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ORIGINAL ARTICLE

Fractionation of birch wood biomass into valuable chemicals by the extraction and catalytic processes

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Abstract

For the first time, the process of extraction fractionation of "hemicelluloses-free" birch wood in an ethanol medium into cellulose product and ethanol lignin is studied and optimized. The composition and structure of cellulose product and ethanol lignin obtained by extraction fractionation of "hemicellulose-free" birch wood and other products of their subsequent transformations are characterized by methods of infra-red spectroscopy, nuclear magnetic resonance, X-ray diffractometry, scanning electron microscopy, BET surface area analysis, high-performance liquid chromatography, gel permeation chromatography, gas chromatography, and chemical and elemental analysis. The possibility of producing enterosorbents from birch ethanol lignin that are more effective than the commercial enterosorbents "Polyphepan" based on hydrolyzed lignin is established. A new approach to the biorefinery of birch wood into xylose, levulinic acid and enterosorbents is proposed based on the integration of an optimized process of extraction fractionation of "hemicellulose-free" birch wood in ethanol medium, alkaline isolation of xylan and its hydrolysis to xylose, cellulose product conversion into levulinic acid and ethanol lignin processing to enterosorbents.

Keywords Birch wood · Fractionation · Extraction,•Catalytic · Xylan · Xylose · Levulinic acid · Enterosorbents · Characterization

1 Introduction

Wood is a renewable organic raw material, the processing of which into chemicals and biofuels does not affect the balance of CO_2 in the atmosphere [1]. Woody biomass contains three main components: cellulose, hemicelluloses, and lignin. The conventional chemical technologies of wood processing use mainly cellulosic component and hemicellulose and lignin remain as a waste. With this in mind, the development of new biorefinery processes that ensure the conversion of all the main components of woody biomass into valuable products is an urgent task [2–5].

Complex processing of all components of the lignocellulose biomass is achieved via its catalytic oxidative [6] and reductive [7] fractionation. The composition of wood fractionation products depends on the chemical composition of the biomass, which can be significantly different for coniferous and deciduous trees [8].

Birch is one of the most widespread deciduous trees in Russia. A feature of the chemical composition of its biomass is a high (up to 30 wt.%) content of hemicelluloses consisting mainly of xylan [9]. Xylan is used to produce xylose, xylitol, organic acids, and other valuable products [10].

Xylan is isolated from plant biomass using different methods [11–13]. One of the most efficient methods for isolating xylan from plant materials is the alkaline extraction. An alkali can destroy hydrogen bonds between cellulose and hemicelluloses and ester bonds between hemicelluloses and lignin without damage of the xylan structure [14].

A promising method of fractionation of wood biomass into holocellulose and lignin is the high-temperature extraction with aqueous-organic and organic solvents (ethanol, methanol, ethylene glycol, glycerin, acetic and formic acids) [15].

The new directions in the processing of cellulose products are related to the one-pot catalytic synthesis of valuable monomeric compounds, e.g., levulinic acid (LA). The presence in

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LA of both carbonyl and carboxyl functional groups makes it a platform chemical for the synthesis of many high-demand products [16]. LA and its derivatives are widely used in pharmaceuticals, food industry, and organic synthesis, as plant growth regulators, preservation agents, stabilizers, fragrances, etc. The LA ester additives increase the stability of plastics and improve the characteristics of motor fuels [17]. The catalytic hydrogenation of LA is used to obtain γ-valerolactone (GVL), which serves as a fuel additive, a green solvent, and a raw material to produce new polymers [18].

In contrast to technical lignins, the organosolv lignins do not contain sulfur, have a relatively low molecular weight, and they are characterized by the narrower molecular weight distribution [19, 20]. The high content of hydroxyl, phenolic, and carboxyl groups in the organosolv lignins ensures their effective interaction with functional groups of different toxins [21]. Therefore, organosolv lignins can be used to produce effective enterosorbents.

The literature describes two approaches to the fractionation of birch wood biomass into valuable chemical products [22, 23]. Both of them involve the preliminary removal of hemicelluloses from birch wood in the form of xylan or xylose. Further, the "hemicellulose-free" wood is processed into vanillin, syringe aldehyde, and cellulose by catalytic oxidation with oxygen [22] or into methoxyphenols and microcrystalline cellulose by catalytic hydrogenation with hydrogen [23].

In this paper, for the first time, it is proposed to carry out the biorefinery of birch wood using an optimized method of extraction fractionation of "hemicellulose-free" wood in an ethanol medium into cellulose product and ethanol lignin. Integration of this fractionation process and the known methods of isolation and hydrolysis of xylan, conversion of cellulose product into LA makes it possible to process in a single technological cycle all the main components of woody biomass into xylose, levulinic acid, enterosorbents with a yield and quality comparable to the corresponding products, produced by less economical methods of separate processing of birch wood.

2 Experimental

2.1 Materials and reagents

The sawdust (fraction of 1.0−2.0 mm) of birch (*Betula pendula*) harvested in the suburb of Krasnoyarsk city was used as a starting raw material. The cellulose content in the wood was determined by the Kürschner method. The lignin content was determined by hydrolysis of the sample with sulfuric acid (72 wt.%) at 20 °C for 2.5 h, with subsequent dilution of the reaction mixture with water and boiling for 1 h. The hemicellulose content was determined by hydrolysis of the wood sample with 2 wt.% of HCl at 100 °C for 3 h with the subsequent identification of monosaccharides gas chromatography. The extractives were identified by extracting wood with the alcohol−benzene mixture (1:3) in a Soxhlet extractor for 8 h. Ash was identified gravimetrically by burning the wood sample in a muffle furnace at 550 °C for 3 h.

The contents of the main components in the birch wood were 47.3 wt.% of cellulose, 28.5 wt.% of hemicelluloses, 19.0 wt.% of lignin, 4.9 wt.% of extractives, and 0.3 wt.% of ash.

The reagents used were sodium hydroxide of reagent grade (GOST 4328–77, Russia), ethyl alcohol (95%, Russia), sulfuric acid of reagent grade (GOST 4204–77, Russia), and an Amberlyst-15 solid acid catalyst (dry, Acros Organics). The solutions were prepared using distilled water (GOST 6709–72). The monosaccharides used as chromatography standards were crystalline hydrate glucose (GOST 975–88); Panreac D-xylose 142,080.1208, D-mannose 373,195.1208, and D-sorbitol and Sigma-Aldrich LA (98%).

2.2 Extraction fractionation of birch wood biomass

The scheme of extraction fractionation of birch wood into xylan, cellulose, and ethanol lignin is given in Fig. 1.

Xylan was isolated from birch wood by the alkaline extraction as described in [24]. Birch wood sawdust was pretreated by a boiling water−ethanol mixture (50:50) with a reflux condenser for 1 h at hydromodule 40 to remove fats and waxes. After the treatment, the sawdust was separated from the solution by filtration, washed with distilled water, and dried to the air-dry state at 60 °C for 24 h. Then, xylan was isolated by treatment of the deresined sawdust with a 4% aqueous solution of sodium hydroxide at room temperature at hydromodule 40 for 6 h under stirring. After that, the solution was separated from the precipitate by filtration and the precipitate was washed with distilled water until the neutral pH of washing water. The obtained lignocellulose product was dried at 60 °C for 24 h to the air-dry state.

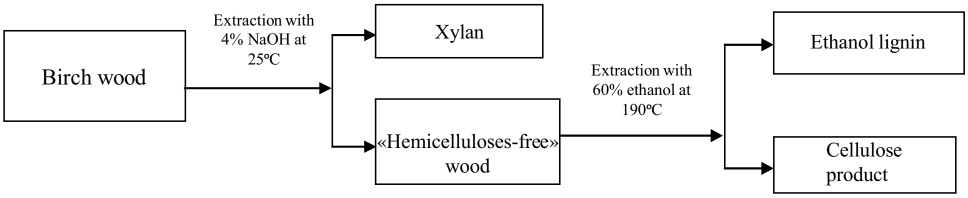


Fig. 1 Scheme of the extraction fractionation of birch wood biomass

The solution was neutralized with acetic acid and xylan was precipitated with 96% ethanol. The solution with the xylan precipitate was kept under cooling (+ 5 °C) for 24 h, then decanted, and kept again in ethanol under cooling for 24 h. Xylan was separated from the solution by centrifugation in an OHAUS Frontier 5816 centrifuge at 8000 rpm for 8 min, kept at a temperature of −18 °C for 24 h, and then dried in an Iney-6 freeze dryer to constant weight.

