



# Article Fractionation of Birch Wood by Integrating Alkaline-Acid Treatments and Hydrogenation in Ethanol over a Bifunctional Ruthenium Catalyst

Boris N. Kuznetsov <sup>1,2,\*</sup>, Sergey V. Baryshnikov <sup>1</sup>, Angelina V. Miroshnikova <sup>1,2</sup>, Aleksandr S. Kazachenko <sup>1,2,\*</sup>, Yuriy N. Malyar <sup>1,2</sup>, Andrey M. Skripnikov <sup>1,2</sup> and Oxana P. Taran <sup>1,2</sup>

- <sup>1</sup> Institute of Chemistry and Chemical Technology Siberian Branch, Russian Academy of Sciences, FRC Krasnoyarsk Science Center SB RAS, Akademgorodok 50, Bld. 24, Krasnoyarsk 660036, Russia; bsv2861@mail.ru (S.V.B.); miroshnikova.av@icct.krasn.ru (A.V.M.); yumalyar@gmail.com (Y.N.M.); and-skripnikov@yandex.ru (A.M.S.); taran.op@icct.krasn.ru (O.P.T.)
- <sup>2</sup> Department of Analytical and Organic Chemistry, Institute of Non-Ferrous Metals and Material Science, Siberian Federal University, pr. Svobodny 79, Krasnoyarsk 660041, Russia
- \* Correspondence: bnk@icct.ru (B.N.K.); leo\_lion\_leo@mail.ru (A.S.K.)

Abstract: For the first time, the fractionation of birch wood into microcrystalline cellulose, xylose and methoxyphenols is suggested based on the integration of alkali-acid pretreatments and hydrogenation in ethanol over a bifunctional Ru/C catalyst. It is established that removal of hemicelluloses during pretreatments of birch wood influences the yields of the liquid, gaseous and solid products of the non-catalytic and catalytic hydrogenation of pretreated samples in ethanol at 225 °C. The bifunctional Ru/carbon catalyst affects in different ways the conversion and yields of products of hydrogenation of the initial and acid- and alkali-pretreated birch wood. The most noticeable influence is characteristic of the hydrogenation of the acid-pretreated wood, where in contrast to the non-catalytic hydrogenation, the wood conversion and the yields of liquid products increase but the yields of the solid and gaseous products decrease. GC-MS, gel permeation chromatography and elemental analysis were used for characterization of the liquid product composition. The molecular mass distribution of the liquid products of hydrogenation of the initial and pretreated wood shifts towards the low-molecular range in the presence of the catalyst. From the GC-MS data, the contents of monomer compounds, predominantly 4-propylsyringol and 4-propanolsyringol, increase in the presence of the ruthenium catalyst. The solid products of catalytic hydrogenation of the pretreated wood contain up to 95 wt% of cellulose with the structure, similar to that of microcrystalline cellulose.

**Keywords:** birch wood; alkali and acid pretreatment; hydrogenation; Ru/carbon catalyst; microcrystalline cellulose; xylose; methoxyphenols

# 1. Introduction

Renewable lignocellulose biomass is an alternative to the traditional oil stock for production of various chemicals [1–3]. Main constituents of wood biomass are polysaccharides (cellulose and hemicelluloses) and lignin (aromatic biopolymer) [4]. Proportions of the main constituents of biomass vary depending on the plant species and age [5]. Birch containing up to 30 wt% of hemicellulose predominates among hardwood trees in Russia.

Hemicelluloses are amorphous branched heteropolymers composed of  $C_5$  and  $C_6$  monosaccharides and uronic acids. The most widespread hemicelluloses in hardwood and non-wood plants is xylan [6]. Lignin forms phenylglicoside bonds with the wood polysaccharides to give the so-called lignocarbohydrate complexes [7]. The chemical bonds between lignin and hemicelluloses considerably affect the reactivity of the wood for its chemical transformations [8]. Chemical pretreatments (acid, alkali) of wood disrupt the initial structure of the lignocarbohydride complexes. The acid pretreatment hydrolyzes



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**Copyright:** © 2021 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). selectively hemicelluloses in the lignocellulose biomass [9], and may lead to considerable changes in the biomass structure [10]. The alkali pretreatment allows the effective delignification and xylan isolation to be achieved under mild conditions [11].

Complex processing of all components of the lignocellulose biomass is achieved via its catalytic fractionation based on the selective oxidation with hydrogen peroxide [12] or oxygen [13], hydrogenation [14–16] or thermal dissolution in supercritical fluids, e.g. in ethanol [17,18]. The reductive catalytic fractionation of the lignocellulose biomass leads to depolymerization of lignin, to produce liquid hydrocarbons without sacrificing the main part of cellulose [19,20].

Heterogeneous metal, acid and bifunctional catalysts bearing acid and metal active sites are used for the reductive catalytic fractionation [21–23].

The development of new methods of lignocellulose biomass fractionation to expand the range of products is an urgent problem.

The urgent task is the development of new extraction—Catalytic methods for "green" fractionation of lignocellulosic biomass, which expands the range of valuable products. Earlier, we showed that the integration of the processes of dihydroquercetin and arabino-galactan extraction from larch wood, oxidation of extracted wood by oxygen to vanillin and cellulose in the presence of catalyst Cu(OH)<sub>2</sub>, arabinogalactan hydrolysis over solid acid catalyst to arabinose and galactose and acid-catalyst conversion of cellulose to levulinic acid makes possible to increase in the number of target products [24].

