

# Green catalytic valorization of hardwood biomass into valuable chemicals with the use of solid catalysts

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## Abstract

Results of the study of green valorization of main components of hard wood biomass into valuable chemicals with the use of solid catalysts were described. The studied heterogeneous catalytic processes of hemicelluloses and cellulose hydrolysis, wood oxidative fractionation, lignin depolymerization in supercritical spirits was suggested to employ for the green biorefinery of hardwood with producing of xylose, pure cellulose, glucose, alcohols and liquid hydrocarbons.

*Keywords:* hardwood biomass, green biorefinery, valuable chemicals, solid catalysts.

## Introduction

In recent years the new processes for obtaining the alternative fuels and chemicals from renewable lignocellulosic biomass are intensively studied (Clark and Deswarte 2008; Nelson 2011). Wood waste and low-quality wood create a reliable source of renewable raw material for large-scale production of chemicals and alternative fuels.

In principle, from main components of wood biomass it is possible to produce all range of products of modern petrochemical synthesis, and also unique natural compounds, like biologically active substances.

Biomass of various tree species consists of cellulose, lignin, hemicelluloses, extracted substances and insignificant quantity of inorganic components (Fengel and Wegener 1984). Cellulose represents the linear polysaccharide constructed of links of glucose, connected by  $\beta$ -1,4 bonds. Hemicelluloses are the branched polysaccharides generally constructed of pentoses and hexoses with shorter, than in cellulose, chains. The lignin is polymer with branched structure which macromolecules are constructed by substituted phenylpropane units.

The specified types of vegetable polymers are structured by complex way in plant cells and therefore are quite stable against chemical reagents and enzymes. In this regard, in

36 traditional processes of lignocellulose biomass conversion the chemically aggressive and  
37 ecologically dangerous reagents, increased temperatures and pressures are applied.

38 For this reason, the traditional technologies of wood processing have a low productivity,  
39 produce only limited range of products and negatively influence on an environment. In  
40 particular, conventional technologies of cellulose production use the ecologically dangerous  
41 sulfur and chlorine-containing delignification agents (Sixta 2006). Also they don't allow to  
42 provide simultaneous producing the commodity products from such wood components, as lignin,  
43 hemicelluloses, extractive substances.

44 Traditional technologies of wood hydrolysis use mineral acids as catalysts and they  
45 became outdated and don't meet the modern requirements for productivity, power consumption,  
46 resource-saving and ecological purity.

47 New effective methods for the production valuable chemicals, functional polymers and  
48 biofuels from lignocellulose biomass are based on the use of effective catalysts and "green"  
49 reagents (Bessone et al. 2014; Serrano-Ruiz and Dumesic 2011; Zakzeski et al. 2010).

50 The studies, directed on integrated catalytic processing of biomass into biofuels and  
51 chemicals are intensified in the last decade (Cherubini et al. 2009; de Long et al. 2013). The  
52 most perspective integrated processes include, as a key stage, biomass fractionation on  
53 polysaccharides and lignin. Their further conversion allows to produce various chemicals and  
54 liquid biofuels.

55 Known ways of lignocelluloses biomass fractionation can be united into two groups. In  
56 one of them cellulose and hemicelluloses are removed by dissolution, and the lignin remains as  
57 an insoluble rest, another includes methods in which the lignin is dissolved. The first group  
58 includes wood hydrolysis processes, and the second – processes of cellulose isolation from  
59 wood.

60 Single-stage processes of wood fractionation on cellulose and soluble lignin by oxidative  
61 depolymerization of lignin in "hydrogen peroxide-acetic acid-water" medium at 120–130 °C in  
62 the presence of different catalysts were studied (Kuznetsov et al. 2008a). At optimum conditions  
63 of wood delignification by hydrogen peroxide in the presence of H<sub>2</sub>SO<sub>4</sub> catalysts (2 wt%) and  
64 TiO<sub>2</sub> (0,5 wt%) the cellulosic products containing less than 1 % of a residual lignin can be  
65 obtained with an acceptable yield (44–48 wt% on abs. dry wood).

66 Perspective directions of lignocellulosic biomass processing are connected with the use of  
67 solid catalysts which have a number of technological advantages in comparison with the  
68 dissolved catalytic systems (Van de Vyver et al. 2011; Maki-Arvela et al. 2007; Raveendran and  
69 Guliants 2009).

70 This presentation describes results of the study of heterogeneous catalytic processes of  
71 green valorization of low-quality birch and aspen wood to valuable chemicals, namely hydrolysis  
72 of hemicelluloses into xylose, oxidative fractionation of wood on pure cellulose and soluble  
73 lignin, hydrolysis of cellulose into glucose, depolymerization of acetone-lignin in supercritical  
74 butanol with the formation of liquid hydrocarbons. The combination of studied processes in a  
75 single technological cycle can be employed for the green biorefinery of hardwood into valuable  
76 chemicals.

77

## 78 **Experimental**

79 Air dry sawdust (fraction 2–5 mm) of birch wood (*Betula pendula*) with composition  
80 (wt%): cellulose – 46.5, hemicelluloses – 27.2, lignin 21.8 and aspen wood (*Populus tremula* L.)  
81 with composition (wt%): cellulose 46.3, hemicelluloses 24.5, lignin 21.9 were used in  
82 experiments.

83 Acetone-lignin, isolated by boiling acetone from aspen wood after hydrolysis of wood  
84 hemicelluloses (Boeriu et al. 2014) was used in experiments on the lignin depolymerization in  
85 supercritical butanol. Yield of acetone-lignin is 21 wt% from amount of lignin in aspen wood.  
86 Obtained acetone-lignin is completely dissolved in twofold excess of boiling butanol. Acetone-  
87 lignin chemical composition (wt%): C – 67.2, H – 6.7, O – 25.1, ash – 0.4.

88 The catalytic processes of wood hemicelluloses and cellulose hydrolysis oxidative  
89 fractionation of wood on cellulose and lignin, lignin conversion in supercritical butanol were  
90 studied with the use of batch stirring reactors and rotating autoclaves.

91

### 92 *Hydrolysis of wood hemicelluloses*

93 In hydrolysis with H<sub>2</sub>SO<sub>4</sub> catalyst the glass batch reactor of 500 cm<sup>3</sup> volume supplied by  
94 mechanical stirrer, condenser and thermometer was used. Air-dry wood sawdust (fraction 2–5  
95 mm) in the amount 10 g and 80 ml 1–4 wt% H<sub>2</sub>SO<sub>4</sub> (GOST 4204-77) were placed into the  
96 reactor. The reaction mixture was vigorously stirred (700 rpm) at 100 °C during 1–5 h. When the  
97 reaction was completed, the reaction mixture was cooled to room temperature and filtered under  
98 vacuum using a Buchner funnel. Obtained hydrolysate was analysed on gas chromatograph  
99 “VARIAN-450”. Solid wood residue was washed with distilled water and dried at 105 °C until  
100 constant weight. Conversion of wood was estimated by the gravimetric method.