The fractionation of "hemicellulose-free" birch wood into soluble lignin and cellulose was performed in a ChemRe SYStem R-201 autoclave reactor (Republic of Korea). The lignocellulose sample (10 g) was added to 100 ml of 60% ethanol and the obtained mixture was loaded into a steel autoclave reactor with a volume of 300 ml. The autoclave was sealed, triply purged with argon, and heated to a specified temperature. After holding for a required time, the reactor was cooled to room temperature and the solid cellulose product was separated by filtration on a white ribbon filter and washed with 60% ethanol before discoloration of the washing solution [25]. The cellulose precipitate was dried at a temperature of 105 °C to a constant weight.

The filtrate was combined with a flushing water and cooled in a refrigerator to 13 °C. Ethanol lignin was precipitated from the solution by fivefold dilution with distilled water at + 4 °C. After aging in the refrigerator for 24 h, ethanol lignin was separated from the solution by centrifugation at 8000 rpm for 8 min, kept at a temperature of −18 °C for 24 h, and dried to a constant weight in the freeze dryer.

2.3 Conversion of cellulose product to levulinic acid

Levulinic acid was obtained by hydrolysis of cellulose product isolated from "hemicellulose-free" birch wood using a rotary steel autoclave (a rotation rate of 11 rpm) equipped with an internal fluoroplastic 35 ml tube. Cellulose (0.25 g) was placed in a tube, then 10 ml of 5% H_2SO_4 was added and the hydrolysis was carried out at temperatures of 180 and 200 °C for 2, 3, and 4 h. The obtained hydrolysate was analyzed for the LA content using a high-performance liquid chromatography (HPLC). Before performing the analysis, the hydrolysate was neutralized with sodium carbonate to pH 5 and extracted with ethyl acetate. The LA content in the ethyl acetate solution was calculated using the calibration curve.

2.4 Hydrolysis of xylan

Hydrolysis of xylan was carried out at temperatures of 110, 130, and 150 °C in a steel rotary autoclave (a rotation rate 11 rpm) equipped with an internal fluoroplastic 35 ml tube. The catalysts used were 0.1 M H_2SO_4 and an Amberlyst-15 solid acid. Xylan (0.075 g) was placed in a tube, then 15 ml of 0.1 M H_2SO_4 was added. The hydrolysis was carried out at temperatures 110 °C, 130 °C, and 150 °C with varying duration from 1 to 12 h. When using the solid catalyst, a mixture of xylan (0.075 g) and the catalyst (0.075 g) was placed in a tube, then 15 ml of distilled water was added. The hydrolysis temperature and time ranged within the same limits as in a case of 0.1 M H_2SO_4 catalyst.

After the specified time, the tube was cooled and the hydrolysate was filtered on a Büchner funnel with a paper filter under vacuum. The solid catalyst was washed with distilled water and dried in an oven at 105 °C and the xylose and furfural contents in the hydrolysate were analyzed.

2.5 Preparation of enterosorbents from ethanol lignin

Enterosorbents were obtained by treating ethanol lignin (10 g) with the 0.4% $NaHCO_3$ solution at room temperature or with water at 95 °C for 30 min at hydromodule 20 [26]. After that, the solid precipitate was separated from the solution by filtration on a Büchner funnel with a blue ribbon paper filter and purified from low-molecular-weight substances using the MF-505–46 MFPI cellophane dialysis bags (US) with a pore size of 0.1 μm. The dialysis time was 8 h; water in the dialysis bag was periodically changed. Then, ethanol lignin was separated from the solution by centrifugation at 8000 rpm for 8 min, kept at a temperature of −18 °C for 24 h, and dried to a constant weight in a freeze dryer.

2.6 Biorefinery of birch wood into xylose, levulinic acid and enterosorbents

The scheme of biorefinery of birch wood into xylose, levulinic acid, and enterosorbents integrates the processes of xylan extraction isolation by birch wood treatment at 25 °C with 4 % NaOH of "hemicellulose-free" wood extraction fractionation with ethanol at 90 °C into cellulose product and ethanol lignin, xylan catalytic hydrolysis to xylose over solid Amberlyst-15 catalyst at 130 °C, cellulose product conversion to levulinic acid over of 5 % H_2SO_4 catalyst at 180 °C and ethanol lignin processing to enterosorbents (Fig. 2).

2.7 Analysis of the products

FTIR spectra were recorded using the Bruker Tensor 27 IR Fourier spectrometer (Germany) in the range of 4000–400 cm^{-1}. The spectral data were processed using the OPUS spectroscopy software, version 5.0. To record FTIR spectra, the pressed tablets containing 4 mg of the sample in a potassium bromide matrix were prepared.

Nuclear magnetic resonance (NMR) spectra were recorded using the Bruker AVANCE III 600 MHz spectrometer at

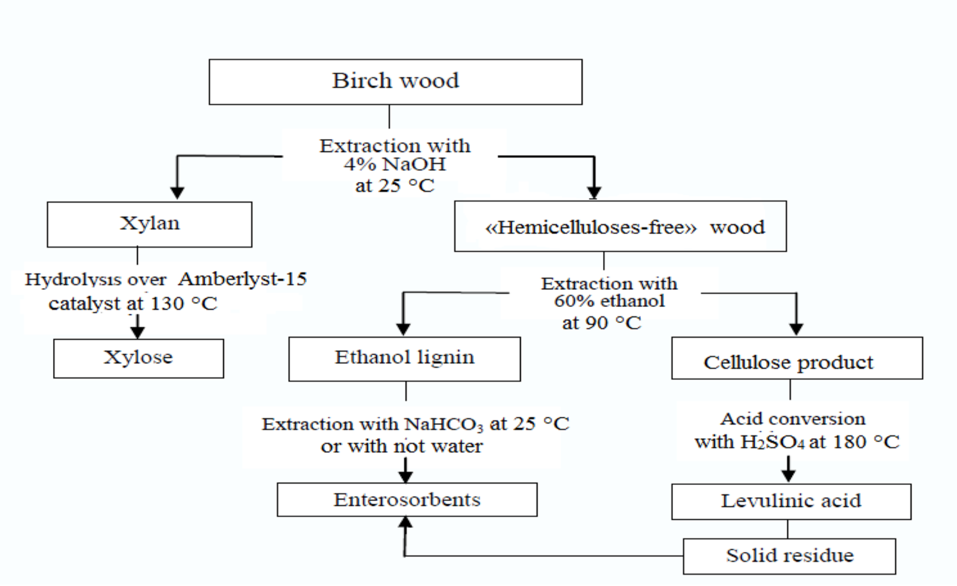


Fig. 2 Biorefinery of birch wood based on the integration of extraction and catalytic fractionation processes

25 °C. The 2D NMR spectrum of xylan dissolved in DMSO-d_6 was recorded on 128 slices for 32 scans with a relaxation delay of 15 s using a variant of the spectral editing technique (hsqcedgp). To obtain the ^{31}P-NMR spectra, ethanol lignin (0.01 g) was dissolved in a mixture of deuterated DMF/pyridine solvents (1:1 v/v). The cyclohexanol was used as a standard. The lignin sample was phosphorylated with 2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxophosphalane.

X-ray diffraction (XRD) patterns of the solid samples were obtained using the PANalytical X'Pert Pro diffractometer (CuKα radiation, $\lambda = 0.154$ nm). The patterns were recorded at the 2θ angles ranging from 10 to 50° with a step of 0.01° in a cell 2.5 cm in diameter.

The surface morphology of the solid samples was studied using the Hitachi TM-1000 scanning electron microscope (Japan) equipped with a SwiftED3000 energy dispersive analyzer (Oxford Instruments Analytical Ltd) at an accelerating voltage of 15 kV and a resolution of 30 µm.

The elemental composition of the samples was determined using the Vario El Cube ELEMENTAR analyzer (Germany).

