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New Methods of Lignin Processing into Low Molecular Mass Organic Compounds and Nanoporous Materials

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Abstract

The development of high-tech methods for the utilization of lignins generated in vast amounts during industrial processes of deep conversion of lignocellulosic raw materials is a relevant task.

The paper considers new promising methods for the utilization of wood lignins and valuable chemicals production being developed at the Institute of Chemistry and Chemical Technology SB RAS, FRC KSC SB RAS.

Aromatic aldehydes and organic acids were obtained by catalytic oxidation of lignins with oxygen and hydrogen peroxide, liquid hydrocarbons – by catalytic conversion of lignins in supercritical alcohols medium.

During the thermal conversion of wood lignins in supercritical ethanol, there were achieved high yields of liquid products when using solid catalysts based on sulphated zirconium dioxide and high silica zeolites in the H-form. In supercritical butanol medium, SiO₂-supported Ni-containing catalysts showed high activities in the conversion of lignin into liquid products.

New methods of synthesis of nanoporous carbon materials from lignin, including carbon molecular sieves and aerogels with unique properties, were developed.

It was demonstrated that thermal-alkaline activation of lignin facilitated the development of the specific surface area to 2700 m²/g and total pore volume to 1.4 cm³/g in the resulting carbon materials. They had high sorption activity and were promising for gaseous mixtures separation and gas and water treatment.

There were proposed methods of synthesis of nanoporous organic and carbon aerogels on the basis of accessible and inexpensive lignin-containing composites, such as lignin-tannin-formaldehyde and lignin-phenol-formaldehyde ones. The resulting aerogels have wide potential application areas as thermal insulation materials, sorbents, catalysts, electrodes, and electrochemical capacitors.

Keywords: lignin, processing, products, aromatic aldehydes, liquid hydrocarbons, nanoporous carbon, aerogels

INTRODUCTION

The yearly increase in vegetable biomass greatly exceeds the annual human needs in fuel and chemicals. In principle, one may obtain the whole range of petrochemical synthesis products from vegetable biomass components, *i.e.* polysaccharides, lignin, and extractive matter [1].

In the near future, there is expected a significant increase in the use of chemicals produced from renewable vegetable raw materials due to the gradual depletion of the most valuable and easily accessible types of fossil fuels, *i.e.* oil and gas. The presence of enormous resources of wood raw materials in the Siberian region stimulates research on the development of more efficient preparation methods of di-

verse chemicals from biomass of wood species most common in Siberia.

Biomass of various wood species mainly comprises of cellulose, lignin, and hemicelluloses [2]. Cellulose is a linear polysaccharide built of components of glucose coupled between themselves by glycosidic bonds. Hemicelluloses are branched polysaccharides constructed of links of pentoses and hexoses. Lignin is an aromatic polymer of a branched structure, macromolecules of which are constructed of substituted phenylpropane moieties interlinked by ether and carbon-carbon bridges.

The development of high-tech methods for the utilization of lignins generated in enormous quantities during industrial processes of the deep processing of lignocellulosic raw materials is a relevant task [3].

In recent years, there has been extensive research on the development of techniques of the deep processing of lignocellulosic biomass into demanded chemical products [4–6].

The most promising of these include, as a key step, the fractionation of biomass into polysaccharides and lignin that are further converted into a variety of chemical products and liquid biofuels. The known methods of lignocellulosic biomass fractionation could be combined into two groups. In one of them, polysaccharides are removed by hydrolysis, and lignin is precipitated in the solid form; others include methods, in which lignin is dissolved, and polysaccharides remain as a solid residue.

Hydrolysis lignin refers to the first group, and alkali lignin and kraft lignin – to the second one. These lignins are significantly different from native lignins from wood according to their composition and structure. Organosolv lignins produced by organic solvent extraction of wood are less modified compared to native ones [7–9]. The former do not contain sulphur, which significantly expands the range of potential catalysts for their processing into low molecular mass products; in particular, liquid phenolic and aromatic hydrocarbons that may be used as components of motor fuels [5, 10].

The present paper summarizes the results of research carried out in recent years at the Institute of Chemistry and Chemical Technology SB RAS, FRC KSC SB RAS in the area of development of new efficient methods for processing lignin into low molecular mass organic compounds and nanoporous materials.