101 For wood hemicelluloses hydrolysis with solid catalysts the rotating steel autoclave with  
102 an inner Teflon tube of 35 ml volume was used. The mixture of wood sawdust activated in  
103 planetary mill AGO-2 during 30 min and solid catalyst (fraction less 0.5 mm) with weight ratio  
104 1:1 was placed into Teflon tube and distilled water was added. The concentration of wood in

105 water was 40 g/l. The hydrolysis reaction was carried out at 110–170 °C at the speed of rotation  
106 of the autoclave 120 rpm. The procedures of reaction mixture fractionation and analysis were the  
107 same as in the case of wood hydrolysis with H<sub>2</sub>SO<sub>4</sub>.

108

#### 109 *Hydrolysis of cellulose with acid solid catalysts*

110 Rotating steel autoclave with an inner Teflon tube of 35 ml volume was used for cellulose  
111 hydrolysis at 150 °C and 170 °C. Cellulose (0.45 g) and solid catalyst (0.45 g) were placed into  
112 Teflon tube and distilled water was added. Procedures of cellulose hydrolysis and hydrolysates  
113 analysis were the same as in the case of hemicelluloses hydrolysis with solid acid catalysts.

114

#### 115 *Conversion of lignin in butanol*

116 The thermal conversion of acetone-lignin in supercritical butanol was carried out at 250–  
117 350 °C in a rotating autoclave (Autoclave Engineers, USA) of 300 cm<sup>3</sup> volume. A mixture 3 g  
118 lignin and 0.3 g catalyst crushed to the size of the particles < 0.1 mm and 15 ml of butanol was  
119 placed in the autoclave. The autoclave was hermetically sealed. Air was removed from the  
120 autoclave by purging it with argon through its stop valves. Thereafter, the autoclave was heated  
121 at a rate of 10 C/min to the desired temperature and was kept at this temperature for 1 h under  
122 vigorous mixing (850 rpm). Under these conditions, the pressure in the autoclave was 4.8–5.0  
123 MPa. Then the autoclave was cooled to room temperature and the products were quantitatively  
124 washed out of the autoclave with hexane. The condensed products were filtered through a filter  
125 paper (blue ribbon) in a vacuum using a Büchner funnel. The filtration residue was sequentially  
126 extracted with hexane, diethyl ether and acetone. The extract was brought to constant weight by  
127 drying under vacuum at room temperature. Yield of extracts and solid residues were determined  
128 by the gravimetric method after solvent removal.

129

#### 130 *Oxidative fractionation of wood*

131 Catalytic delignification of wood sawdust by H<sub>2</sub>O<sub>2</sub> was carried out as in (Kuznetsov et al.  
132 2013a) using 250 cm<sup>3</sup> glass reactor equipped with mechanical stirrer, reflux condenser and  
133 thermometer. Wood sawdust (10 g) was placed to glass reactor. Then, a mixture of glacial acetic  
134 acid, hydrogen peroxide, distilled water and TiO<sub>2</sub> was added. The reaction mixture was  
135 vigorously stirred (700 rpm) at selected temperature (70–100 °C) during 1–4 h. Composition of  
136 the of reaction mixture was varied in the following range: hydrogen peroxide 3–7 wt%, acetic  
137 acid 15–40 wt%, liquid/wood ratio (LWR) –10–15. Concentration of TiO<sub>2</sub> catalyst was at 1 wt%.  
138 Commercial TiO<sub>2</sub> (GOST 9808-84) with an average particle size of about 10 microns, rutile  
139 phase composition and BET surface area 3 m<sup>2</sup> /g was used as the catalyst. When the reaction was

140 completed, the solid product was separated under vacuum using Buchner funnel, following by  
141 washing distilled water and drying at 105 °C until constant weight.

142 Such parameter as the residual lignin content in cellulosic product was used to evaluate  
143 the delignification activity of TiO<sub>2</sub> catalyst.

144 The cellulosic product yield was estimated by gravimetric method and calculated as  
145 follows:  $Y = (m/m_0) \times 100$ , where Y – yield of cellulosic product, wt%; m – weight of abs. dry  
146 cellulosic product, g; m<sub>0</sub> – weight of abs. dry wood, g.

147

## 148 **Analysis of liquid and solid products**

### 149 *Analysis of hydrolysates*

150 Individual composition and content of monosaccharides in hydrolysates obtained from  
151 hemicelluloses and cellulose were determined using a gas chromatograph “VARIAN-450 GC”  
152 with a flame ionization detector and with capillary column VF-624 ms 30 m length, inner  
153 diameter 0.32 mm. Conditions of the analysis: carrier gas helium, temperature of injector 250 °C,  
154 temperature of detector 280 °C, initial temperature of column 50 °C, temperature rise up to 180  
155 °C at a speed 10 °C/min, aging at 180 °C during 37 min. The duration of chromatographic  
156 separation of monosaccharides was 55 min. To register the release of oligosaccharides the  
157 temperature of column was raised up to 250 °C and kept 30 min. Total time of hydrolysates  
158 analysis was 92 min. Before analysis the sample of hydrolysate was subjected to derivatization  
159 with the formation of trimethylsilyl derivatives of monosaccharides using the mixture of  
160 trimethylchlorosilan and hexamethyldisilazane in pyridine medium according to [Ruiz-Matute et  
161 al. 2011). Sorbitol was used as an inner standart.

162 Impurities of furfural, 5-hydroxymethyl-furfural and levulinic acid in hydrolysates were  
163 determined by HPLC method using chromatograph “Milichrom A-02” (Econova, Novosibirsk)  
164 with scanning spectrophotometric detector UV range 190–360 nm. Column made of stainless  
165 steel (2.0×75 mm) and packed with silica gel Pronto SIL-120-5-C18 AQ with a grain size of  
166 5.0 μm was used. Temperature of the column 35 °C was kept. Mobile phase: acetonitrile and  
167 deionized water (3:97), flow rate 100 ml/min. The time of analysis 17 min. Standarts for the  
168 analysis of hydrolysates are glucose (GOST 975-88), D-xylose 142080.1208 (Panreac),  
169 D-mannose 373195.1208 (Panreac), D-sorbit (Panreac), furfural (GOST 10930-74),  
170 5-hydroxymethyl-2-furaldehyde, 99 % (Aldrich), levulinic acid, 99 % (Aldrich).

171 The liquid hydrocarbon products were analyzed by GC-MS using Agilent 7890A  
172 chromatograph fitted with an Agilent 7000A Triple Quad mass-selective detector (Agilent,  
173 United States) by recording the total ion current. The products were separated in an HP-5MS

174 capillary column (30 m in length, 0.25 mm in inner diameter) in the temperature programmed  
175 mode while raising the temperature from 40 to 250°C at a rate of 3°C/min.

176 X-ray diffraction analysis was carried out on PANalytical X'Pert Pro diffractometer using  
177 Cu-K $\alpha$  source ( $\lambda = 0,154$  nm) in the  $2\theta$  range 5–70 ° and scanning step width of 0,01 °/scan. The  
178 cellulose samples were analyzed by the powder method in cuvette with 2,5 cm diameter.  
179 Crystallinity index (CI) was calculated from the ratio of the height between the intensity of the  
180 crystalline peak and total intensity after subtraction of the background signal (Park et al. 2010):  $CI$   
181 =  $(I_{002} - I_{AM}) / (I_{002})$ , where  $I_{002}$  – is the height of the 002 peak;  $I_{AM}$  – is the height of the  
182 minimum between the 002 and the 101 peaks.