Weight-average molecular weight M_w, number-average molecular weight M_n, and polydispersity (PD) of the ethanol lignin samples were determined by gel permeation chromatography (GPC) using the Agilent 1260 Infinity II Multi-Detector GPC/SEC system with triple detection (refractometer RI, viscometer VS, and light scattering LS). The separation was made on a PLgel Mixed-E column with tetrahydrofuran (THF) stabilized with 250 ppm butyl hydroxytoluene (BHT) as an eluent. The column was calibrated using the polydisperse polystyrene standards (Agilent, USA). The eluent flow rate was 1 ml/min and the injected sample volume was 100 µl. Before the analysis, the samples were dissolved in THF (5 mg/ml) and filtered through a 0.45-µm Millipore PES membrane filter. The data collection and processing were performed using the Agilent GPC/SEC MDS software.

The texture characteristics of the samples were determined from the nitrogen adsorption and desorption isotherms measured at −196 °C under relative pressures P/P_0 from 0.005 to 0.995 using the Micromeritics ASAP 2020 adsorption automatic analyzer (USA). Before the measurements, the samples were degassed at a temperature of 80 °C for 24 h under vacuum. The porous structure of the samples was characterized by the Brunauer–Emmett–Teller (BET) specific surface area (S_{BET}) determined from the absorption branch of the isotherm and by the total pore volume (V_{tot}) calculated from the sorbed nitrogen volume at a relative pressure of $P/P_0 \geq 0.995$.

The individual composition and content of monosaccharides were determined using the VARIAN-450 gas chromatograph with a flame ionization detector and with VF-624 ms capillary column with a length of 30 m and an inner diameter of 0.32 mm. The monosaccharides were preliminarily derivatized with the formation of trimethylsilyl derivatives using the procedure [27].

3 Results and discussion

Although the separate methods of birch wood processing to produce xylan, xylose, levulinic acid, and organosolv lignin are well known, the possibility of integrating these methods in a single technological cycle in order to utilize all the main components of wood biomass and to reduce the cost of target products is studied for the first time.

It can also be expected that the yield, composition, and structure of products obtained from wood using an integrated process may differ from those produced by separate methods.

3.1 Extraction fractionation of birch wood biomass into xylan and lignocellulose

Xylan is isolated from plant biomass using different methods [11–13]. Alkaline hydrolysis was reported to be advantageous over acid hydrolysis or autohydrolysis (steam explosion) to extract long chain hemicelluloses [28]. Alkaline hydrolysis at low temperature allows to produce the high molecular weight hemicelluloses. High temperatures (100–240 °C) and pressures under steam explosion conditions lead to the dissolution of hemicelluloses and partly of lignin [29]. Besides, at temperatures above 200 °C, cellulose decomposes to form cellooligosaccharides, glucose, 5-hydroxymethylfurfural, etc. [30].

The method employed in this work makes it possible to obtain pharmaceutical grade xylan with a high yield at a low temperature using an available and cheap reagent NaOH [24].

The yield and composition of xylanes isolated from various types of plant raw materials may vary. The yield of xylan extracted under the same conditions from Acacia sawdust [31] was 23.5 wt.%, from sugarcane bagasse [32] — 19.6 wt.%, and from eucalyptus [33] — 16.1 wt.%.

The yield and composition of the isolated xylans can also vary in the case of birch trees of different species.

In this study, the *Betula pendula* birch wood was fractionated into xylan and the lignocellulose product under the optimal extraction conditions established in [24]: the NaOH concentration 4 wt.%, the process temperature 100 °C, and the process time was 1 h. Using the alkaline extraction of *Betula pendula* wood and the subsequent precipitation with ethanol, the xylan was isolated with a yield of 23% on the weight of absolutely dry wood (82.4% on the wood hemicelluloses weight) and the cellulose product with a yield of 67.5% on the weight of absolutely dry wood. Under the same conditions, the yield of xylane from *Betula pubescens* wood was 19.6 wt.% [24].

The sample of xylan isolated from *Betula pendula* wood by the alkaline extraction was characterized by the elemental analysis, FTIR, 2D NMR, and XRD methods.

The FTIR spectrum of xylan (Fig. 3) is similar to the spectrum of commercial birch wood xylan [33]. The absorption band at 1044 cm^{-1} corresponds to the stretching vibrations of the C–C bond, at 1166 cm^{-1} – to the stretching vibrations of the C – O – C bond between xylopyranose units, at 1579 and 1410 cm^{-1} – to symmetric vibrations of the –COO group of glucuronic acid, at 3427 cm^{-1} – to stretching vibrations of the xylan O–H groups involved in hydrogen bonds, at 2927 cm^{-1} – to the C–H stretching vibrations. The absorption band at 895 cm^{-1} proves β-configuration of the glycosidic bond 1 → 4 between the xylopyranose units of the main chain of xylan.

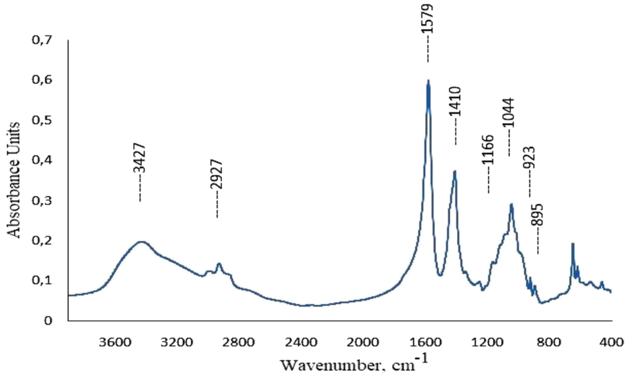
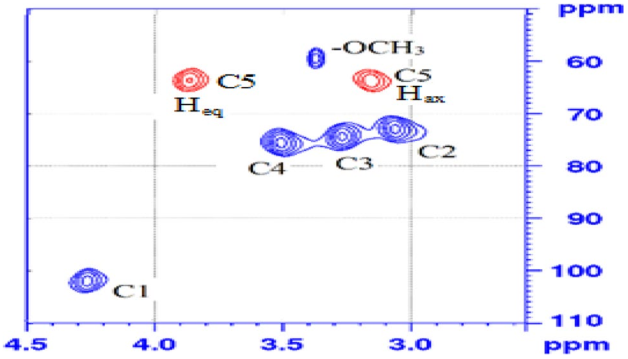


Fig. 3 FTIR spectrum of xylan isolated from birch wood



Heq - equatorial hydrogen atom at C5
Hax - axial hydrogen atom at C5

Fig. 4 2D NMR spectrum of xylan isolated from birch wood

The 2D NMR spectrum of birch wood xylan (Fig. 4) contains cross peaks characteristic of (1 → 4) -β-D- xylopyranose and it is similar to the spectrum presented in [33]. The presence of methyl group of 4-O-methyl-D- glucuronic acid is indicated by signals at 58.6/3.35 ppm.

As was shown in [34], xylan with a low content of uronic acid units and acetyl groups tend to form crystal structures. The XRD pattern of xylan isolated from birch wood by the alkaline extraction contains several small peaks indicative of a partially crystalline state of this biopolymer (Fig. 5).

The elemental composition of isolated xylan (Table 1) is similar to the composition of commercial xylan with a purity of > 99% described in [33].

The high oxygen content and O/C atomic ratio in isolated xylan as compared to that in commercial xylan are due to the

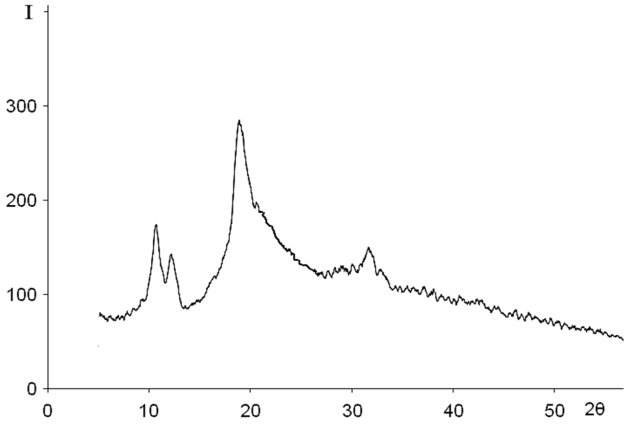


Fig. 5 X-ray diffraction patterns of the xylan isolated from birch wood

Table 1 Elemental composition of the xylan samples

Sample	Composition, wt.%			H/C	O/C
	C	H	O (in difference)		
Isolated xylan	39.14	5.88	54.98	1.80	1.05
Commercial xylan	40.68	6.68	52.65	1.98	0.97

presence of D-glucuronopyranose in the side chains of this biopolymer, which is consistent with FTIR and 2D NMR data (Figs. 3, 4).