SYNTHESIS OF CHEMICALS BY CATALYTIC OXIDATION OF NATIVE LIGNINS

Peroxide oxidation of wood accompanied by preparation of microcrystal cellulose and organic acids

Wood cellulose mainly comprises of crystallites (ordered sections) interlinked by amorphous interlayers. Microcrystal cellulose is obtained by the removal of the amorphous portion of wood cellulose. Currently, microcrystal cellulose (MCC) is widely used in copper, pharmaceutical, food, chemical, cosmetics, and perfume industries due to such properties as non-toxicity, biocompatibility, the ability to biological degradation, high mechanical strength, and a large surface area [11, 12].

Traditional methods for the preparation of MCC from wood raw materials are multi-step and are based on the integration of environmentally hazardous processes of cellulose cooking and bleaching and acid hydrolysis of its amorphous portion [13].

Earlier, the authors described methods for one-step preparation of microcrystal cellulose. The techniques were based on oxidative delignification of deciduous and coniferous wood in hydrogen peroxide, acetic acid, and water, as medium, in the presence of sulphuric acid catalyst [14, 15] that were carried out at elevated temperatures (120–130 °C) and pressure. Recent papers suggested improved one-step processes, wherein suspended and environmentally safe TiO_2 catalyst was used as a catalytic agent for peroxide delignification of wood. It made it possible to obtain MCC from deciduous and coniferous wood under soft conditions (temperature of 100 °C and atmospheric pressure) [16–18].

Experimental and mathematical optimization of MCC preparation processes by peroxide catalytic delignification of sawdust of deciduous (aspen and birch) and coniferous (fir and larch) wood was carried out. There were determined the following optimum modes of MCC preparation with a yield of 36.3–42.0 mass % of absolutely dry wood: a temperature of 100 °C, atmospheric pressure, a concentration of H_2O_2 of 5–6 mass %, of acetic acid of 25–30 mass %, process modulus (liquid/solid ratio) of 10–15, and time of 2–3 hours.

It was found by IR, XPA, and SEM methods that the content and structure of cellulose samples produced under optimum conditions

of catalytic peroxidase delignification of aspen, birch, fir, and larch wood were similar to the composition of industrial microcrystal cellulose (Table 1).

According to electron microscopy data, microcrystal cellulose produced by aspen wood delignification comprises of microfibrils of different length. Some of them are combined into aggregates from 140 to 270 μm in length. The morphology of particles is in many respects similar to that of industrial microcrystal cellulose Vivapur, wherein the length of microfibril aggregates is 100–160 μm .

Thus, the developed catalytic method makes it possible to produce MCC samples from aspen, birch, fir, and larch wood in one step under soft conditions.

Concentrating waste liquor during peroxide delignification of wood followed by water addition thereto is not accompanied by the precipitation of the dissolved lignin. This points to its deep oxidation with generating low-molecular water-soluble substances. Hemicelluloses are precipitated when an excess of ethanol is added to waste liquor.

The composition of soluble products of lignin delignification using hydrogen peroxide was explored by GC-MS. It was found that alongside with hemicelluloses, they contained aromatic (4-hydroxybenzoic, 3-hydroxy-4-methoxybenzoic, and 4-hydroxy-3,5-methoxybenzoic) and aliphatic organic acids (fumaric, azelaic, and malic).

There were explored kinetic regularities of hydrogen peroxide depolymerization processes of native lignins from deciduous (aspen and birch) and coniferous (fir and pine) wood in $\text{CH}_3\text{COOH-H}_2\text{O}$ medium in the presence of a suspension of TiO_2 catalyst (Fig. 1 and Table 2).