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

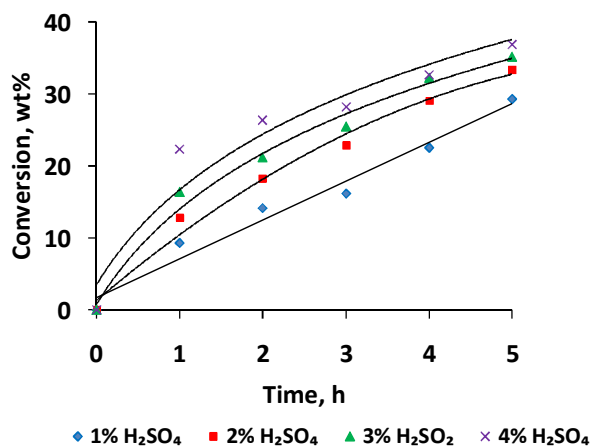
187 The content of cellulose, hemicelluloses and lignin in the products was defined by  
188 chemical methods generally accepted in wood chemistry (Sjoöstroöm and Alern 1999).

189

## 190 **Results and discussion**

### 191 *Catalytic hydrolysis of birch wood hemicelluloses*

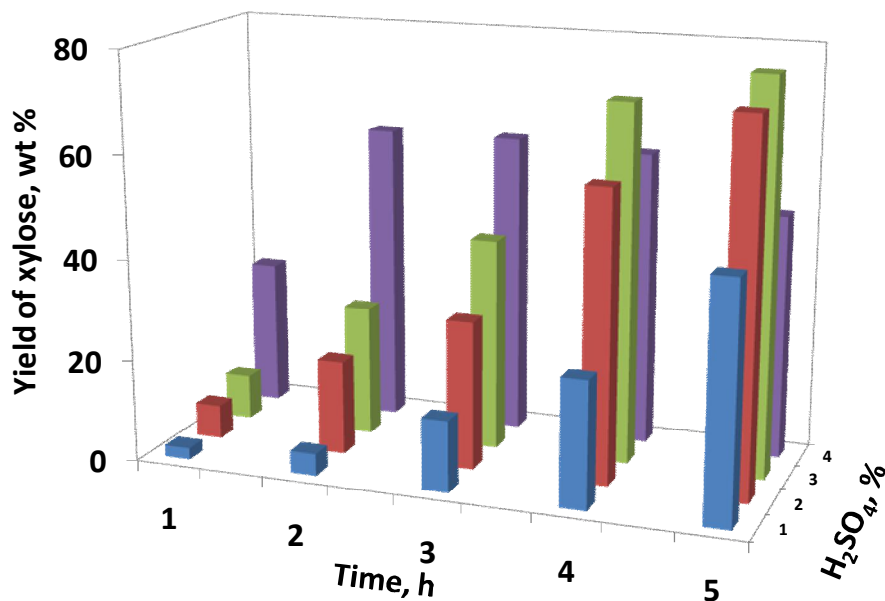
192 In order to select the conditions of hydrolysis of birch wood hemicelluloses, providing a  
193 high yield of xylose the catalytic properties of sulfuric acid and solid acid catalysts were  
194 compared. At fixed temperature 100 °C and liquid wood ratio 8 the concentration of sulfuric acid  
195 catalyst was varied between 1–4 wt% and time of hydrolysis from 1 to 5 h. It was found that the  
196 conversion of wood increases with increasing duration of hydrolysis and concentration of H<sub>2</sub>SO<sub>4</sub>  
197 catalyst (Fig. 1). Conversion of wood reaches 35.1–36.9 wt% at H<sub>2</sub>SO<sub>4</sub> concentration 3 and 4  
198 wt% and time of hydrolysis 5 h.



199

200 **Fig. 1** Impact of H<sub>2</sub>SO<sub>4</sub> catalyst concentration on the conversion of birch wood in hydrolysis at  
201 100 °C

202 The yield of xylose at temperature 100 °C is increased with the growth of H<sub>2</sub>SO<sub>4</sub>  
203 concentration and hydrolysis time reaching 77 % for 3 % H<sub>2</sub>SO<sub>4</sub> after 5 h (Fig. 2).



204

205 **Fig. 2** Influence of H<sub>2</sub>SO<sub>4</sub> concentration and time of birch wood hydrolysis at 100 °C on the  
206 yield of xylose

207

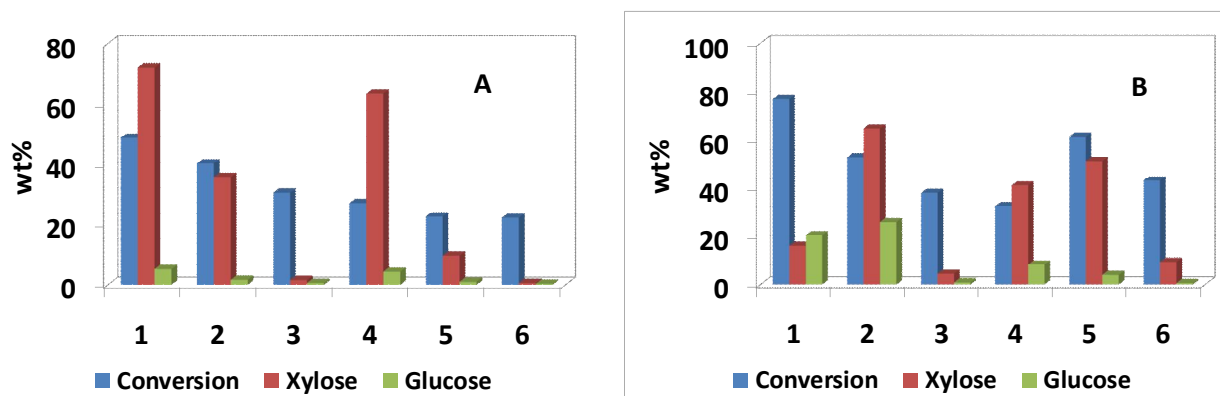
208 Catalyst 4 % H<sub>2</sub>SO<sub>4</sub> gives the high yields of xylose (58.2–59.2 wt%) after hydrolysis  
209 during 2–4 h. But the increase of hydrolysis time to 5 h reduces the yield of xylose to 48 wt%  
210 due to its further transformation into furan compounds (Taherzadeh and Karimi 2007).

211 The following sugars are also formed: mannose (0.12–3.6 wt%) and glycose  
212 (0.9–12.7 wt%) depending on wood hydrolysis conditions.