3.2 Extraction fractionation of "hemicellulose-free" birch wood on cellulose product and ethanol lignin

Extraction of lignocellulose biomass with organic solvents is widely used for the isolation of organosolv lignins [35, 36]. The resulting organosolv lignins do not contain sulfur and have a higher reactivity compared to traditional technical lignins.

In the present study, the extraction fractionation of the "hemicellulose-free" birch wood (lignocellulose) into cellulose and soluble ethanol lignin was carried out in a water–ethanol medium. The effect of temperature and time of the fractionation process on the yield of ethanol lignin and the yield and composition of the cellulose product was examined (Figs. 6, 7).

As the extraction process time varies from 3 to 5 h, the ethanol lignin yield increases from 9.9 to 13.7 wt.% at a temperature of 150 °C and from 15.8 to 16.8 wt.% at a temperature of 190 °C. The highest yield of ethanol lignin (17.1 wt.%) was observed at 210 °C and an extraction time of 3 h. Further increase in the time of extraction at 210 °C decreases the yield of ethanol lignin (Fig. 6).

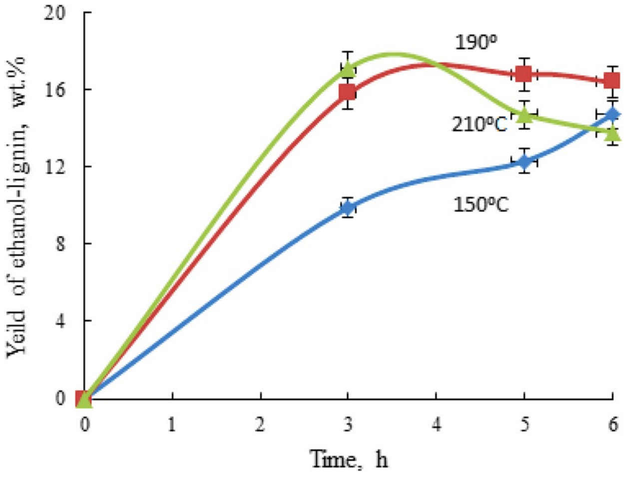


Fig. 6 Effect of birch lignocellulose fractionation temperature and time on ethanol lignin yield

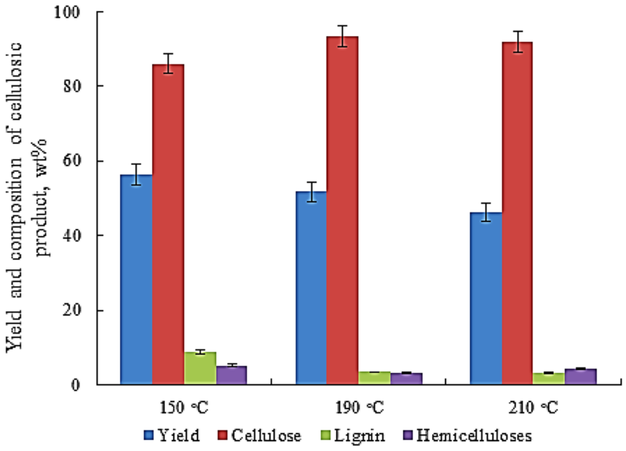


Fig. 7 Effect of birch lignocellulose fractionation temperature on cellulose product yield and composition (extraction time 5 h)

The cellulose product with the highest cellulose content (93.3 wt.%) and low content of residual lignin (3.4 wt.%) was obtained at an extraction temperature of 190 °C and a time of 4 h. At an extraction temperature of 210 °C the highest yield of ethanol lignin was obtained, but the cellulose content in the cellulose product decreased to 92.0 wt.%.

To establish the optimal conditions of the process of lignocellulose extraction fractionation providing the high yields of both the cellulose product with a low residual lignin content and the soluble ethanol lignin, the process was mathematically optimized using the Statgraphics software package [37].

The factors chosen as independent parameters were extraction temperature X_1 (°C) and extraction time X_2 (h). The output parameters chosen for the optimization were cellulose yield Y_1 (wt.%), ethanol lignin yield Y_2 (wt.%), and residual lignin content Y_3 in the cellulose product (wt.%). The constant parameters were hydromodule 10 and the ethanol:water ratio 60:40.

The optimization was made using the generalized parameter W_a calculated as in [37].

Data on the conditions and results of experiments for calculating the generalized optimization parameter are presented in Table 2. The yields of cellulose and lignin are both very important parameters, so the value of their weights δ is 1. The content lignin in the cellulose is the less important and the value of its weight δ is 0.5.

Analysis of variances showed that the factor X_1 (temperature) contributes significantly to the generalized parameter of optimizations. This is indicated by the high values of dispersion ratios in lines A and AA. The influence of the source of variance on the output parameter is considered statistically significant if the P-Value level is less than 0.05. This condition is also satisfied for factors B and AB (Table 3).

After the mathematical processing, the following regression equation was obtained:

$$Wa = -9.979 + 0.096 \bullet X_1 + 0.585 \bullet X_2 - 0.002 \bullet X_1 \bullet X_2 - 0.019 \bullet {X_2}^2$$

The regression equations can be used as a mathematical model for the extraction fractionation of lignocellulose with a water-ethanol mixture.

The predictive properties of the resulting equation are clearly demonstrated in Fig. 8, which compares the experimental values of the output parameter Wa (observed) with the values predicted by the model (predicted). The straight line corresponds to the calculated (predicted) values of Wa, the dots correspond to the experimental results. The rather high value of calculated coefficient of determination (R2 = 97.3%) indicates a good approximation quality of the regression equation.

Figure 9 shows the dependence of the output parameter Wa on the variable factors X_1 and X_2 in the form of a response surface.

The non-linear dependence of Wa on the process temperature (the optimum value of Wa is observed at a temperature of 190 °C) indicates that with a further increase in the temperature, the side reactions of depolymerization of both cellulose and lignin increase. It leads to a decrease in their yield. The calculated optimal parameters of the process of birch lignocellulose fractionation are the following: temperature 190 °C, time 5.2 h, hydromodule 10 and ethanol:water ratio 60:40. At these process conditions, the yields of cellulose product and ethanol lignin are 52.3 wt.% and 15.6 wt.%, respectively. The cellulose product contains 93.3 wt.% of cellulose.

Table 2 Matrix for optimizing the extraction fractionation of birch lignocellulose and the results of its application

T°C (X_1)	t, h (X_2)	Yield of cellulose (Y_1)	Yield of lignin (Y_2)	Content of lignin in the cellulose(Y_3)	d_1	d_2	d_3	Wa
150	3.0	60.0	9.9	12.0	0.0556	0.0125	0.4427	0.1158
150	4,5	56.8	11.9	8,0	0.2556	0.2625	0.4727	0.3018
150	6.0	55.3	13.7	5.4	0.3167	0.4625	0.6909	0.4499
180	3.0	52.0	14,7	4.1	0.5000	0.6375	0.8091	0.6168
180	4,5	51.8	16.3	3.2	0.5111	0.8500	0.8909	0.8391
180	6.0	50.8	16.0	3.1	0.5667	0.7500	0.9000	0.7606
210	3.0	47.4	17.1	3.0	0.7556	0.8875	0.9091	0.7267
210	4,5	45.0	14.5	3.1	0.8889	0.5625	0.9000	0.7067
210	6.0	44.2	12.3	3.4	0.9333	0.2875	0.8727	0.6629
$Y^{(-)}$		61	10	13				
$Y^{(+)}$		43	18	2				
δ		1	1	0.5				

Table 3 Analysis of variance for the generalized parameter Wa

Source	Sum of squares	DF	Mean square	F-Ratio	P-Value
A: Temperature (X_1)	0.251658	1	0.251658	**92.77**	**0.0024**
B: Time (X_2)	0.028579	1	0.028579	10.54	0.0476
AA	0.119919	1	0.119919	**44.20**	**0.0069**
AB	0.039581	1	0.039581	14.59	0.0316
BB	0.007300	1	0.007300	2.69	0.1994