In the present work, a new method was suggested for fractionation of birch wood into xylose, microcrystalline cellulose and liquid hydrocarbons rich in methoxyphenols based on integration of its alkali-acid treatments followed by hydrogenation of the hemicelluloses-free treated wood in ethanol over a bifunctional Ru/carbon catalyst at 225 °C. The influence of the alkali and acid treatments of birch wood on the yields and compositions of the products of non-catalytic and catalytic hydrogenation of original and treated wood in ethanol was established.

#### 2. Results and Discussion

## 2.1. Hydrogenation of Initial and Pretreated Birch Wood in Ethanol

Processes of catalytic hydrogenation of lignocellulose biomass are used for the fractionation of the main components into liquid, solid and gaseous products [23,25]. A new process is suggested in the present work for the fractionation of birch wood, which has a high content of hemicelluloses. This process integrates removal of hemicelluloses and the following catalytic hydrogenation of lignocellulose. Two procedures are used for the removal of hemicelluloses from birch wood: acid hydrolysis to monosaccharides and alkali extraction in the form of xylan.

Chemical analysis revealed that alkali and acid pretreatments led to the removal of a significant portion of hemicelluloses from birch wood, as well as an increase in the contents of cellulose (up to 63.6–64.2 wt%) and lignin (up to 28.2–30.2 wt%) in the treated wood (Table 1).

Sample of Wood	* Yield	* Chemical Composition, wt%		
Sample of Wood	wt%	Cellulose	Lignin	Hemicelluloses
Initial	-	47.3	19.0	28.5
Alkali treatment	74.3	64.2	28.2	7.6
Acid treatment 2.5 h	86.7	63.4	29.7	7.0
Acid treatment 5 h	70.0	63.6	30.2	6.2

Table 1. Chemical analysis of processed and initial birch wood.

\* From absolutely dry sample.

Comparable yields and compositions of liquid, solid and gaseous products of noncatalytic and catalytic hydrogenation (ethanol medium, 225 °C, operation pressure 10 MPa) of the initial birch wood and the wood after removal of a significant part of hemicelluloses are shown in Table 2.

Hydrogenation	Yield, wt% *			
Conditions	Liquid Products	Solid Product	Gases	
* non-catalytic <sup>a</sup>	50.0	33.0	10.5	
** non-catalytic <sup>b</sup>	48.0	44.5	9.8	
** non-catalytic <sup>c</sup>	42.0	58.0	5.6	
* Ru/C <sup>a</sup>	49.0	29.0	16.0	
** Ru/C <sup>b</sup>	52.0	41.6	8.4	
** Ru/C <sup>c</sup>	47.5	49.0	3.5	

**Table 2.** The yields of products of hydrogenation in ethanol at 225 °C: initial wood (<sup>a</sup>), alkali-treated wood (<sup>b</sup>), acid-treated wood (<sup>c</sup>).

\* From initial absolutely dry wood; \*\* from treated absolutely dry wood.

Among the products of non-catalytic hydrogenation of initial birch wood, there are 50.0 wt% of liquid, 33.0 wt% of solid, 10.5 wt% of gaseous products. When hemicelluloses have been removed from the wood by the alkali treatment, the yield of solid hydrogenation products increases up to 44.5 wt%, while the yields of the liquid and gaseous products decrease down to 48 and 9.8 wt%, respectively. Hydrolytic removal of hemicelluloses results in a decrease in the yields of liquid and gaseous products (42.0 and 5.6 wt%, respectively), and an increase in the yield of solid products (58.0 wt%).

The ruthenium catalyst influences different ways the yields of liquid, solid and gaseous products of hydrogenation of initial, alkali- and acid-treated birch wood (Table 2).

In catalytic hydrogenation of the initial birch wood, the yield of gaseous products increases (16.0 wt%), the yield of solid products decreases (29.0 wt%), the yield of liquid products practically does not change (Table 2).

Less influence of the catalyst on the yield of gaseous products is observed during hydrogenation of pretreated wood. The Ru/C catalyst has a greater impact on the yields of liquid and solid products. If compare to the non-catalytic hydrogenation process, the catalyst increases the liquid product yield from 48.0 to 52.0 wt% in the case of alkali-treated wood and from 42.0 to 47.5 wt% from the acid-treated wood. At the same time, the solid product yield decreases from 44.5 to 41.6 wt% in the case of alkali-treated wood, and from 58.0 to 49.0 wt% for acid-treated wood (Table 2).

The yield of liquid products of catalytic hydrogenation of lignocellulose biomass is known to increase due to intensification of the reaction of depolymerization of native lignin in the presence of bifunctional catalysts [26]. The acid sites cause cleavage of ether and C-C bonds on the acid sites [26], and metal sites favor stabilization of low-molecular products of the lignin depolymerization in the presence of hydrogen [19]. This results in improvement of the liquid product yields and a decrease in the solid residue yield.

#### 2.2. Composition of Liquid Products of Birch Wood Hydrogenation

GC-MS, GPC and elemental analysis techniques were used for determining compositions of liquid products of catalytic and non-catalytic hydrogenation of the initial and pretreated birch wood in ethanol at 225  $^{\circ}$ C.

Data on the elemental composition of products of the initial and pretreated birch wood are summarized in Table 3.

There are higher proportions of carbon and hydrogen but lower proportions of oxygen in the liquid products of non-catalytic and catalytic hydrogenation of the pretreated wood against those producing by hydrogenation of the initial wood. The greatest decrease in the oxygen content is observed for liquid products of catalytic hydrogenation of the acid-pretreated wood. Hence, the bifunctional ruthenium catalyst, as well as alkali and acid treatments, result in intensification of the reactions of hydrodeoxygenation of liquid products.