213 Solid catalysts were active in hydrolysis of beech wood hemicelluloses only at  
214 temperatures higher 100 °C. Catalytic properties of SBA-15 with –SO<sub>3</sub>H groups (S<sub>BET</sub> 417 m<sup>2</sup>/g),  
215 ZrO<sub>2</sub> with SO<sub>4</sub><sup>2-</sup> groups (S<sub>BET</sub> 110 m<sup>2</sup>/g), ion exchange resins Amberlite ® IR 120, Amberlyst ®  
216 15 dry (S<sub>BET</sub> 53 m<sup>2</sup>/g) and KU-2-8 were studied in birch wood hemicelluloses hydrolysis at 110–  
217 170 °C.

218 To ensure the effective contact between wood and solid catalyst the mixture before  
219 reaction was ground to a particle size of 0.1–0.25 mm in the mill-activator AGO-2 during 0.5 h.

220 The maximum yield of xylose (72 wt%) was obtained at 150 °C with sulphated ZrO<sub>2</sub>  
221 catalyst (Fig. 3). This yield is comparable to that obtained in the case of wood hydrolysis with  
222 3 % H<sub>2</sub>SO<sub>4</sub> catalyst at 100 °C. At temperature 170 °C the hydrolysis of cellulose also takes place  
223 with the formation of glucose.



224  
 225 **Fig. 3** Effect of solid catalysts on the conversion of birch wood and on the yield of xylose and  
 226 glucose at 150 °C (A) and at 170 °C (B) (wood/catalyst wt. ratio = 1)  
 227 1 – ZrO<sub>2</sub>/SO<sub>4</sub><sup>2-</sup>, 2 – SBA-15 with –SO<sub>3</sub>H, 3 – Amberlite ®IR120 with –SO<sub>3</sub>H, 4 - Amberlyst ®  
 228 15 dry with –SO<sub>3</sub>H, 5 – KU-2-8 with –SO<sub>3</sub>H, 6 –without catalyst  
 229

### 230 *Oxidative fractionation of birch wood*

231 The processes of organosolv delignification with environmentally safe oxidants (O<sub>2</sub>,  
 232 H<sub>2</sub>O<sub>2</sub>) (Suchy and Argyropoulos 2001) can be successfully used for wood fractionation on  
 233 cellulose and lignin for their subsequent processing to chemicals and biofuels.

234 Some complexes of the transition metals, for example polyoxometalates, can catalyze the  
 235 processes of pulp and wood delignification by oxygen (Gaspar et al. 2007). However the  
 236 application of these catalysts is complicated by their high cost and complexity of regeneration  
 237 for the reuse.

238 In oxidative delignification of wood by H<sub>2</sub>O<sub>2</sub> in acetic acid–water solvent, sulfuric acid  
 239 catalyst is used [Kuznetsov et al. 2013a). But H<sub>2</sub>SO<sub>4</sub> catalyst has such technological  
 240 disadvantages as high toxicity and corrosion activity. At elevated temperature (120–130 °c) the  
 241 more technologically convenient solid TiO<sub>2</sub> can be applied in delignification of wood by H<sub>2</sub>O<sub>2</sub>  
 242 (Kuznetsov et al 2008b). Advantages of TiO<sub>2</sub> application as delignification catalyst are stipulated  
 243 by the absence of corrosion activity and toxicity, by its availability, low cost and lack of need for  
 244 its separation from reaction products.

245 In wood delignification processes at elevated temperatures the side reactions of soluble  
 246 mass products condensation with the formation of so-called “pseudo-lignin” (Hu et al. 2012)  
 247 take place. The contribution of condensation reactions can be reduced by the acceleration of a  
 248 diffusion of lignin depolymerization products from wood particles into solution and by reduction  
 249 of delignification temperature.

250 It was shown that the use of small particles of wood, high liquid to wood ratio (LWR)  
 251 and the intensive mixing of the reaction solution allows to reduce the externally diffusion  
 252 limitations and to provide a high rate of aspen wood delignification by H<sub>2</sub>O<sub>2</sub> under mild

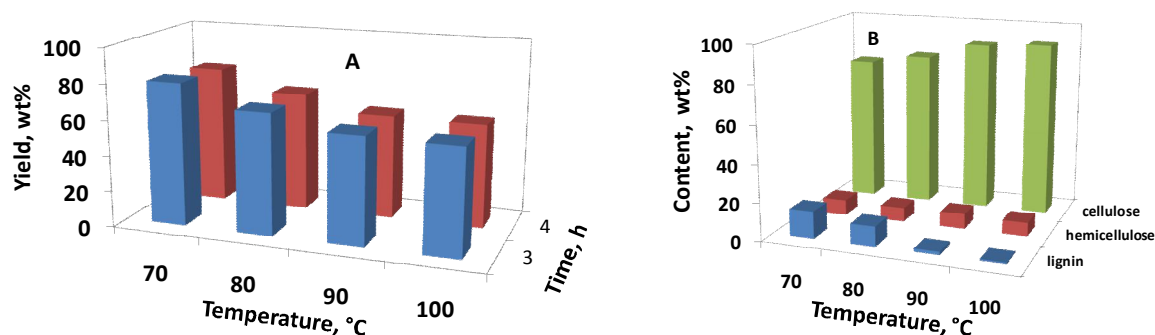


253 conditions (70–100 °C, atmospheric pressure) in the presence of 2 % H<sub>2</sub>SO<sub>4</sub> catalyst (Kuznetsov  
 254 et al 2013a).

255 The possibility of successful replacement under mild conditions the H<sub>2</sub>SO<sub>4</sub> catalyst on  
 256 non-toxic and non-corrosive solid TiO<sub>2</sub> catalyst in the oxidative fractionation of birch wood on  
 257 cellulose and soluble lignin was shown in the present paper. The optimal process conditions  
 258 providing a high yield of pure cellulose were determined.

259 To optimize the process of birch wood oxidative fractionation over mild conditions in the  
 260 presence of TiO<sub>2</sub> catalyst the influence of temperature, concentrations of hydrogen peroxide and  
 261 acetic acid, liquid/wood ratio, time on the dynamics of lignin removal from wood was studied.

262 The increase of temperature, concentrations of H<sub>2</sub>O<sub>2</sub> and CH<sub>3</sub>COOH in the reaction  
 263 mixture significantly reduces the content of residual lignin and of hemicelluloses in the cellulosic  
 264 product (Fig. 4, Table 1). But at the same time the yield of cellulosic product is decreased.



265  
 266 **Fig. 4** Effect of delignification temperature on the yield (A) and composition (B) of cellulosic  
 267 product from birch wood (CH<sub>3</sub>COOH 25 wt%, H<sub>2</sub>O<sub>2</sub> 5 wt%, TiO<sub>2</sub> 1 wt%, LWR = 10)  
 268

269 **Table 1** Effect of concentration of H<sub>2</sub>O<sub>2</sub> and CH<sub>3</sub>COOH on the yield and composition of  
 270 cellulosic product obtained from birch wood at 100 °C and time 4 h

	H <sub>2</sub> O <sub>2</sub> , wt%				CH <sub>3</sub> COOH, wt%		
	3	4	5	6	15	25	35
Yield, wt%	67.5	60.8	56.7	56.5	73.3	56.7	58.2
Composition, wt%:							
cellulose	82.1	87.8	90.7	92.3	83.7	90.7	92.3
hemicelluloses	9.8	8.2	7.5	6.7	8.8	7.5	6.9
lignin	7.8	3.7	1.5	0.7	7.2	1.5	0.5

271  
 272 The increase of temperature from 70 °C to 100 °C reduces the contents of lignin and  
 273 hemicelluloses in the cellulosic product and the yield of product.