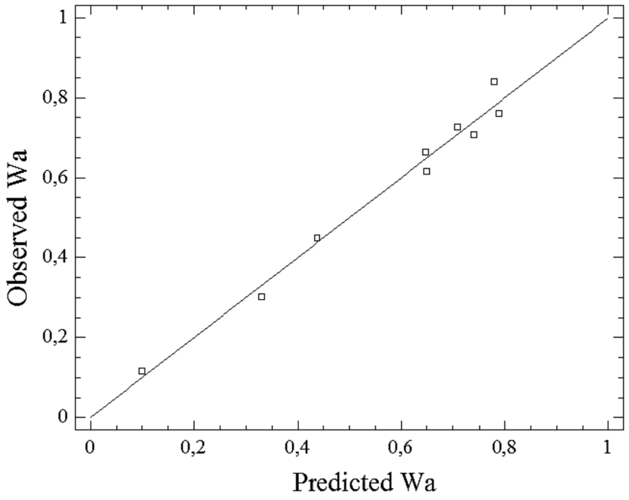


Fig. 8 Graph of comparison of the experimental values of the observed output parameter Wa, with the values predicted by the mathematical model

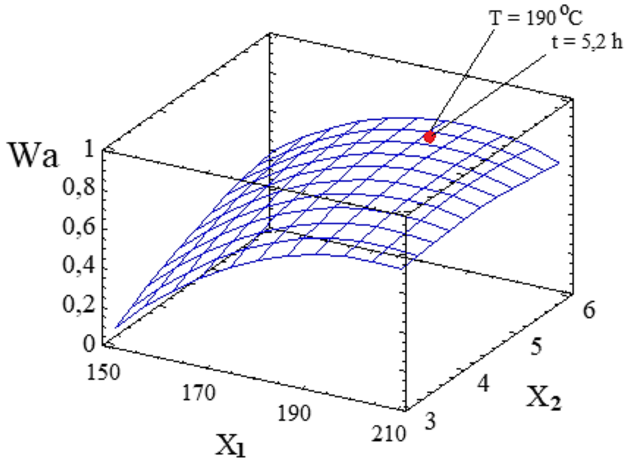


Fig. 9 Response surface of generalized parameter *Wa* for the optimization of the process of extractive fractionation of birch lignocellulose by ethanol–water mixture. X_1 is the extraction temperature and X_2 is the extraction time

3.3 Characterization of cellulose product and ethanol lignin isolated by ethanol from "hemicellulose-free" birch wood

In the present work, the composition and structure of cellulose product and ethanol lignin isolated from "hemicellulose-free" birch wood by ethanol at 190 °C were studied for the first time.

According to chemical analysis data, the isolated cellulose product contains 93.3 wt.% of cellulose, 4.2 wt.% of hemicellulose, and 3.4 wt.% of lignin.

The FTIR spectrum of the cellulose sample is characteristic of the structure of cellulose I [38]. The spectrum contains neither absorption bands in the range of 1700−1740 cm^{-1} corresponding to acetyl or uronic ether groups of hemicelluloses, nor absorption bands corresponding to phenylpropane structural units of lignin (1605−1593, 1515−1495, and 1470−1460 cm^{-1}). That confirms the removal of these biopolymers during the extraction fractionation of birch wood (Fig. 10).

The XRD pattern of cellulose product (Fig. 11) contains maxima at 2θ angles of 15.2°, 16.2°, 22.5°, and 34.6° corresponding to the reflections from the 110, 101, 002, and 040 crystal planes characteristic of the structural modification of cellulose I [39]. The crystallinity index calculated from the formula presented in [40] is 0.68. The average cellulose crystallite size calculated using the Scherrer equation [40] is 2.3 nm.

The cellulose morphology was characterized by scanning electron microscopy (SEM). It can be seen in the electron microscopy image shown in Fig. 12 that cellulose consists of short loose fibers with numerous kinks and tears.

The presence of short defect fibers complicates the use of cellulose product isolated from birch wood by the extraction fractionation in the conventional processes of fibrous cellulose materials production. However, this cellulose can be chemically converted into valuable monomeric compounds: glucose, levulinic acid, 5-hydroxymethylfurfural, ethanol, and others.

Ethanol lignin isolated by the extraction fractionation of birch wood at 190 °C for 5 h is a light-brown fine powder with a density of 1.42 g/cm^3. The molecular weight distribution (MWD) of birch ethanol lignin was established using GPC method (Fig. 13).

The ethanol lignin MWD curve contains a broad (main) peak and a small shoulder. The analysis of the MWD curve showed that most of the molecular weight of ethanol lignin does not exceed 5000 g/mol and the high molecular weight substances are almost absent.

The isolated birch ethanol lignin has a number-average molecular weight (M_n) of 750 g/mol, weight-average molecular weight (M_w) of 1625 Da and polydispersity index (PDI) of 2.17.

Some characteristics of the porous structure of birch ethanol lignin were determined by the BET analysis.

The nitrogen adsorption−desorption isotherm observed for the ethanol lignin sample (Fig. 14) corresponds to the type-IV isotherm [41] which is typical for the meso-macroporous materials. The narrow hysteresis loop is indicative of a narrow pore size distribution in the ethanol lignin sample.

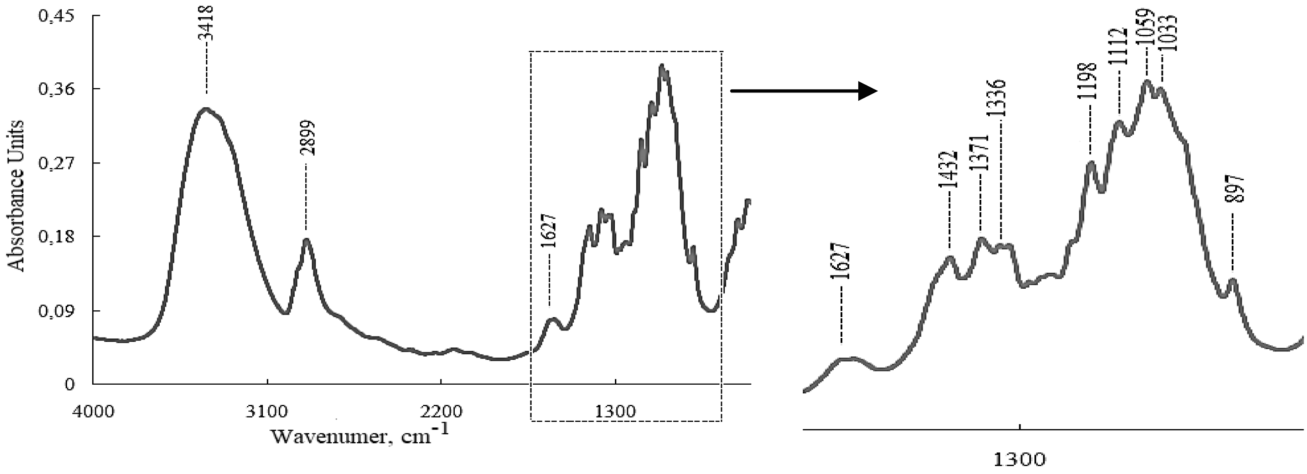


Fig. 10 FTIR spectrum of cellulose product obtained by extraction fractionation of “hemicellulose-free” birch wood

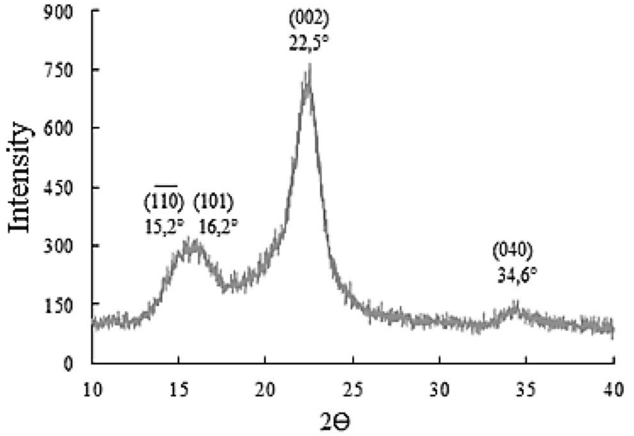


Fig. 11 X-ray diffraction patterns of cellulose product isolated from “hemicellulose-free” birch wood