Hydrogenation Conditions	C, wt%	H, wt%	O, wt%
non-catalytic <sup>a</sup>	59.2	8.3	32.5
non-catalytic <sup>b</sup>	60.3	6.9	32.8
non-catalytic <sup>c</sup>	61.1	8.2	30.7
Ru/C <sup>a</sup>	60.8	8.8	30.4
Ru/C <sup>b</sup>	62.9	7.3	29.8
Ru/C <sup>c</sup>	68.0	8.5	23.5
Initial wood	49.9	6.1	44.0

**Table 3.** Elemental composition of liquid products of hydrogenation of the initial (<sup>a</sup>), alkali-pretreated (<sup>b</sup>) and acid-pretreated (<sup>c</sup>) birch wood.

Gel permeation chromatography was used to obtain data on the molecular mass distribution of the liquid products of hydrogenation of the initial and pretreated birch wood (Table 4). The mass-average molecular mass of 1588 Da and polydispersity of 2.275 was established for the liquid products at non-catalytic hydrogenation of the initial birch wood.

**Table 4.** Molecular mass characteristics of the liquid products of hydrogenation of initial wood (<sup>a</sup>), alkali-treated wood (<sup>b</sup>), acid-treated wood (<sup>c</sup>).

Hydrogenation Conditions	Number-Average Molecular Mass Mn(Da)	Mass-Average Molecular Mass Mw(Da)	Polydispersity PD
non-catalytic <sup>a</sup>	698	1588	2.275
non-catalytic <sup>b</sup>	573	1508	2.632
non-catalytic <sup>c</sup>	701	1481	1.481
Ru/C <sup>a</sup>	374	524	1.401
Ru/C <sup>b</sup>	401	668	1.666
Ru/C <sup>c</sup>	390	664	1.703

The alkali pretreatment of the wood leads to a decrease in the average molecular mass of the liquid products of non-catalytic hydrogenation to 1508 Da and an increase in the polydispersity to 2.632 against those in the liquid products of the initial wood hydrogenation (1588 Da and 2.275, respectively), while the range of MM remains broad enough (more than 1000 Da). The acid pretreatment of the wood results in more considerable decrease in MM (down to 1481 Da) and polydispersity (down to 1.481) of the liquid products of non-catalytic hydrogenation.

In the presence of the ruthenium catalyst, the curves of the molecular mass distribution of the liquid products both of initial and alkali- and acid-pretreated wood are shifted to the range of lower molecular masses (524–668 Da), their polydispersity also being decreased to 1.401–1.703 (Table 4).

In the curves of molecular mass distributions of liquid products of birch wood hydrogenation, the peaks at ~178 Da and ~290 Da (initial wood), ~285 Da (alkali-treated) and ~275 Da (acid treated) are observed, which are assigned to the monomer compounds (Figure 1).

In general, broader ranges of molecular mass distribution are characteristic of the liquid products of hydrogenation of alkali- and acid-treated birch wood, rather than those of hydrogenation of the initial birch wood.

GC-MS data show that the liquid products of wood hydrogenation contain mainly methoxyphenol derivatives formed via lignin depolymerization, as well as minor quantities of products of polysaccharide conversion.

The composition of the phenol compounds in the liquid products of the hydrogenation of birch wood is shown in Table 5. The total contents of methoxyphenols in the liquid products of hydrogenation of the initial and acid-treated wood are 5.03–5.14%, in respect of the lignin weight. In the products of hydrogenation of alkali-treated wood, the proportion of methyxyphenols increases up to 12.09 wt%.



**Figure 1.** Molecular mass distributions of liquid products of hydrogenation of the initial (**a**), alkali-treated (**b**) and acid-treated (**c**) wood.

The following compounds are detected in most appreciable amounts among the phenolic products of non-catalytic hydrogenation: 4-propylsyringol (3.18 wt%) for initial birch wood, syringol (4.65 wt%), 4-propylsyringol (2.58 wt%), 4-propenylsyringol (1.50 wt%), 4-ethylsyringol (1.16 wt%) for alkali-pretreated wood and 4-propenylsyringol (2.97 wt%) for acid-pretreated wood.

The total content of methoxyphenols in the liquid products increases considerably (up to twice) in the presence of the ruthenium catalyst (Table 5). The maximal content of methoxyphenols (24.46 wt%) is detected in the liquid products of the catalytic hydrogenation of alkali-treated birch wood.

The catalyst also considerably affects the composition of the phenolic products to increase the contents of 4-propylsyringol (up to 9.80–7.55 wt%), 4-propanolsyringol (up to 9.71–3.54 wt%) and 4-propylguaiacol (up to 2.60–1.65 wt%), but to decrease the contents of syringol and 4-propenylsyringol in the products of the initial and pretreated wood (Table 5).