274 Acetic acid is used in the reaction mixture to facilitate the dissolution of the products of  
 275 lignin oxidative depolymerization. When CH<sub>3</sub>COOH concentration in reaction medium is less  
 276 than 20 wt% the obtained cellulosic product has a high content of residual lignin.

277 The increase of LWR from 5 to 15 only slightly affects on the yield and composition of  
278 cellulosic product.

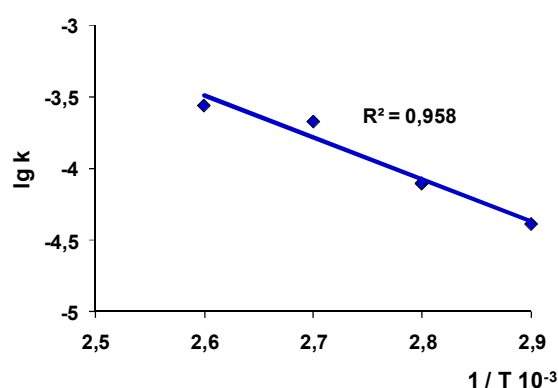
279 The kinetic study of birch wood delignification by H<sub>2</sub>O<sub>2</sub> with TiO<sub>2</sub> catalyst in the  
280 temperature range 70–100 °C was accomplished. The variation of lignin concentration in the  
281 cellulosic product was used for calculating the rate constants of delignification process. It was  
282 found that the process of oxidative delignification of birch wood by H<sub>2</sub>O<sub>2</sub> in the presence of TiO<sub>2</sub>  
283 catalyst is described satisfactory by the first order equations.

284 The calculated rate constants of birch wood oxidative delignification with catalyst TiO<sub>2</sub>  
285 are presented in Table 2.

286  
287 **Table 2** Rate constants of birch wood delignification (reaction conditions: H<sub>2</sub>O<sub>2</sub> – 5 wt%,  
288 CH<sub>3</sub>COOH – 25 wt%, catalyst TiO<sub>2</sub> – 1 wt%, LWR – 15)

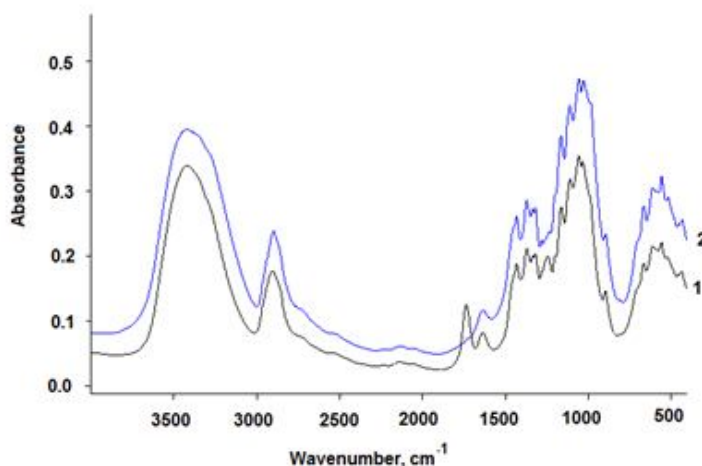
Temperature, °C	k · 10 <sup>-4</sup> , c <sup>-1</sup>
70	0.40
80	0.78
90	2.10
100	2.72

289  
290 The activation energy of birch wood oxidative delignification process was determined  
291 using temperature dependence of the rate constants in Arrhenius coordinates (Fig. 5). The rather  
292 high value of activation energy (84 kJ·mol<sup>-1</sup>) points on the absence a noticeable effect of external  
293 diffusion limitations at the used conditions of birch wood oxidative delignification with TiO<sub>2</sub>  
294 catalyst.



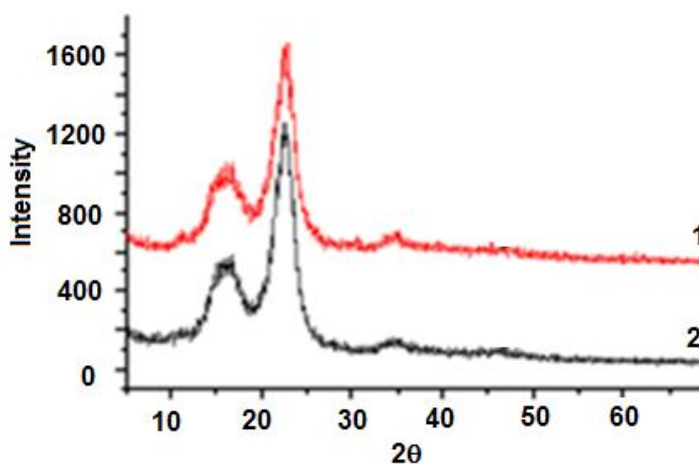
295  
296 **Fig. 5** Temperature dependence of rate constants of birch-wood delignification

297  
298 Cellulosic product obtained by oxidative fractionation of birch wood sawdust at optimal  
299 condition (100 °C, H<sub>2</sub>O<sub>2</sub> – 5 wt%, CH<sub>3</sub>COOH – 25 wt%, LWR – 15) with an yield 48.2 wt% was  
300 studied. The composition of cellulosic product (wt%): cellulose 93.7, hemicelluloses 5.5, lignin  
301 0.5. According to the FTIR and XRD data the structure of cellulose obtained at optimal  
302 conditions of birch-wood fractionation corresponds to that of commercial microcrystalline  
303 cellulose (Fig. 6, 7).



304  
305  
306  
307

**Fig. 6** FTIR spectra of cellulose from birch wood (1) and commercial microcrystalline cellulose Vivapur (2)



308  
309

310 **Fig. 7** Diffraction patterns of cellulose from birch wood (1) and commercial microcrystalline  
311 cellulose Vivapur (2)  
312

313 Crystallinity index of cellulose from birch wood, calculated from the ratio of height  
314 between the intensity of the crystalline peak and total intensity (Park et al. 2010) is equal to 0.75.  
315 According to GC-MS data the soluble products of birch wood oxidative fractionation contain  
316 only small amounts of aromatic compounds, indicating deep oxidation of phenylpropane units of  
317 lignin at studied process conditions. It is possible that the hydroxyl and peroxide radicals  
318 generated from  $H_2O_2$  on the surface of  $TiO_2$  catalyst can diffuse through the liquid reaction  
319 medium to the wood particles and to execute the oxidative destruction of lignin via homolytic  
320 mechanism.

321 Thus, the results of the study demonstrate the possibility of effective fractionation of hard  
322 wood biomass into pure cellulose and soluble products from lignin under mild conditions  
323 ( $100^\circ C$ , atmospheric pressure) in the medium " $H_2O_2-CH_3COOH-H_2O-TiO_2$  catalyst".