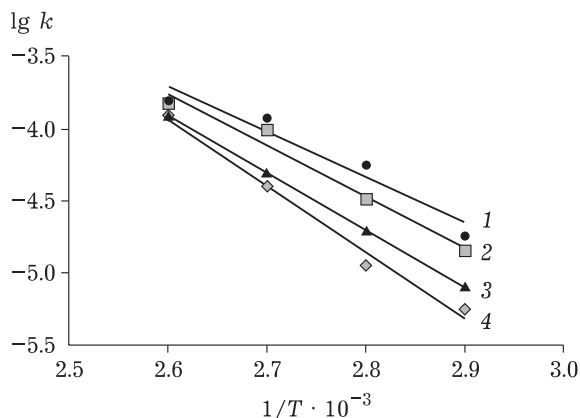


Fig. 1. Temperature versus rate constants of peroxide delignification of sawdust of different wood species in the presence of 1% TiO_2 catalyst (H_2O_2 – 5 mass %, CH_3COOH – 25 mass %, hydromodulus 15). 1 – aspen, 2 – birch, 3 – fir, 4 – pine.

Processes for hydrogen peroxide delignification of all explored tree species are properly described by first-order equations. Process activation energies vary between 76–94 kJ/mol (Table 2). However, hydrogen peroxide delignification of deciduous wood proceeds with a higher rate than of that of coniferous one, probably due to the fact that guaiacyl structural fragments of coniferous lignins are more tightly packed than deciduous lignins, wherein syringyl structures are prevailing.

As coniferous tree species contain more lignin than deciduous varieties do, a higher concentration of hydrogen peroxide is required for their deep delignification.

Sufficiently high values of activation energies point to the lack of significant diffusion limitations during catalytic delignification of sawdust by hydrogen peroxide under examined conditions.

TABLE 1

Chemical composition and crystallinity index (CI) of wood cellulose samples produced from different wood species under optimum conditions of peroxide delignification process

Wood	Composition, mass %			CI
	Cellulose	Lignin	Hemicellulose	
Fir	93.0	1.0	5.7	0.73
Larch	93.8	<1.0	4.5	0.70
Aspen	92.5	<1.0	5.4	0.68
Birch	93.7	<1.0	5.5	0.71
MCC Vivapur 101	94.8	<1.0	5.2	0.75

TABLE 2

Rate constants and activation energies of peroxide delignification processes of sawdust of different tree species in the presence of 1 % TiO₂ catalyst (H₂O₂ – 5 mass %, CH₃COOH – 25 mass %, hydromodulus 15)

Temperature, °C	$k \cdot 10^{-4}, \text{c}^{-1}$	Activation energy, kJ/mol
Aspen wood		
70	0.18	76
80	0.56	76
90	1.19	76
100	1.56	76
Birch wood		
70	0.14	82
80	0.32	82
90	0.98	82
100	1.49	82
Fir wood		
70	0.08	86
80	0.19	86
90	0.49	86
100	1.23	86
Pine wood		
70	0.07	94
80	9.20	94
90	0.62	94
100	2.17	94

Oxidation of wood by oxygen with synthesis of aromatic aldehydes

Aromatic aldehydes are valuable raw materials for pharmaceutical, food, and perfume industries [19, 20]. The presence of reactive functional groups in vanillin ensures an opportunity to produce derivatives with biological activity and antiseptic, bactericidal, and antioxidant properties therefrom [21]. In turn, syringaldehyde can be used for the production of Trimethoprim, Bactrim, Biseptol, and other pharmaceuticals [22].

Nitrobenzene oxidation of lignins allows reaching the aromatic aldehydes yield extremely close to theoretically possible from the standpoint of lignin structure [23]. Oxidation by molecular oxygen is more preferable in technological terms than with nitrobenzene, though less selective. This is primarily related to the significant contribution of side reactions of radical-chain oxidation [24].

Aldehydes yields during oxidation of lignins by molecular oxygen are increased when using certain catalysts [25]. It is found that the most active catalyst is a suspension of Cu(OH)₂. Vanillin is mainly formed during the catalytic oxidation of coniferous lignins containing guaiacyl structures. Foliate lignins containing syringyl and guaiacyl structures yield a mixture of syringaldehyde and vanillin during catalytic oxidation with O₂, wherein the first of the two is prevailing.

Native lignins from foliate species produce higher total yields of aldehydes (42–50 %) than coniferous lignins (20–27 %). An explanation of this fact lies in greater stability of syringyl fragments compared to guaiacyl ones both in processes of delignification and oxidation into aldehydes. The aromatic aldehydes yield passes through a maximum with increasing temperature and duration of catalytic oxidation of lignins with O₂.