The increasing yield of phenol monomers in the presence of the bifunctional ruthenium catalyst can be explained in terms of the following mechanism. In the course of the lignin depolymerization in the presence of acids, there occurs the cleavage of  $\beta$ -O-4 bonds [27] via several steps (Figure 2). The first step is the removal of OH-group from the  $\alpha$ -position to form the benzyl carbocation. The carbocation gives enol ether as an intermediate; hydrogenolysis of its C–O bonds produces C2-aldehydes and C3-ketones [28]. Ketones can enter reactions of condensation under hydrogenation conditions [20,27]. Metal sites of the catalyst favor hydrogenation of ketones with hydrogen to form non-condensed compounds (4-propylsyringol, 4-propylguaiacol, 4-propanolsyringol and 4-propanolguaiacol), depending on the catalyst nature and the reaction conditions (Figure 2). RT

Compound

		Content,	wt% *		
Non- cat. <sup>a</sup>	Non- cat. <sup>b</sup>	Non- cat. <sup>c</sup>	Ru/C <sup>a</sup>	Ru/C <sup>b</sup>	Ru/C <sup>c</sup>
0.05	0.26	0.03	0.2	0.42	0.24
no	4.65	0.43	0.7	0.58	0.37

Table 5. Composition and content of phenolic compo (<sup>b</sup>) acid-treated (<sup>c</sup>) birch wood.

			cat.	cat.	cat.			
24.39	4-ethylguaiacol	HO H <sub>3</sub> CO	0.05	0.26	0.03	0.2	0.42	0.24
26.53	Syringol	HO H <sub>3</sub> CO	no	4.65	0.43	0.7	0.58	0.37
26.84	4-propylguaiacol	HO H <sub>3</sub> CO	0.02	0.27	0.05	2.6	1.65	2.07
27.93	4-propenylguaiacol	HO H <sub>3</sub> CO	0.31	0.67	0.77	0.2	0.02	0.36
28.97	4-methylsyringol	HO H <sub>3</sub> CO	0.04	0.35	0.15	0.2	0.04	0.29
30.92	4-ethylsyringol	HO H <sub>3</sub> CO	0.11	1.16	0.2	1.4	1.33	0.93
32.72	4-propenylsyringol	HO Ho H <sub>3</sub> CO	1.32	1.5	2.97	0.6	no	0.27
32.88	4-propylsyringol	HO H3CO	3.18	2.58	0.54	9.8	8.64	7.55
33.92	4-propanolguaiacol	HO H <sub>3</sub> CO OCH	no	no	no	no	2.07	no
39.17	4-propanolsyringol	HO H <sub>3</sub> CO	no	0.65	no	4.1	9.71	3.54
	Total content of alkylph	nenols	5.03	12.09	5.14	19.8	24.46	15.62
	Other methoxyphen	ols	0.68	1.94	0.8	0.28	0.41	0.48

-calculated per lignin weight in the wood.



Figure 2. Scheme of lignin hydrolysis via cleavage of β-O-4 bonds and hydrogenation of intermediates in the presence of Ru-containing catalysts [27].

> 4-Propanolsyringol is formed due to hydrogenation of the C=C bond of monolignol resulting from hydrogenolysis of the  $\beta$ -O-4 bond. The further dehydration of



4-propanolsyringol to 4-propenylsyringol, followed by hydrogenation, gives 4-propylsyringol (Figure 3) [27,29].

**Figure 3.** Formation of 4-Propylsyringol via cleavage of  $\beta$ -O-4 bonds followed by hydrogenation and dehydration of sinapyl alcohol.

It is known that propyl-substituted phenolic compounds are preferably formed in the presence of ruthenium catalysts [30,31]. However, the increased content of 4propanolsyringol in the liquid products of hydrogenation of alkali-pretreated birch wood may be accounted for by the fact that the removal of hemicelluloses from wood makes easier cleavage of the  $\beta$ -O-4 bonds of lignin and the formation of sinapyl alcohol to be hydrogenated for 4-propanolsyringol (Figure 3).

The data in Table 5 demonstrate that the acid pretreatment of the wood leads to a decrease in the content of monomer phenolic compounds in the liquid products of wood hydrogenation. The acid hydrolysis of the wood probably contributes reactions of lignin condensation to decrease the content of the  $\beta$ -O-4 bonds, which reduces the yield of the monomers during hydrogenation. In contrast, the alkali pretreatment of the wood under mild conditions allows much of  $\beta$ -O-4 bonds in lignin to be preserved [32,33]. The alkali pretreatment of the wood results in removal of hemicelluloses to facilitate depolymerization of lignin during hydrogenation, and favors an increase in the yields of monomer methoxyphenols.

The influence of the time of acid treatment of birch wood on the yield of monomer methoxyphenols at the catalytic hydrogenation was studied (Figure 4). It was established that the total yield of methoxyphenols reduces with increasing the time of the acid treatment from 2.5 to 5 h. The time of the acid treatment also influences the composition of methoxyphenols formed. No 4-propanolsyringol but the maximal yield of 4-propylsyringol is observed after 2.5. h treatment (Figure 4).



**Figure 4.** Influence of the time of the acid treatment of birch wood on the content of phenolic compounds in the liquid products of Ru/C catalyzed hydrogenation of initial (1), 2.5 h acid-pretreated (2) and 5 h acid-pretreated (3) wood.

The increase the time of the acid treatment of birch wood probably leads to strengthening of the condensation processes to decrease the number of reactive  $\beta$ -O-4 bonds in lignin, which results in a reduce in the yield of monomer methoxyphenols during hydrogenation.

Along with the lignin depolymerization, wood polysaccharides are transformed during hydrogenation. The products of the polysaccharide transformation contain mainly furan derivatives, ethers, alcohols, ketones and monosaccharides. However, the total yield of these compounds is far lower of the yield of methoxyphenols, being no more than several percent.

## 2.3. Composition and Structure of Solid Products of Birch Wood Hydrogenation

The solid product of non-catalytic hydrogenation of birch wood contains 71.8 wt% of cellulose, 18.8 wt% of lignin and 9.4 wt% of hemicelluloses. In the solid product of catalytic hydrogenation of the wood, the cellulose content increases up to 87 wt%, while contents of lignin and hemicelluloses decrease down to 7.8 and 5.2 wt%, respectively (Table 6).