324 *Catalytic hydrolysis of cellulose to glucose*

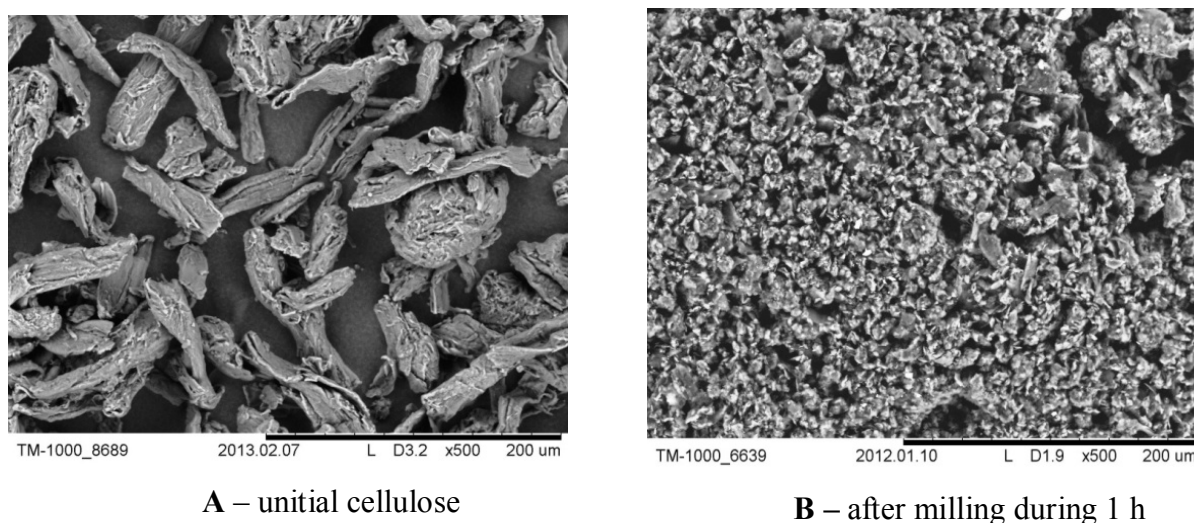
325 The glucose-containing hydrolysates for biotechnological synthesis are mainly produced  
326 in industry by high-temperature catalytic hydrolysis of wood with dilute sulfuric or hydrochloric  
327 acid (Zheng et al. 2009). The resulting hydrolysates are contaminated by products of lignin and  
328 hemicelluloses destruction, that requires time and labor consuming purification of wood  
329 hydrolysates before using.

330 The yeast used in the enzymatic synthesis of ethanol can assimilate only hexose sugars,  
331 while pentose sugars inhibit the process. It is, therefore, necessary to remove the pentosan-  
332 containing hemicelluloses from lignocellulosic biomass for increasing the ethanol yield.

333 Cellulose obtained by catalytic oxidative fractionation of wood can be used for the  
334 production of pure glucose hydrolysates for alcohols synthesis. As known from the literature  
335 [Besson et al. 2014] the solid acid catalysts are active in hydrolysis of cellulose at 150–180 °C.  
336 The used catalysts should be stable in water under elevated temperatures. In this paper the  
337 catalytic properties of mesoporous catalyst SBA-15, containing –SO<sub>3</sub>H groups were studied in  
338 the hydrolysis of cellulose at 150 °C. Texture characteristics of acid SBA-15 catalyst: surface  
339 area 370 m<sup>2</sup>/g, total volume of pores 0.2 cm<sup>3</sup>/g, average diameter of pores 2.0 nm.

340 The mechanical treatment of cellulose was used to decrease the cellulose crystallinity.  
341 Mechanical activation of cellulose in planetary mill AGO-2 during 1 h reduces the degree of its  
342 polymerization from 350 to 185 and the crystallinity index from 0.75 to 0.35. It was established  
343 by scanning microscopy that the structure of cellulose after activation becomes more  
344 homogeneous and the average particle size decreased from 60–70 μm to 10–15 μm (Fig. 8).

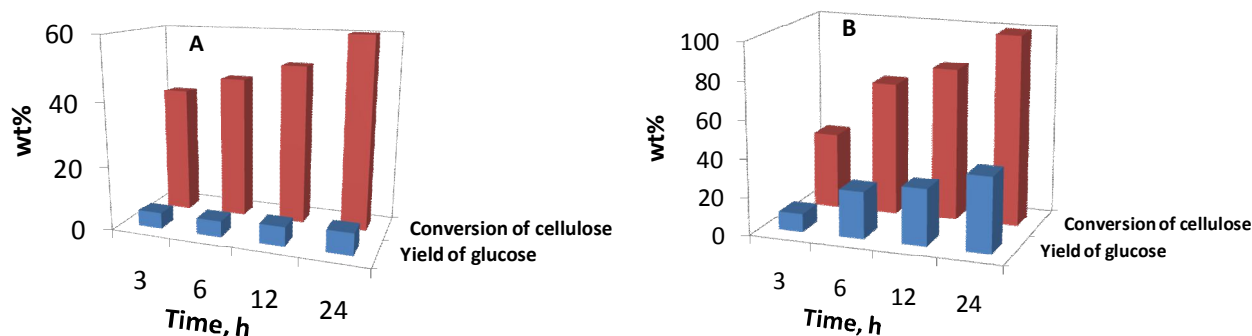
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**Fig. 8** SEM images of cellulose from birch wood (A) and cellulose after milling in planetary mill during 1 h

346

347 Cellulose in the absence of a catalyst not to be subjected to hydrolysis in water at 150 °C  
 348 during 24 h. At these conditions the conversion of cellulose is 66 wt% in the presence of acid  
 349 SBA-15 catalyst but oligosaccharides were mainly formed and the yield of glucose was only  
 350 8 wt% (Fig. 9a). The mechanical activation cellulose significantly increases its reactivity in  
 351 hydrolysis and the almost 100 % conversion of cellulose in the presence of acid SBA-15 catalyst  
 352 reaches at 150 °C and reaction time 24 h. At these conditions the yield of glucose is 42 wt%  
 353 (Fig. 9 b).



354 **Fig. 9** Impact of time of hydrolysis of cellulose from birch wood (A) and cellulose after milling  
 355 (B) on the conversion and yield of glucose in the presence of acid SBA-15 catalyst at 150 °C and  
 356 LWR 24

357  
 358 GC study of composition of hydrolysates from activated cellulose showed that the  
 359 elevated temperatures (150-170 °C) intensify the formation of furfural, 5-HMF and levulinic  
 360 acid, which inhibit the fermentation of glucose to bioethanol.

361 Concentration of toxic components in the hydrolysates for bioethanol synthesis should  
 362 not exceed (g/l): 0.5 – for furfural, 1.0 – for 5-HMF and 15.0 – for levulinic acid) (Huang et al.  
 363 2011; Zha et al.; Zha et al. 2012). In hydrolysates obtained from activated cellulose at 150 °C  
 364 with acid SBA-15 catalyst the content of these toxic components are below the permissible  
 365 values.