The results of the undertaken research allow making recommendations on the selection of vegetable raw materials, most appropriate to produce vanillin, syringaldehyde, levulinic acid, and other valuable products.

To produce vanillin as the sole product, coniferous lignins are required. The most appropriate lignin-containing raw materials to manufacture vanillin may be lignins from enzymatic hydrolysis of coniferous wood, wherein to 10 mass % of product per raw may be produced [26]. This is one and a half times higher than the best indicators for the oxidation of lignosulphonates. In this case, vanillin can be obtained as a by-product of biobutanol production, in the same way as in sulphite cellulose manufacture technology.

It is preferable to produce syringaldehyde derivable in a mixture with vanillin during oxidation of lignins of foliate species from birch wood, as the latter has a better syringaldehyde/vanillin ratio compared to aspen [27].

Any scheme for wood complex processing oriented toward aromatic aldehydes should include the step of removal of hemicelluloses, which allows reducing the costs of reagents in catalytic oxidation step and obtaining furfural, 5-hydroxymethylfurfural, and levulinic acid as additional products. To process into levulinic acid 5-hydroxymethylfurfural from cellulose obtained during oxidation of wood into aromatic aldehydes, a wood species is not essential.

Technical lignins are not very suitable to produce syringaldehyde, except for enzymatic hydrolysis lignin [28]. Thus, from the standpoint of tech-

nological advantages, syringaldehyde should be produced during birch wood complex processing or catalytic oxidation of enzymatic lignins from foliate species.

Resulting from the research undertaken, efficient catalytic methods for oxidative fractionation of lignocellulosic biomass were developed and cellulose and low molecular mass organic products were obtained from lignin. Catalytic peroxide delignification processes allow fractionation of wood biomass onto microcrystalline cellulose, aromatic and aliphatic organic acids. Catalytic oxidation by molecular oxygen ensures an opportunity for fractionation of lignocellulosic biomass into cellulose and aromatic aldehydes. Products of oxidative fractionation of biomass can be used for the synthesis of other valuable chemical compounds: sugars, 5-hydroxymethylfurfural, levulinic acid, bioalcohols, etc. This allows reaching complex processing of the main components of lignocellulosic biomass into a variety of demanded chemicals.

SYNTHESIS OF LIQUID HYDROCARBONS BY CATALYTIC DEPOLYMERIZATION OF LIGNINS IN SUPERCRITICAL ALCOHOLS

A promising trend of the utilization of lignins is their catalytic depolymerization and the production of liquid fuels [5, 29].

Lately, there has been an increasing interest in the use of organosolv lignins isolated from wood by organic solvent extraction as research objects [30–33]. Unlike technical lignins, they are soluble and do not contain sulphur that poisons sulphur catalysts and other catalytic poisons. This allows broadening the range of the catalysts used and increasing their efficiency due to a significant decrease in the contribution of diffusion limitations that become apparent during catalytic depolymerization of solid technical lignins.

Efficient depolymerization of lignin may be carried out by its thermal conversion in lower aliphatic alcohols found in the supercritical state [34–36]. Selection of alcohols is driven by the fact that the values of their critical temperatures are lower or close to the optimum lignin thermal degradation temperature range. During thermal dissolution, alcohols not only extract lignin thermal fragmentation products but are also able to alkylate them, preventing secondary reactions of the formation of high

molecular mass compounds. Furthermore, bioalcohols are produced by wood hydrolysis process, the waste of which is lignin. This fact allows organizing *in situ* lignin processing without the use of additional reagents.

Resulting from the research undertaken, it has been found that the method of lignin isolation from wood has a significant effect on the value of its conversion and liquid products yield during thermal dissolution in supercritical ethanol medium (Fig. 2).

At a temperature of 400 °C and a pressure of 5 MPa, maximum conversion values (in 57.6 mass %) were reached when using acetic acid lignin. The highest yields of liquid products (38.9 mass %) were acquired for alkali lignin. Sulphuric acid lignin with the most condensed structure is the least reactive one.

During the thermal dissolution of ethanol-lignin in supercritical ethanol, process temperature has a substantial impact on the yield and composition of liquid, gaseous, and solid products [37]. Maximum liquid products yield appears at 280–300 °C.

