. Kim, J.W. Choi, Energy Fuels. 29 (8) (2015) 5154–5163.

- [17] M.R. Sturgeon, M. H. O'Brien, P.N. Ciesielski, R. Katahira, J.S. Kruger, S.C. Chmely, J. Hamlin, K. Lawrence, G. B. Hunsinger, T.D. Foust, R.M. Baldwin, M. J. Bidy, G.T. Beckham, *Green Chem.* 16 (2014) 824–835.
- [18] Q Song, F. Wang, J. Cai, Y. Wang, J. Zhang, W. Yu, J. Xu, *Energy Environ. Sci.* 6 (2013) 994–1007.
- [19] A.B. Ayusheev, O.P. Taran, I.I. Afinigenova, T.I. Mishchenko, M.V. Shashkov, K.A. Sashkina, V.S. Semeikina, E.V. Parkhomchuk, V.E. Agabekov, V.N. Parmon, *J. Sib. Fed. Univ. Chem.* 3 (2016) 353–370.
- [20] S. Van den Bosch, W. Schutyser, R. Vanholme, T. Drissen, S.F. Koelewijn, T. Renders, B. De Meester, W.J.J. Huijgen, W. Dehaen, C.M. Courtin, B. Lagrain, W. Boerjan, B.F. Sels, *Energy Environ. Sci.* 8 (2015) 1748–1763.
- [21] W. Schutyser, Van der Bosch, T. Renders, T. De Boe, S.F. Koelewijn, A. Dewaele, T. Ennaert, O. Vikindereb, B. Goderis, C.M. Courtin, B.F. Sels, *Green Chem.* 17(2015) 5035–5045.
- [22] E.M. Anderson, R. Katahira, M. Reed, M.G. Resch, E.M. Karp, G.T. Beckham, Yu. Roman-Leshkov, *ACS Sus. Chem. & Engineering.* 4 (2016) 6940–6950.
- [23] B.N. Kuznetsov, V.E. Tarabanko, S.A. Kuznetsova, *Kinet. Catal.* 49 (2008) 517–526.
- [24] B.N. Kuznetsov, I.G. Sudakova, N.V. Garyntseva, L. Djakovitch, C. Pinel, *Reac. Kinet. Mech. Cat.* 110 (2013) 271–280.
- [25] U.V. Karyakin, I.I. Angelov, *Pure chemical materials, Chemistry, Moscow*, 1974.
- [26] M.A. Ermakova, D.Yu. Ermakov, *Appl. Catal. A: General.* 245(2003) 277–288.
- [27] M.V. Bykova, D.Yu. Ermakov, S.A. Khromova, A.A. Smirnov, M.Yu. Lebedev, V.A. Yakovlev, *Catal. Today* 220–222 (2014) 21–31.
- [28] E. Sjöström, R. Alern, *Analytical methods of wood chemistry. Pulping and Papermaking*, Springer-Verlag, Berlin, 1999.
- [29] J. Quesada-Medina, F.J. López-Cremades, P. Olivares-Carrillo, *Bioresource Technology.* 101 (2010) 8252–8260.
- [30] C. Arato, E. Kendall Pye, G. Gjennestad, *The Lignol, Appl. Biochem. Biotech.* 1 (2005) 121–124.
- [31] B.N. Kuznetsov, N.V. Chesnokov, O.V. Yatsenkova, V.I. Sharypov, N.V. Garyntseva, N.M. Ivanchenko, V.A. Yakovlev, *Wood Sci. Technol.* 51(2017) 1189–1208.
- [32] B.N. Kuznetsov, V.I. Sharypov, N.V. Chesnokov, N.G. Beregotsova, S.V. Baryshnikov, A.V. Lavrenov, A.V. Vosmerikov, V.E. Agabekov, *Kinet. Catal.* 56 (2015) 434–441.
- [33] S. Park S, J.O. Baker, M.E. Himmel, P.A. Parilla, D.K. Jonson, *Biotechnol Biofuels* 3(2010) 10.