### 366 367 *Lignin conversion in supercritical alcohols*

368 The use of supercritical alcohols allows to raise the yield of the extractable products from  
 369 lignin (Huang et al. 2014; Ma R., Hao et al. 2014). Lower aliphatic alcohols (ethanol, butanol)  
 370 are mainly chosen for lignin depolymerization for the reason that their critical temperatures are  
 371 lower or close to the temperature range of lignin thermal destruction. In addition, bioethanol and  
 372 biobutanol are produced by hydrolysis process in which lignin is wasted. Therefore, no  
 373 additional chemicals should be used for lignin depolymerization into valuable chemicals.

374 The alcohols not only extract products of the thermal fragmentation of lignin but also can  
 375 alkylate these products, preventing repolymerization processes (Heitner et al. 2010; Kim et al.  
 376 2015).

377 In paper (Kuznetsov et al. 2015) the effects of sulfated  $ZrO_2$  and  $ZrO_2-Al_2O_3$  catalysts  
 378 and acidic zeolite catalysts with various Si/Al ratios on the thermal conversion of alkali lignin in  
 379 supercritical ethanol at 300 °C and on the composition of the resulting products have been  
 380 investigated. All of the catalysts increased lignin conversion into liquid products at 350–400 °C.  
 381 The catalysts reduced the concentration of phenol and its derivatives and increased the  
 382 concentration of ethers in the liquid products. The highest lignin conversion and a highest yield  
 383 of low-boiling liquid products were achieved at 350°C with the zeolite catalyst with Si/Al = 30,  
 384 which contains a high concentration of acid sites.

385 In the present paper the thermal conversion of acetone-lignin isolated from aspen wood  
 386 was studied in supercritical butanol in the presence of NiCuMo/SiO<sub>2</sub> catalyst. Butanol is not  
 387 converted to hydrocarbons in the absence of catalysts at temperatures 280–350 °C. But at these  
 388 conditions the catalyst NiCuMo/SiO<sub>2</sub> intensify the conversion of butanol and acetone-lignin to  
 389 hydrocarbons. Some characteristics of used catalysts are given in Table 3.

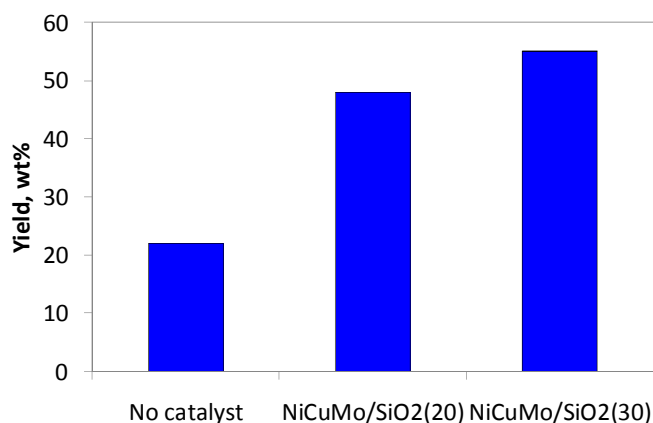
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391 **Table 3** Catalysts for conversion of acetone-lignin in supercritical butanol

Catalyst	Catalyst composition, wt%.	Specific surface area, m <sup>2</sup> /g	Pore volume, sm <sup>3</sup> /g
NiCuMo/SiO <sub>2</sub> 20	Ni – 46; Cu – 6.7; Mo – 11.7; Si – 15 (red. 500 °C)	109	0.23
NiCuMo/SiO <sub>2</sub> 30	Ni – 41; Cu – 6.0; Mo – 17.8; Si – 13.3 (red. 500 °C)	104	0.22

392 Catalysts NiCu/SiO<sub>2</sub> and NiCuMo/SiO<sub>2</sub> were developed for the process of bio-oil  
 393 hydrotreatment (Bulavchenko et al. 2010; Bykova et al. 2014). In the previous paper (Sharypov  
 394 et al. 2015) the composition of liquid products of acetone-lignin conversion over NiCu/SiO<sub>2</sub>  
 395 catalysts in supercritical butanol at 300 °C and pressure 2.4–5.0 MPa was studied by GC-MS  
 396 method. It was found that the catalysts NiCu/SiO<sub>2</sub> intensify the reactions of butanol conversion  
 397 and increase by 1.8 times the yield of hexane-soluble products. Liquid products of catalytic  
 398 conversion of acetone-lignin have a high content of esters and a reduced concentration of  
 399 methoxyphenols as compared to liquid products obtained in the absence of catalyst.

400 It was found that catalysts NiCuMo/SiO<sub>2</sub> are more active in acetone-lignin conversion  
 401 than NiCu/SiO<sub>2</sub> catalysts (Fig. 10). The best of NiCu/SiO<sub>2</sub> catalyst allows to achieve the yield of  
 402 hexane-soluble products up to 44 wt% (Sharypov et al. 2015) while catalyst NiCuMo/SiO<sub>2</sub>  
 403 containing 30 wt% of Mo – up to 55 wt%



404

405 **Fig. 10** Yield of hexane-soluble products obtained by acetone-lignin conversion in supercritical  
 406 butanol at 300 °C over NiCuMo catalysts

407

408 *Integrated processing of hard wood*

409 Perspective directions in the development of innovative technologies of wood complex  
 410 processing into valuable products are connected with a design of integrated processes which  
 411 ensure the total utilization of all main components of a biomass (Cherubini et al. 200;. de Long et  
 412 al. 2013; Dajiang et al. 2014; Xu et al. 2016).

413 In particular, an integrated catalytic processing of hard wood based on wood catalytic  
 414 oxidation with dioxygen to obtain a mixture of vanillin and syringaldehyde from lignin and  
 415 levulinic acid from cellulose (Kuznetsov et al. 2008a).

416 An integrated process for obtaining liquid biofuels from aspen wood was also reported  
 417 (Kuznetsov et al. 2013b). The process is based on the separation of a lignocellulosic feedstock  
 418 into cellulose and low-molecular weight lignin (LMWL) followed by their conversion into two  
 419 types of liquid biofuels, namely, hydrocarbon mixtures from lignin and bioethanol from  
 420 cellulose.