It is found that solid acid catalysts enhance the lignin thermal dissolution process in supercritical ethanol and have an effect on the composition of the resulting liquid and gaseous products [38]. During thermal conversion of aspen wood lignin in supercritical ethanol medium, the highest yield of the fraction of liquid products boiling below 180 °C is reached in the presence of sulphated ZrO₂-based catalysts at 400 °C [39], and that of the fraction of liquid products boiling above 180 °C – for zeolite catalysts at 350 °C [40].

At 400 °C, sulphated ZrO₂-containing catalysts increase the degree of conversion of lignin into liquid and gaseous products by 1.5 times. Herewith, the yield of the fraction of liquid products boiling above 180 °C sharply increases and 1,1-diethoxyethane content in liquid products rises with a significant decrease in the content of phenol and its derivatives.

In the presence of a zeolite catalyst with the silicate module of 30, the maximum lignin conversion values (71 mass %) and the yield of the low-boiling (<180 °C) fraction of liquid products (44 mass %) are acquired at 350 °C. The use of zeolite catalysts during lignin thermal conversion is preferred, as gaseous products

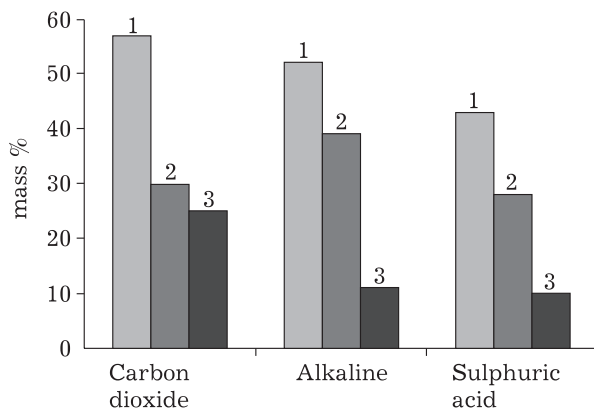


Fig. 2. Effect of lignin extraction method from aspen wood on conversion value (1), fraction yield of liquid products (2) and gas (3) during its thermal dissolution in ethanol at 400 °C and 5 MPa.

are generated in high yields over ZrO_2 -containing catalysts.

Liquid products of non-catalytic conversion of alkali lignin are mainly comprised of phenolic compounds, among which ethyl-substituted analogues and esters are prevailing. Apparently, they are produced resulting from reactions of alkylation by ethanol of lignin and its depolymerization products.

Sulphated ZrO_2 and $ZrO_2-Al_2O_3$ catalysts reduce the content of phenolic compounds in liquid products by 4.6 and 3 times, respectively, with simultaneous increasing the yield of aliphatic alcohols (mainly butanols) and 1,1-diethoxyethane. The phenolic portion of liquid products of lignin conversion over zeolite catalysts at 350 °C is mainly presented by methoxyphenol species of syringyl and guaiacyl types and their methyl and ethyl analogues.

During the non-catalytic conversion of acetone-lignin in supercritical ethanol at 300 °C, the yield of the hexane-soluble fraction of liquid products is 22 mass %. The NiCu/SiO₂ and NiCu-Mo/SiO₂ catalysts increase the yield of hexane-soluble products to 54.6 mass % under these conditions [41, 42]. Herewith, the total yield of liquid products of catalytic conversion of acetone-lignin sequentially extracted with hexane, diethyl ether, and acetone reaches 89 mass %. Re-use (to 3 cycles) of NiCuMo/SiO₂ catalyst during the thermal transformation of acetone-lignin does not result in worsening its catalytic properties.

As demonstrated by the results of the exploration of hexane-soluble products by GC-MS, they comprise of oxygen-containing com-

pounds, such as phenols, esters, and methoxybenzene derivatives. There is a decrease in the relative content of methoxyphenol species, in particular, syringol – from 8 to 14 times, under the action of Ni-containing catalysts.

Maximum liquid products yield of non-catalytic thermal transformation of pine ethanol-lignin (60 mass %) is reached at 300 °C. According to GC-MS data, ethanol-soluble products are mainly presented by derivatives of phenol and methoxyphenol and ethyl esters.