- [34] B.N. Kuznetsov, I.G. Sudakova, N.V. Garyntseva, L. Djakovitch, C. Pinel, *Reac. Kinet. Mech. Cat.* 120 (1) (2017) 81–94.
- [35] C.L. Chen, E.A. Capanema, H.Z. Gracz, *J. Agric. Food Chem.* 51(2003) 1932–1941.
- [36] V. Alves, E. Capanema, Ch-L. Chen, J. Gratzl, *J. Mol. Catal. A: Chem.* 206 (1–2) (2003) 37–5.
- [37] C. Fernández-Rodríguez, J.M. Dona-Rodríguez, O. González-Díaza, I. Secka, D. Zerbani, D. Portillo, J. Perez-Pena, *Appl. Catal. B: Environmental.* 125 (2012) 383-389.
- [38] B.N. Kuznetsov, V.G. Danilov, S.A. Kuznetsova, O.V. Yatsenkova, N.B. Aleksandrova, *Theor. Found. Chem. Eng.* 43 (2009) 499–503.
- [39] A.M. Adel, Z.H. El-Wahab, A.A. Ibrahim, M.T. Al-Shemy, *Carbohydr. Polym.* 83 (2001) 676-687.
- [40] M. Fan, D. Dai, B. Huang, Fourier transform infrared spectroscopy for natural fibres, in Salih S. (Eds.), *Fourier transform – material analysis*, In Tech, Rejeka, 2012, pp. 45-68.
- [41] S. Shankar, J.W. Rhim, *Carbohydr. Polym.* 148 (2016)18-26.
- [42] L.Y.Xiang, M.A.P. Mohammed, A.S. Bahrudin, *Carbohydr. Polym.* 148 (2016) 11-20.
- [43] Y. Nishiyama, P. Langan, H. Chanzy, *J. Am. Chem. Soc.* 124(31) (2002) 9074-9082.
- [44] C. Vailiu-opera, J. Nicoleanu, *Polym. Plast. Technol. Eng.* 32(3) (1993) 181-214.
- [45] C. Crestini, M. Crucianelli, M. Orlandi, R. Saladini, *Catal. Today.* 156 (2010) 8–22.
- [46] B. Saake, R. Lehen, *Lignin. Ullmann's Encyclopedia of Industrial Chemistry*, Weinheim, Germany: Wiley-VCH Verlas, Gmb&Co, 2007.
- [47] D. Watkins, Md. Nuruddin, M. Hosur, A. Tcherbi-Narteh, Sh. Jeelani, *J. Mater. Res. Technol.* 4(1) (2015) 26–32.
- [48] J. Domínguez-Robles, R. Sánchez, P. Díaz-Carrasco, E. Espinosa, M.T. García-Domínguez, A. Rodríguez, *Int. J. Biol. Macromol.* 104 (2017) 909-918.
- [49] J. Rencoret, G. Marques, A. Gutierrez, L. Nieto, J. I. Santos, J. Jimenez-Barbero, A.T. Martinez, J.C. del Río, *Holzforchung.* 63 (2009) 691–698.
- [50] J. Zeng, G.L. Helms, X. Gao, S.Chen, *J. Agric. Food Chem.* 61(46) (2013) 10848–10857.
- [51] G. Hu, C. Cateto, Y. Pu, R. Samuel, A.J. Ragauskas, *Energy Fuels.* 26 (1) (2012) 740–745.
- [52] J.L. Wen, Sh. L. Sun, T.Q. Yuan, F. Xu, R.C. Sun, *J. Agric. Food Chem.* 61 (2013) 11067–11075.
- [53] N.G. Beregovtsova, V.I. Sharypov, S.V. Baryshnikov, L.I. Grishechko, A.V. Vos'merikov, B.N. Kuznetsov, *J. Sib. Fed. Univ. Chem.* 7(2) (2014) 242–251.