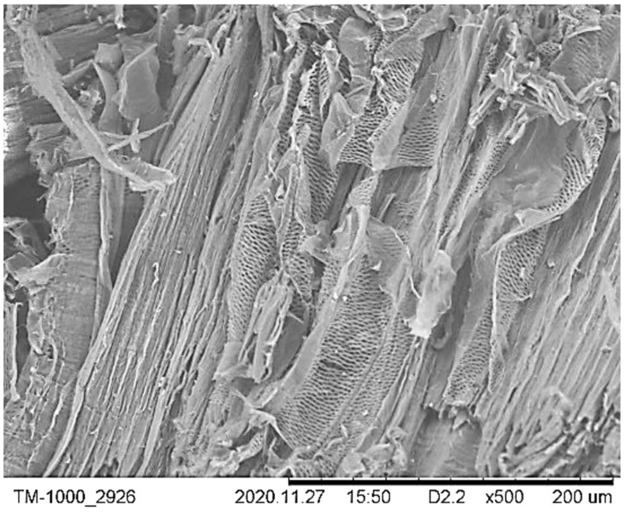


Fig. 12 Scanning electron microscopy image of the cellulose product isolated from “hemicellulose-free” birch wood

The BET specific surface area of the birch ethanol lignin sample is 42 m^2/g, the total pore volume is 0.12 cm^3/g, and the average pore diameter is 3.2 nm.

The FTIR spectrum of birch ethanol lignin (Fig. 15) includes absorption bands typical for the guaiacyl–syringyl type of lignin [42]. A broad band with a maximum at 3457 cm^{-1} corresponds to stretching vibrations of–OH groups involved in the intermolecular hydrogen bonds. The absorption bands at 2936 and 2844 cm^{-1} correspond to the asymmetric and symmetric stretching vibrations of C–H bonds in methyl groups. The band at 1710 cm^{-1} corresponds to carboxyl groups. Skeletal vibrations of the aromatic ring are reflected in the absorption bands at 1593, 1512, 1461, and 1422 cm^{-1} [43]. The absorption band at 1123 cm^{-1} can be attributed to bending vibrations of the C–H bond in the aromatic ring and to stretching vibrations of the C–O bond in secondary alcohols. Stretching vibrations of the C–O bond in primary alcohols manifest themselves in the absorption band at 1034 cm^{-1}. The band at 834 cm^{-1} corresponds to bending vibrations of C–H bonds in positions 2 and 6 of the syringyl ring.

Hydroxyl functional groups in ethanol lignin were identified by the ^{31}P-NMR method (Fig. 16). The phosphorylating agent 2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane (TMDP) was used for derivatization. The cyclohexanol was used as an internal standard.

Table 4 gives the integration regions used to determine signals and the content of hydroxyl groups in ethanol lignin calculated as in [44, 45].

The data obtained show that the content of different hydroxyl groups in ethanol lignin increases in the sequence carboxylic $<$ aliphatic $<$ phenolic.

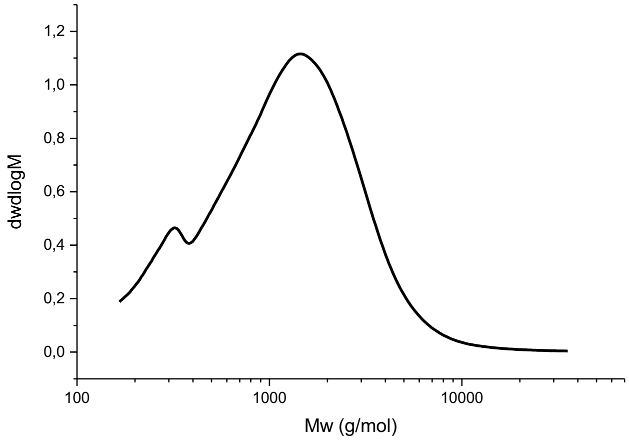


Fig. 13 Molecular weight distribution of ethanol lignin isolated from "hemicellulose-free" birch wood

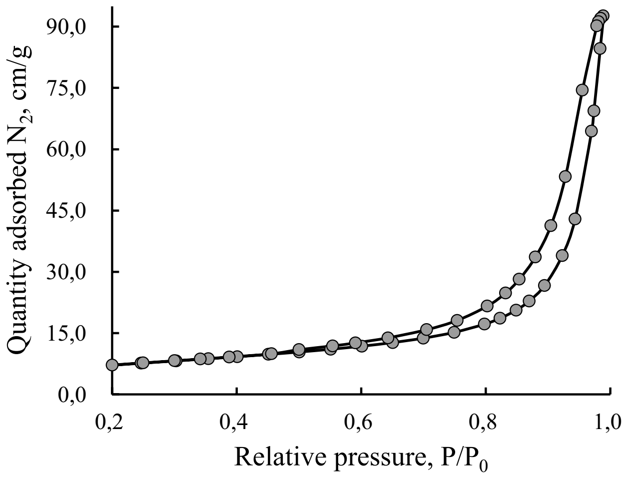


Fig. 14 Nitrogen adsorption−desorption isotherm observed for the sample of ethanol lignin

3.4 Extraction-catalytic fractionation of birch wood biomass into xylose, levulinic acid, and enterosorbents

We proposed to convert the products of birch wood extraction fractionation (xylan, cellulose product and ethanol lignin) into xylose, levulinic acid (LA), and enterosorbents using the known catalytic and extraction processes. The integration of the processes of extraction isolation of xylan, cellulose product, ethanol lignin and their subsequent conversion into xylose, LA, and enterosorbents ensures the complex processing (biorefinery) of birch wood according to the scheme shown in Fig. 2.

According to a proposed scheme birch wood biorefinery, the xylose is obtained by acid hydrolysis of xylan; LA — by the acidic transformation of cellulose product and enterosorbents — by treatment of ethanol lignin with a NaHCO$_3$ solution or hot water.

3.5 Hydrolysis of birch xylan

Xylose is used as a substitute for citric acid, to produce xylitol, furfurol, trioxyglutaric acid, feed additives. Xylose is produced by acid-catalyzed hydrolysis of xylane [46–48].

Earlier, it was proposed to carry out the hydrolysis of arabinogalactan in the presence of acid catalysts 0.1 M H$_2$SO$_4$ and Amberlyst-15 [49]. Using a sulfuric acid catalyst, a high yield of monosaccharides was obtained at a temperature of 130 °C for 1.5 h. In the presence of a solid acid catalyst Amberlyst-15, the complete hydrolysis of arabinogalactan was observed at a temperature of 150 °C and a process time of 4 h.

In this study, the activity of these catalysts was compared in the hydrolysis of xylan isolated from birch wood. To select the optimal of conditions xylan hydrolysis that ensure high yield of xylose the process temperature and time were varied (Fig. 17).

The catalytic hydrolysis of xylan in the presence of sulfuric acid catalyst gives a xylose yield 70 wt.% at a temperature of 110 °C and time of 4 h. (Fig. 17A).

Further increase in the hydrolysis temperature and time is impractical, since a part of xylose is converted to other products (Fig. 17).

In contrast to the sulfuric acid catalyst, the solid acid catalyst Amberlyst-15 is low active in the hydrolysis of xylan at 110 °C. However, at a hydrolysis temperature of 130 °C and a time of 10 h, the xylose yield in the presence of Amberlyst-15 catalyst reaches 62 wt.% (Fig. 18A). This yield is comparable to the yield of xylose observed at the hydrolysis of xylan at 110 °C for 4 h in the presence 0.1 M H$_2$SO$_4$ catalyst (70 wt.%). The hydrolysis of xylan in the presence of the Amberlyst-15 catalyst at a temperature of 150 °C, yields 60 wt.% of xylose after 12 h. Under these conditions, the furfural yield noticeably (up to 6 wt.%) increases (Fig. 18B).

Thus, the hydrolysis of xylan at a temperature of 130 °C in the presence of the solid acid catalyst Amberlyst-15 makes it possible to produce xylose with an yield of 62 wt.% with a slight formation of furfural.

It was found that the Amberlyst-15 catalyst retains its initial catalytic activity during 4 catalytic cycles. The results obtained indicate the potential possibility to replacing a toxic and corrosive sulfuric acid catalyst with a safe solid acid catalyst Amberlyst-15.