**Table 6.** Chemical composition of solid products of hydrogenation of initial (<sup>a</sup>), alkali-pretreated (<sup>b</sup>), acid-pretreated (<sup>c</sup>) birch wood.

Hydrogonation Conditions	Composition of the Solid Product, wt%				
Hydrogenation Conditions	Cellulose	Lignin	Hemicelluloses		
non-cat. <sup>a</sup>	71.8	18.8	9.4		
non-cat. <sup>b</sup>	78.7	14.2	7.1		
non-cat. <sup>c</sup>	84.4	12.7	2.9		
Ru/C <sup>a</sup>	87.0	7.8	5.2		
Ru/C <sup>b</sup>	94.7	5.3	1.4		
Ru/C <sup>c</sup>	95.0	3.8	1.2		

In the solid products of non-catalytic hydrogenation of the alkali- and acid-pretreated wood, the cellulose content increases up to 78.7–84.4 wt%, the contents of lignin and hemicelluloses decrease down to 14.2–12.7 wt% and 7.1–2.9 wt%, respectively (Table 6).

In the solid products of catalytic hydrogenation of the-pretreated birch wood, the contents of lignin and hemicelluloses decrease down to 5.3–3.8 wt% and to 1.4–1.2 wt%, respectively, while the content of cellulose reaches 95 wt% (Table 6). Hence, alkali or acid pretreatments of birch wood allow the solid products with high content of cellulose to be obtained by the catalytic hydrogenation of the-pretreated wood in ethanol at 225 °C.

IR spectroscopy and XRD techniques were used for studying the structure of the solid products of the wood hydrogenation. Figure 5 shows IR spectra of the initial wood and of the solid products of its hydrogenation.

In the IR spectrum of the initial wood, there are absorption bands of its main structural constituents, as well as bands assigned to bonds between macromolecules of cellulose, lignin and hemicelluloses [34]. The absorption band at  $1734 \text{ cm}^{-1}$  is assigned to the stretching vibrations of the C=O group in the ester group of uronic acid of hemicelluloses [35]. The band at  $1734 \text{ cm}^{-1}$  is far less intense in the solid product (sample 2) of hydrogenation of the initial birch wood (curve 2 in Figure 5), and practically disappears in the spectra of the solid products of the hydrogenation of the initial and pretreated wood (curves 3–5 in Figure 5). The absorption bands at 1593 and 1505 cm<sup>-1</sup> in the IR spectra of the initial birch wood and of the solid hydrogenation products are assigned to stretching vibrations of the C–C bonds of syringol and guaiacol rings [36]. The decrease in the intensity of these absorption bands argues for a reduce in the lignin contents in the solid hydrogenation products.

Absorption bands at 1500–900 cm<sup>-1</sup> are assigned to vibrations of the C–H bonds in the methyl and methylene groups, to C–O and O-H bonds, to vibrations of the glycoside bond and glucopyranose ring of cellulose [37]. If compared to the spectra of the initial birch wood, the spectra of the solid hydrogenation products show more intense absorption bands at 1455 and 1421 cm<sup>-1</sup> related to cellulose. Considerably more intense absorption bands at



1421 cm<sup>-1</sup> in the spectra of the solid products compared to the initial wood characterize the high cellulose crystallinity in these samples [38].

**Figure 5.** IR spectra of the initial birch wood (1), solid product of non-catalytic hydrogenation of the initial wood (2), solid residue of catalytic hydrogenation of the initial wood (3), solid product of catalytic hydrogenation of the alkali-pretreated wood (4) and solid product of catalytic hydrogenation of the acid-pretreated wood (5).

Diffraction patterns of the initial and-pretreated birch wood and of the solid products of their hydrogenation are shown in Figure 6.



**Figure 6.** Diffraction patterns of the samples birch wood (**A**): initial (1), alkali-treated (2), acid-treated (3) and of the solid products of catalytic hydrogenation of the birch wood (**B**): initial (1), alkali-pretreated (2) and acid-pretreated (3).

Diffraction patterns of all the samples under study contain two peaks with maxima at 2 $\theta$  equal to 22.5° and 16° (Figure 6) assigned to reflections of atoms in plane (002) and overlapped reflections of atoms in planes (101) and (101), respectively, of the cellulose

crystal lattice [39]. The widths of the diffraction peaks depend on the size of crystallinity regions referred to as the coherent scattering ranges. Pronounced peak at the diffraction angle  $2\theta$  near  $22.5^{\circ}$  is the criterion of the cellulose crystallinity, and characterizes the proportion of closely densed cellulose molecules [40]. The diffraction patterns were used for calculating crystallinity indices (CI) of the samples of birch wood and solid products (Table 7).

**Table 7.** Crystallinity indices of the samples of birch wood and solid product of its hydrogenation initial (<sup>a</sup>), alkali-pretreated (<sup>b</sup>) and acid-pretreated (<sup>c</sup>) wood.

Sample	Crystallinity Index
Birch wood <sup>a</sup>	0.59
Birch wood <sup>b</sup>	0.51
Birch wood <sup>a</sup>	0.69
Solid product <sup>b</sup>	0.64
Solid product <sup>b</sup>	0.54
Solid product <sup>c</sup>	0.70
Solid product Ru/C <sup>a</sup>	0.70
Solid product Ru/C <sup>b</sup>	0.62
Solid product Ru/C <sup>c</sup>	0.74

The crystallinity index of the initial birch wood equals 0.59, but decreases to 0.51 for the alkali-pretreated wood. The acid pretreatment increases CI to 0.69 owing to hydrolysis of the amorphous part of cellulose.