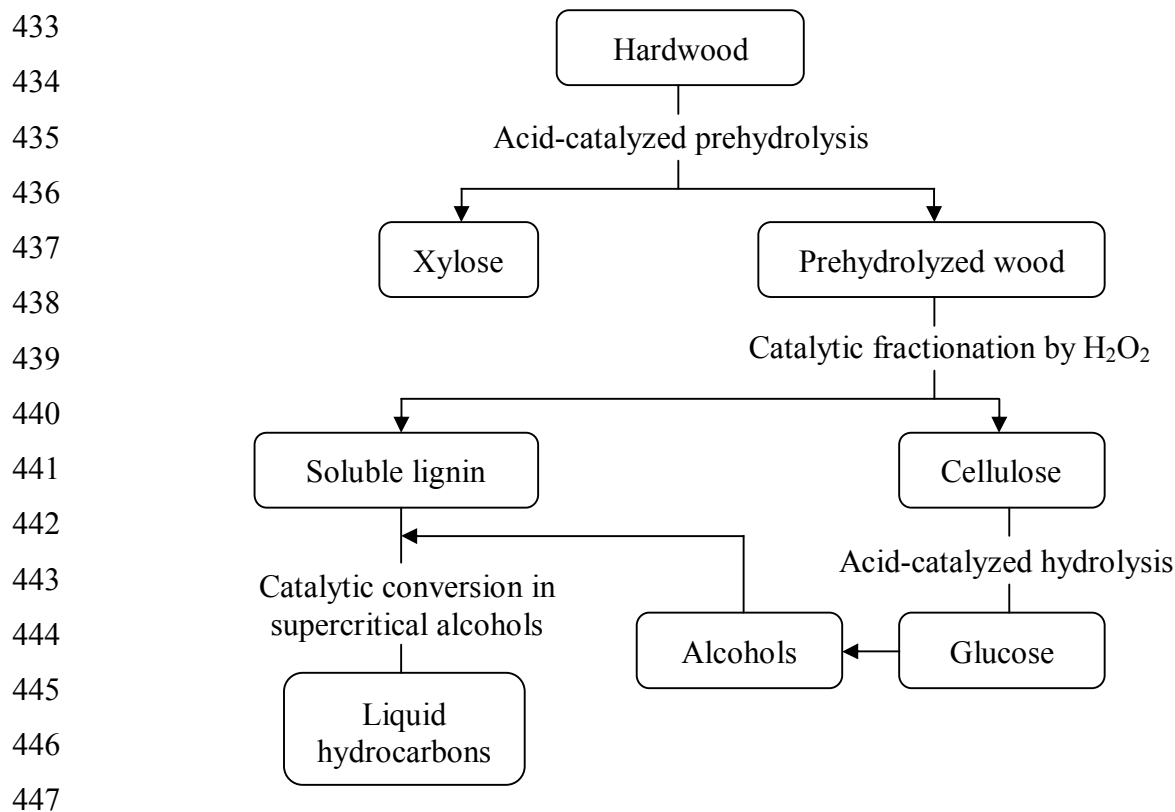
421 In this paper the conversions of main components of hardwood biomass into valuable  
 422 chemicals with the use of solid catalysts were described. The separate catalytic processes of  
 423 hemicelluloses hydrolysis to xylose, wood oxidative fractionation into cellulose and soluble  
 424 lignin, hydrolysis of cellulose to glucose for alcohols synthesis and lignin depolymerization in  
 425 supercritical alcohols to liquid hydrocarbons can be employed for the biorefinery of hard wood,  
 426 according to scheme, presented on Fig. 11.

427 Further improvement of the integrated processing of hardwood with the production of  
 428 xylose, pure cellulose, glucose, alcohols and liquid hydrocarbons needs the development of more  
 429 efficient solid catalysts for depolymerization of hemicelluloses, cellulose and lignin.

430

431

432



448 **Fig. 11** Scheme of hardwood biorefinery based on heterogeneous catalysis processes

449

450 For catalytic conversion of lignin in supercritical alcohols the solid acidic and

451 bifunctional catalysts employed in petrochemical processes can be used. Since the processes of

452 cellulose and hemicelluloses hydrolysis are carried out in aqueous media, the solid catalysts

453 should be resistant to water and its surface should have optimum hydrolytic/hydrophobic

454 properties (Toshio 2002.).

455

### 456 **Conclusion**

457 Results of the study of green valorization of main components of hardwood biomass to

458 valuable chemicals with the use solid catalysts were described in this paper.

459 To select the conditions of hydrolysis of birch wood hemicelluloses, providing a high

460 yield of xylose the properties of sulfuric acid and solid acid catalysts  $ZrO_2/SO_4^{2-}$ , SBA-15 with –

461  $SO_3H$  groups, Amberlite®IR 120, Amberlyst®15 dry, KU-2-8 were compared. The yield of

462 xylose at temperature 100 °C is increased with the growth of  $H_2SO_4$  concentration from 1 % to

463 3 % reaching 77 wt% in the case of wood hydrolysis with 3 %  $H_2SO_4$  catalyst. Solid catalysts are

464 active in hydrolysis of birch wood hemicelluloses only at temperatures higher 100 °C. The

465 maximum yield of xylose (72 wt%) is obtained at 150 °C with sulphated  $ZrO_2$  catalyst. This

466 yield is comparable to that obtained in the case of wood hydrolysis with 3 %  $H_2SO_4$  catalyst at

467 100 °C.



468 To optimize the process of birch wood oxidative fractionation over mild conditions in the  
469 presence of TiO<sub>2</sub> catalyst the influence of temperature, concentration of H<sub>2</sub>O<sub>2</sub>, CH<sub>3</sub>COOH,  
470 liquid/wood ratio and time on the dynamics of lignin removal from wood was studied. Cellulosic  
471 product obtained at optimal conditions of birch wood fractionation (100 °C, H<sub>2</sub>O<sub>2</sub> – 0.5 wt%,  
472 CH<sub>3</sub>COOH – 25 wt%, LWR – 15) with an yield 48.2 wt% contains (wt%): cellulose 93.7,  
473 hemicelluloses 5.5, lignin 0.5. The structure of birch wood cellulose corresponds to that of  
474 commercial microcrystalline cellulose. The soluble products of birch wood oxidative  
475 fractionation contain only small amounts of aromatic compounds, indicating deep oxidation of  
476 phenylpropane units of lignin at studied process conditions.

477 Cellulose obtained by catalytic oxidative fractionation of wood was used for the  
478 production of pure glucose hydrolysates for alcohols synthesis. The conversion of cellulose in  
479 hydrolysis at 150 °C during 24 h is 66 wt% in the presence of SBA-15 catalyst with –SO<sub>3</sub>H  
480 groups. But the oligosaccharides are mainly formed (yield of glucose is only 8 wt%). At these  
481 conditions the conversion of cellulose mechanically activated in planetary mill reaches the  
482 almost 100 % and the yield of glucose is 42 wt%. In hydrolysates obtained from activated  
483 cellulose at 150 °C with acid SBA-15 catalyst the content of components which inhibit the  
484 fermentation of glucose to bioethanol (furfural, 5-HMF, levulinic acid) are below the permissible  
485 values.

486 The thermal conversion of acetone-lignin isolated from aspen wood was studied in  
487 supercritical butanol in the presence of NiCuMo/SiO<sub>2</sub> catalysts. Butanol is not converted to  
488 hydrocarbons in the absence of catalysts at temperatures 280–350 °C. But the catalysts intensify  
489 the conversion of butanol and acetone-lignin to hydrocarbons at these temperatures. The best  
490 NiCuMo/SiO<sub>2</sub> catalyst which contain 30 wt% of Mo allows to achieve the yield of hexane-  
491 soluble products up to 55 wt%.

492 The studied heterogeneous catalytic processes of hemicelluloses and cellulose acid  
493 hydrolysis, wood oxidative fractionation, lignin depolymerization in supercritical alcohols can be  
494 employed for the green biorefinery of hardwood with producing of xylose, pure cellulose,  
495 glucose alcohols and liquid hydrocarbons.

496

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