3.6 Acid conversion of birch cellulose product

Levulinic acid (LA) is a platform product for speciality chemical and fuels, which are widely used in

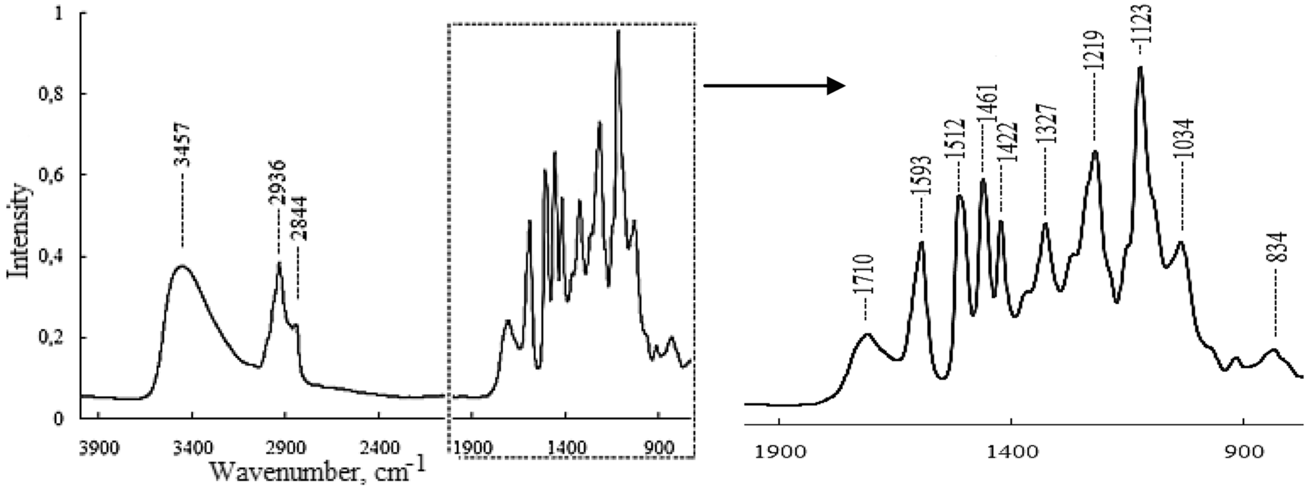


Fig. 15 FTIR spectrum of ethanol-lignin isolated from birch wood

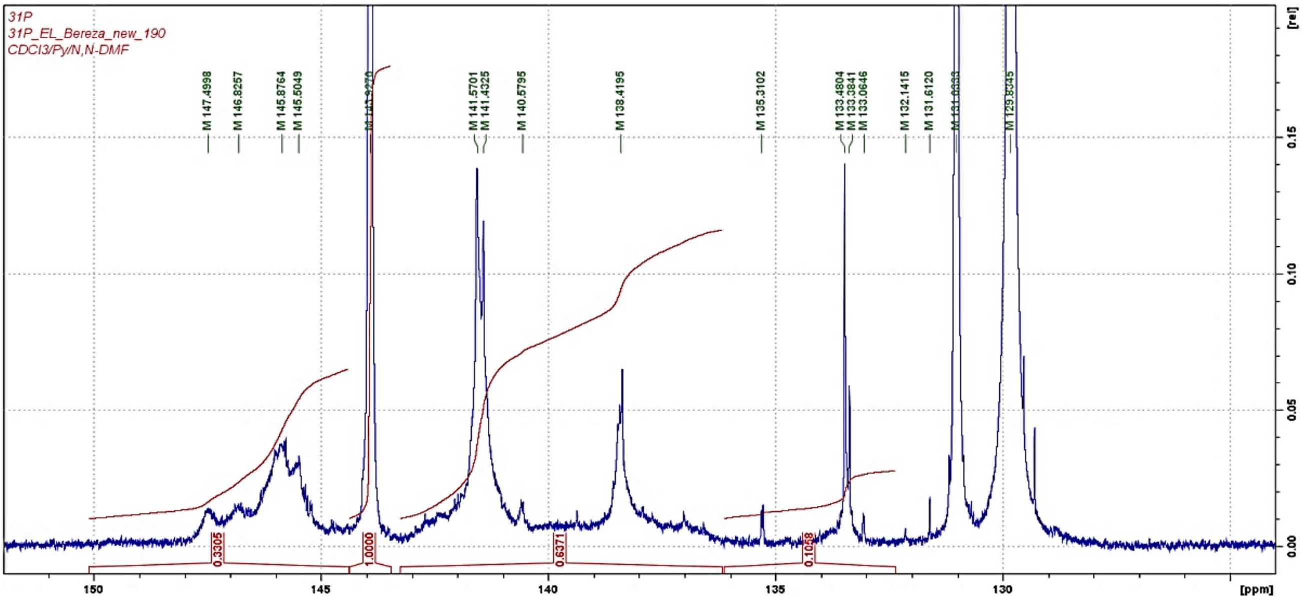


Fig. 16 ^{31}P-NMR spectrum of ethanol lignin isolated from birch wood

Table 4 Integration regions used in the of analysis ^{31}P-NMR spectrum of ethanol lignin and content of hydroxyl groups

Hydroxyl groups	δ ^{31}P–NMR, ppm	Content, mmol/g
Aliphatic	150.0–145.5	1.8547
Cyclohexanol (internal standard)	144.7–145.5	–
Phenolic	136.6–144.7	3.5753
Carboxylic	133.6–136.6	0.5936

pharmaceuticals, food industry and organic synthesis [50]. LA is produced by acid-catalyzed hydrolysis of cellulose [51–53]. For this purpose, dissolved mineral acids and solid acid catalysts can be applied. Since the dissolved acid catalysts are more active, then solid acid catalysts, we used 5% H_2SO_4 for hydrolysis of cellulose product isolated from “hemicellulose-free” birch wood. The low content of lignin and hemicelluloses in the cellulose product obtained by the extraction fractionation of “hemicellulose-free” birch wood makes it promising to use for production of LA. The effect of temperature and time of cellulose product hydrolysis with a 5% H_2SO_4 on the LA yield was examined (Fig. 19).

It was found that both the temperature and time of the acid conversion of cellulose product significantly affect the LA yield. The highest LA yield (31.0 wt.%) was observed at a process temperature of 180 °C and a time of 2 h (Fig. 19).

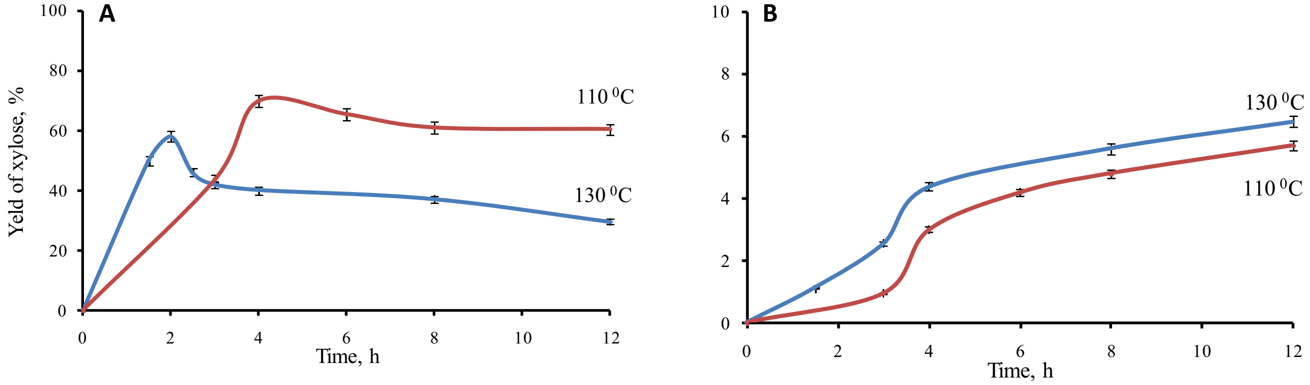


Fig. 17 Effect of temperature and time of xylan hydrolysis in the presence of 0.1 M H_2SO_4 catalyst on the yield of xylose (**A**) and furfural (**B**)