The crystallinity indices of the solid products of hydrogenation of the initial andpretreated wood are the higher of those of the initial and-pretreated wood (Table 7). The reason is the removal of a considerable part of hemicelluloses, amorphous cellulose and lignin during wood hydrogenation.

The highest crystallinity index CI (0.74) comparable to CI of microcrystalline cellulose (0.75) [41] is characteristic of the solid product of catalytic hydrogenation of the acid-pretreated wood.

#### 2.4. Composition of Gaseous Products of Hydrogenation of Birch Wood

Gaseous products of hydrogenation of the initial and-pretreated birch wood contain mainly carbon dioxide (Figure 7). An increase in the proportions of CO and CH<sub>4</sub> at a decrease in the proportion of CO<sub>2</sub> is observed at the catalytic hydrogenation of the wood. The increasing yield of CO is supposedly due to intensification of the acid-catalyzed hydrolysis of ester bonds between lignin fragments. The ketones thus formed undergo decarbonylation over the metal sites of the catalyst to release CO [42]. The increase in the methane yield is thought to result from the intensified hydrocracking of methoxyphenols formed during the catalytic depolymerization of lignin [43].

## 2.5. Fractionation of Birch Wood into Microcrystalline Cellulose, Xylose and Methoxyphenols

The results obtained allowed us to suggest two ways of birch wood fractionation (Figure 8). One of them integrates the stages of hemicelluloses hydrolysis to xylose by acid treatment and the subsequent hydrogenation of "hemicellulose-free" wood in ethanol at 225 °C in presence of bifunctional catalyst Ru/Carbon. The other way includes the stages of alkali treatment of wood to remove hemicelluloses in the form of xylan and the subsequent catalytic hydrogenation of the treated wood.

Individual stages of the suggested complex processing of birch wood were optimized. It was previously was established [44] that the high yield of xylose (72.4–77.1 wt% of the hemicellulose content in the birch wood) was achieved at wood hydrolysis with 3% H<sub>2</sub>SO<sub>4</sub> at 100 °C for 5 h.



**Figure 7.** Composition of gaseous products of hydrogenation of the initial (a), alkali-pretreated (b) and acid-pretreated (c) wood.

At the present work, the high yield of xylan (up to 82.0 wt% from the hemicelluloses content in the birch wood) was observed at wood pretreatment with 4% NaOH at 25 °C for 6 h. In order to produce xylose by hydrolysis of the obtained xylan, an ecologically sound solid acid catalyst Amberlyst-15 was suggested to be used instead of the toxic and corrosive sulfuric acid catalyst. It was established that xylan is completely hydrolyzed to xylose during 6 h at 130 °C, and during 3 h at 150 °C. The content of furfural in the produced hydrolysates is lower by an order of magnitude than the content of xylose.

The highest yield of microcrystalline cellulose (MCC) (49 wt% from the-treated wood) was obtained by catalytic hydrogenation of acid-pretreated birch wood. The MCC sample with the crystallinity index of 0.74 comprised 95.0 wt% of cellulose, 3.8 wt% of lignin, 1.2 wt% of hemicellulose. The composition and structure of produced cellulose corresponded to the commercial MCC.

The maximal amount of methoxyphenols (24.5 wt%) is contained in the liquid products of catalytic hydrogenation of alkali-pretreated birch wood.

The products of the complex processing of birch wood are in demand for many areas. Due to such unique properties of microcrystalline cellulose as nontoxicity, biodegradability, high mechanical strength, large surface area and biocompatibility, this material is commonly used in medicine and in the pharmaceutical, food, chemical, cosmetic and fragrance industries [45]. Microcrystalline cellulose is used in thin-layer chromatography, for the production of sorbents, biocomposites, polymer-based reinforced materials and other products [46].

Xylose is used as a substitute at citric acid in the production of xylitol and furfural in the microbiological industry. Methoxyphenols are used for the production of additives and components of motor fuels in the chemical industry [47].

The industrial processes of microcrystalline cellulose (MCC) production are multistage, resource-consuming and environmentally harmful due to the use of toxic reagents at the stages of pulping, bleaching and acidizing cellulose [48]. Only the cellulose component of wood is used in the conventional production of MCC, but lignin and hemicelluloses remain as unused waste. Taking all these into account, the developed method of birch wood fractionation into MCC, xylose, methoxyphenols and polyols is much more effective in the respect to product yield, overall environmental friendless and economic outlook.



Figure 8. Scheme of complex processing of birch wood.

## 3. Materials and Methods

## 3.1. Initial Wood

Birch wood (*Betula pendula*) was used for the studies. Components of the wood (expressed as weight percentage in the absolutely dry wood) were: 47.3% cellulose, 19.0% lignin, 28.5% hemicelluloses, 4.9% extractants and 0.3% ash. The wood was crushed using a vibration machine VR-2 to obtain submillimeter particles, deresinated successively with petroleum ether and acetone (according to the standard ANSI/ASTM D 1105 method) and dried at 80 °C to constant weight.

# 3.2. Catalyst Ru/Carbon

A bifunctional catalyst 3% wt Ru was prepared by impregnation of the acid carbon support Sibunit (fraction 0.056–0.094 mm) with an aqueous solution of Ru(NO)(NO<sub>3</sub>)<sub>4</sub>.

The carbon support was acid-modified by oxidation with a mixture of  $O_2$  and  $N_2$  (20:80 vol%) in the presence of water vapor (saturation at 90 °C, vapor pressure 70.1 kPa, flow rate 200 mL/min) at 450°C for 2 h according to procedure [49].

The ruthenium catalysts were dried at room temperature for 2-3 h, then at 60 °C for 12 h and reduced in flowing hydrogen (30 mL/min) at 300 °C for 2 h. After cooling down to room temperature in hydrogen, the catalyst was passivated using a gas mixture of 1% of  $O_2$  in  $N_2$  flow 30 mL/min [50].

Textural characteristics of the samples were determined from the  $N_2$  adsorption isotherms at 77 K with an automatic analyzer of specific surface area and porosity instrument (Micromeritics ASAP-2020 Plus, Norcross, GA, USA, 2018).

High-resolution electron microscopy images and the size distribution of ruthenium particles were acquired using a transmission electron microscope HT7700 (Hitachi, Tokyo, Japan, 2014) at the accelerating voltage of 110 kV and resolution of 2 Å. Particle size distribution histograms were obtained by statistical (500-800 particles) analysis of the TEM images. Linear ( $<d_1>$ ) and weight-average diameters ( $<d_s>$ ) were calculated by formulae

$$\langle d_l \rangle = \Sigma d_i / N, \langle d_s \rangle = \Sigma d_i^3 / \Sigma d_i^2$$
<sup>(1)</sup>

where d<sub>i</sub> is the diameter of a deposited particle and N is the total number of particles.

The ruthenium dispersion DRu in the catalysts was calculated by a formula

$$D_{Ru} = 6 \cdot \frac{M_{Ru}}{\alpha_{Ru} \cdot \rho \cdot N_0 \cdot \langle d_s \rangle}$$
<sup>(2)</sup>

where  $M_{Ru} = 0.101 \text{ kg/mol}$  is the ruthenium molar weight,  $\rho = 12410 \text{ kg/m}^3$  is the ruthenium metal density,  $a_{Ru} = 6.13 \cdot 10^{-20}$  is the average effective area of the metal atom on the surface (m<sup>2</sup>), N<sub>0</sub> is the Avogadro number and d<sub>s</sub> is the weight-average diameter of ruthenium particles [50].

The catalyst acidity was estimated by the pH point of zero charge (pzc) by the Sorenson–de Bruyn method [51].  $pH_{pzc}$  has been proved to correlate with total amount of acid surface species in previous work [49].

Characteristics of the ruthenium catalyst: average particle size of ruthenium  $\langle d_l \rangle$ 1.13 ± 0.01 nm; dispersion of ruthenium D<sub>Ru</sub>-0.94; specific surface area (S<sub>BET</sub>) = 341 m<sup>2</sup>/g; pore volume (V<sub>pore</sub>) = 0.50 cm<sup>3</sup>/g; average pore size  $\langle d_{pore} \rangle$  5.88 nm; pH<sub>pzc</sub> 6.89.

The resulting ruthenium catalyst contained both acid and metal active sites, and was therefore bifunctional.

#### 3.3. Acid Hydrolysis of Hemicelluloses

Birch wood was treated with 3% sulfuric acid under optimal conditions determined before [44]: 100  $^{\circ}$ C, 5 h. The yield of xylose reached 77 wt% of the initial hemicellulose content in the birch wood. Glucose and mannose were only in minor quantities in the hydrolyzate.

## 3.4. Isolation of Xylan

Xylan was extracted from birch wood via treatment with 4% sodium hydroxide (chemical purity grade) solution at room temperature, water duty 40, for 4 h under continuous stirring. The solution was filtered using a Buchner funnel, and the solid precipitate ion the filter was washed with 50 mL of water. The solution of xylan was neutralized with 35% acetic acid (chemical purity grade) until flocculation. Then, the solution and the precipitation with 96% ethanol added at the ratio of 1:1 was maintained cooled (+5 °C) for 20 h. The obtained xylan was separated from ethanol by centrifuging at 8000 rps for 8 min using centrifuge OHAUS Frontier 5816, frosted and lyophilizated using a drier Iney-6.

#### 3.5. Hydrogenation of Birch Wood

Birch wood was hydrogenated using a 300 mL autoclave ChemReSYStem R-201 (Korea) (see the scheme in Figure 9). Ethanol (60 mL), the substrate (3.0 g) and catalyst

(0.3 g) were loaded into the reactor. The autoclave was sealed hermetically and blown with argon to remove air. Hydrogen started to feed at the pressure of 4 MPa. The process was conducted at 225 °C for 4.5 h with constant stirring at a rate of 800 rpm. The conditions were chosen based on the experimental results reported elsewhere [52]. Temperature was elevated at the rate of 10 °C/min, the required temperature was reached in 20–25 min. The operation pressure was 10 MPa. Upon cooling the reaction mixture down to room temperature, the gas-phase products were collected to a gasometer, and the volume was measured. The composition at gases was determined by GC analysis. The soluble and solid reaction products were uploaded quantitatively from the autoclave with ethanol and separated by filtration (Figure 9).





A rotary evaporator was used for removing the solvent from the soluble products. The liquid products were dried to constant weight in vacuum (1 mm Hg) at room temperature. The solid product was washed with ethanol until the solvent discoloration and dried to constant weight at 80 °C. The yields of liquid ( $\alpha_1$ ), solid ( $\alpha_2$ ), gaseous ( $\alpha_3$ ) products and the conversion of birch wood ( $X_{init}$ ) were determined by Formulas (3)–(6)

$$a_1 = \frac{m_1(g)}{m_{init}(g)} \times 100\%$$
(3)

$$a_2 = \frac{m_s(g) - m_{cat}(g)}{m_{init}(g)} \times 100\%$$
(4)

$$a_3 = \frac{m_g(g)}{m_{init}(g)} \times 100\%$$
 (5)

$$X_{init} = \frac{m_{init}(g) - m_s(g)}{m_{init}(g)}$$
(6)

where  $m_1(g)$  is the mass of liquid products,  $m_{init}(g)$  the mass of the initial absolutely dry wood or of the processed absolutely dry wood,  $m_s(g)$  the solid product mass,  $m_{cat}(g)$  the catalyst mass and  $m_g(g)$  the mass of gaseous products.