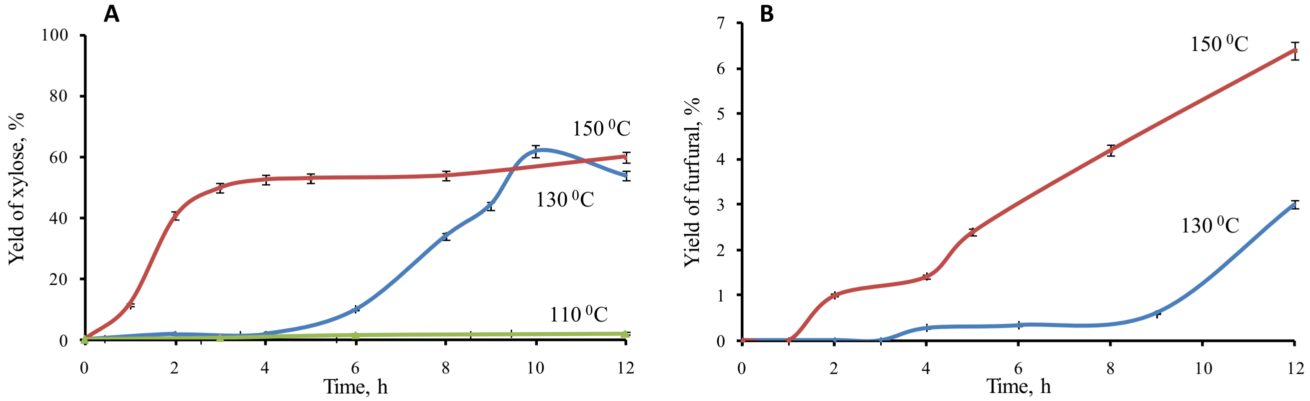


Fig. 18 Effect of temperature and time of xylan hydrolysis in the presence of an Amberlyst-15 catalyst on the yield of xylose (**A**) and furfural (**B**)

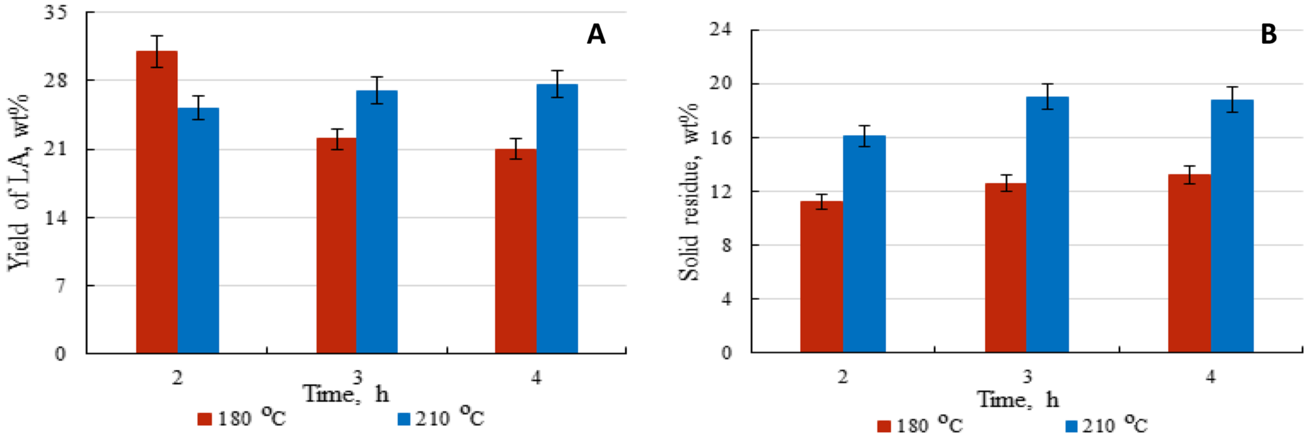


Fig. 19 Effect of temperature and time of cellulose product hydrolysis on the yield of levulinic acid (**A**) and solid residue (**B**)

With a further increase in temperature and time of the acid conversion of cellulose, the LA yield decreases due to the intensification of secondary reactions, in particular, the formation of solid residues of a humic nature. The yield of humic substances varies from 11.2 to 19.0% from the cellulose weight depending on the process conditions (Fig. 19).

The elemental composition of solid residues ranges within 65.11−67.26% for C and 4.55−4.66% for H. It is similar to the elemental composition of humic substances (63.1 of C and 4.2 of H) [54]. The solid residue of a humic nature can be used for preparation of enterosorbents.

3.7 Enterosorbents production from birch ethanol lignin

The hydrolysis lignin is traditionally used for production of commercial enterosorbents "Polyphepan".

The absence of sulfur in birch ethanol lignin, the low ash content, and a high concentration of hydroxyl groups make this product promising for the production of enterosorbents. To remove unwanted impurities from ethanol lignin, two regimes of its treatment were used: with a 0.4% aqueous solution of $NaHCO_3$ and with hot water.

The enterosorbent yield after treatment of ethanol lignin by $NaHCO_3$ at 25 °C was 85.8 wt.% (9.8% from wood weight) and after treatment with hot water — 90.4 wt.% (10.3% from wood weight).

The adsorption capacity of enterosorbents was studied using substances of different molecular weight and chemical nature. Iodine and methylene blue represent a class of low-molecular-weight toxicants and gelatin — a class of high-molecular-weight substances with a protein-binding activity (microorganisms, toxins, proteins). A commercial enterosorbent Polyphepan (ZAO Saintek, St. Petersburg) produced from hydrolyzes lignin was chosen as a reference sample.

The characteristics of the studied enterosorbents and their sorption properties are given in Tables 5 and 6.

All enterosorbents demonstrate a high sorption capacity for marker substances. Their high sorption capacity for iodine (39.8–45.4%) indicates a microporous structure of these enterosorbents.

The enterosorbents produced from ethanol lignin surpass the commercial enterosorbent Polyphepan by a factor of 1.5−2.5 in the capacity for methylene blue and by a factor of 1.5 in the capacity for gelatin. The high sorption capacity of enterosorbents from ethanol lignin is due to the high concentration of oxygen-containing functional groups capable of binding various molecules.

According to the pharmacological regulations, the content of water-soluble substances in enterosorbents should be no higher than 5%. The data given in Table 5 show that both enterosorbents produced from ethanol lignin meet the pharmacopoeia requirements for the content of water-soluble substances and ash.

Table 5 The yield of enterosorbents from ethanol lignin and the content of water-soluble substances and ash in them

Method of ethanol lignin treatment	Yield of enterosorbent, wt.%	Content in enterosorbent wt.%	
		Water-soluble substances	Ash
By 0.4% $NaHCO_3$, 30 min	85.8	3.7	0.19
By hot water, 30 min	90.4	4.1	0.15

Table 6 Sorption characteristics of the enterosorbents produced from a birch ethanol lignin

Method of ethanol lignin treatment	Sorption capacity		
	Iodine, %	Methylene blue, mg/g	Gelatin, mg/g
By 0.4% $NaHCO_3$	45.4	99.4	198.5
By hot water	39.8	75.6	174.3
Commercial enterosorbent Polyphepan [24]	38.7	44.0	115.0

4 Conclusions

It is first proposed to perform biorefinery of birch wood into xylose, levulinic acid and lignin enterosorbents by integrating the optimized process of extraction fractionation of "hemicellulose-free" birch wood with ethanol into cellulose product and ethanol lignin and the processes of alkaline isolation of xylan and its hydrolysis to xylose over solid catalyst Amberlyst-15 of cellulose product conversion to levulinic acid and of extraction processing of ethanol lignin to enterosorbents. The integration of these processes in a single technological cycle makes it possible to utilize all the main components of wood biomass and to reduce the cost of target products.

The products of birch wood biorefinery were characterized by methods of infrared spectroscopy, nuclear magnetic resonance, X-ray difractometry, scanning electron microscopy, BET surface area analysis, high performance liquid chromatography, gel permeation chromatography, gas chromatography, chemical and elemental analysis. It was established that the yields, composition and structure of target products obtained by integrating processing of birch wood are comparable to those produced by less economical methods of separate processing of birch wood. The products obtained by the extraction catalytic fractionation of birch wood biomass can find application in organic synthesis, medicine, veterinary, and other fields.

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Declarations

Competing of interests The authors declare no competing of interests.

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