## 3.6. Analysis of Liquid Products

An Agilent 7890A chromatograph with an Agilent 7000A TripleQuad detector of selective masses was in a capillary column HP-5MS (30 m) used for GC-MS analysis of liquid products of wood hydrogenation at the temperature programmed between 40 and 250 °C. The constituents were identified using the database of the NIST MS Search 2.0 instrument.

The molecular mass distribution of the liquid products was determined by gelpenetration chromatographic technique using an Agilent 1260 Infinity II Multi-Detector GPC/SEC System chromatograph based on triple detection: with a refractometer (RI), viscosimeter (VS) and light scattering (LS). A PLgelMixed-E column with tetrahydrofuran as the eluent stabilized by 250 ppm of butylhydroxytoluene was used for separation. The column was calibrated using polydisperse polystyrene standards (Agilent, Santa Clara, CA, USA). The eluent was injected by 100  $\mu$ L samples at the rate of 1 mL/min. Samples to be analyzed were dissolved in THF (1 mg/mL), and filtered through a 0.22  $\mu$ m membrane PTFE filter (Millipore). Data were acquired and processed using the Agilent GPC/SEC MDS program package.

### 3.7. Analysis of Gaseous Products

GC analysis of gaseous products of birch wood hydrogenation was carried out using a Cristall 2000 M chromatograph (Chromatec, Yoshkar-Ola, Russia) equipped with a thermal conductivity detector at 170 °C. Helium was used as the gas carrier (15 mL/min). A column with NaX zeolite (3 m  $\times$  2 mm) was used for analysis for CO and CH<sub>4</sub> at 60 °C. A Porapak Q column was used for analysis for CO<sub>2</sub> and hydrocarbon gases at the temperature elevated from 60 to 180 °C at the rate of 10 °C/min.

## 3.8. Analysis of Solid Products

The cellulose content was calculated from the difference between the mass of wood (or solid residue) and the summary contents of hemicelluloses and lignin. To determine the residual lignin content, wood polysaccharides were hydrolyzed with 72%  $H_2SO_4$  at 98 °C [53]. The compositions and concentration of monosaccharides in the solution obtained by hemicelluloses hydrolysis with 4% sulfuric acid were determined by GC [53].

A VARIAN-450 GC gas chromatograph (Varian Inc. Palo Alto, CA, USA), a flame ionization detector, a VF-624 ms capillary column of 30 m length and 0.32 mm inner diameter with helium as the gas carrier at the injector temperature of 250 °C were used for the analysis. Before the analysis, the solution was derivatized according to the procedure described elsewhere [54] to produce trimethylsilyl derivatives. Sorbitol was used as an internal standard. The peaks were identified using the retention times of tautomeric forms of monosaccharides.

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

Infrared spectroscopy analysis (FTIR) was carried out in the transmission mode. Samples of cellulose (4 mg each) were prepared in pellets with matrix KBr. The spectra were acquired with a Bruker Tensor-27 in the range of 4000–400 cm<sup>-1</sup>. Spectral data were processed using the OPUS/YR (version 2.2) program package.

X-ray diffraction (XRD) analysis was carried out using a PANalyticalX'Pert Pro (PANalytical, Netherlands) spectrometer with CuK $\alpha$  radiation ( $\lambda = 0.54$  nm). The analysis was performed in the angle 4 range of  $2\theta = 5^{\circ}-70^{\circ}$  with a step of  $0.1^{\circ}$  on the powder sample in a 2.5-cm diameter cuvette. Crystallinity index (CI) was calculated from the ratio of the height between the intensity of the crystalline peak ( $I_{002}$ – $I_{AM}$ ) and total intensity ( $I_{002}$ ) after subtraction of the background signal

$$CI = \frac{I_{002} - I_{AM}}{I_{002}},\tag{7}$$

where  $I_{002}$  is the height of peak 002;  $I_{AM}$  is the height of the minimum between peaks 002 and 101 [40].

## 4. Conclusions

It is established that the removal of hemicelluloses via alkali- and acid-pretreatment of birch wood improves efficiency of the reductive fractionation of the "hemicelluloses-free" wood in ethanol at 225 °C in the presence of the bifunctional Ru/C catalyst. This way of wood fractionation gives the microcrystalline cellulose and liquid products a high content of methoxyphenols.

The acid pretreatment, rather than the alkali pretreatment, affects more significantly the yield and composition of products of the catalytic hydrogenation of birch wood.

The bifunctional Ru/C catalyst bears both acid and metal active sites increases in the of the methoxyphenols contents in the liquid products of hydrogenation of both initial and pretreated birch wood. The content of saturated alkyl-substituted methoxyphenols (4-propylsyringol and 4-propylguaiacol) is most noticeable, probably due to intensification of hydrogenolysis of  $\beta$ -O-4 bonds and hydrogenation of C=C bonds in lignin.

The fractionation of the birch wood biomass into xylose, microcrystalline cellulose and methoxyphenols is suggested to achieve by integrating processes of alkali-acid pretreatment of the wood and hydrogenation of the-treated wood in ethanol at 225 °C in the presence of a bifunctional Ru/carbon catalyst.

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