The use of catalysts based on borate-containing alumina ($B_2O_3-Al_2O_3$ and $NiO/B_2O_3-Al_2O_3$) during the conversion of ethanol-lignin in supercritical ethanol at 300 °C promotes an increase in the yield of liquid products boiling below 180 °C by over 3 times compared to the non-catalytic process. Herewith, there is a slight decrease (from 59 to 45–48 mass %) in the yield of liquid products boiling above 180 °C (Fig. 3).

The use of catalysts based on borate-containing alumina during the thermal transformation of pine ethanol-lignin results in an increase of the content of methoxyphenol species therein by 1.4–1.7 times. The maximum yield of methoxyphenol compounds is produced in the presence of NiO/ $B_2O_3-Al_2O_3$ catalyst.

An opportunity to combine processes of extraction of ethanol-lignin from wood followed by its depolymerization with the involvement of solid catalysts with generating liquid products has been demonstrated.

It is found that the combined mechanochemical activation of aspen wood and a zeolite catalyst leads to a drastic decrease in particle size of mixture constituents, decomposition of the main structural components of wood, dispersive catalyst distribution along wood surface, and an increase in the degree of aspen wood conversion during thermal transformation in supercritical ethanol medium [43]. At 270 °C and 6.4 MPa, zeolite catalysts increase the yield of liquid products with BP above 180 °C by 2.3–2.5 times and the content of furan derivatives in them compared to the non-catalytic process [44].

A zeolite catalyst with a Si/Al ratio of 30, notable for an elevated concentration of acid sites, demonstrates the highest activity in generating liquid products. The pressure increase from 6 to 17 MPa at a process temperature of 270 °C increases the yield of the hydrocarbon fraction with BP above 180 °C by 2 times and reduces the output of the fraction with BP below 180 °C by 1.5 times (Fig. 4).

Liquid products obtained at wood thermal conversion temperature of 270 °C are mainly presented by compounds formed from wood polysaccharides: furfural, 5-GMF, levulinic acid, and organic acid ethyl esters. The solid residue of thermal conversion of aspen wood at 270 °C mainly contains cellulose and lignin.

Thus, at a temperature of 270 °C, high-silica zeolite catalysts allow fractioning wood biomass in supercritical ethanol onto lignocellulose and soluble organic products from hemicelluloses. At an elevated temperature (350 °C), the yield of soluble products decreases due to the intensification of secondary reactions of their transformation into gases and coke.

A possible mechanism of thermal conversion of the mechanically activated aspen wood in supercritical ethanol medium involves stages of hemicellulose depolymerization and lignin extraction from wood as soluble ethanol lignin. Soluble organic products initially formed undergo further catalytic transformation into a mixture of liquid hydrocarbons.

SYNTHESIS AND PROPERTIES OF NANOPOROUS CARBON MATERIALS FROM LIGNINS

Preparation of nanoporous carbon materials by thermo-alkaline carbonization of lignin

The production of porous carbon materials (PCM) is one of the large-tonnage trends of the

utilization of lumbering and wood processing wastes. Lately, there has been a growing interest in the preparation of nanoporous carbon materials (NPCM) that are able to show molecular-sieve properties [45, 46].

To produce NPCM, methods of chemical activation of initial raw materials based on the introduction of chemical additives therein followed by carbonization in an inert medium are effective. Such compounds as alkali metal hydroxides, carbonates, or oxides; H_3RO_4 , etc. are used as chemical promoters [47, 48].

The mechanism of action of alkali additives lies in the intensification of dehydration/dehydrogenation reactions and intermolecular bonding, which ultimately results in condensation of aromatic fragments.

Oxygen-containing functional groups of lignin play a crucial part in the development of porosity during subsequent alkaline activation. It is assumed that they interact with alkali to form alkali metal phenolates and carboxylates. The latter undergo thermal decomposition and gaseous compounds (CO_2 , CO , etc.) promoting the development of the porous structure of carbon materials are formed [49, 50].

We have explored conditions for alkaline carbonization of lignins isolated from wood via diverse methods versus the structure and sorption properties of the resulting NPCM.

It is found that ethanol-lignin and alkali lignin from fir are significantly different accord-

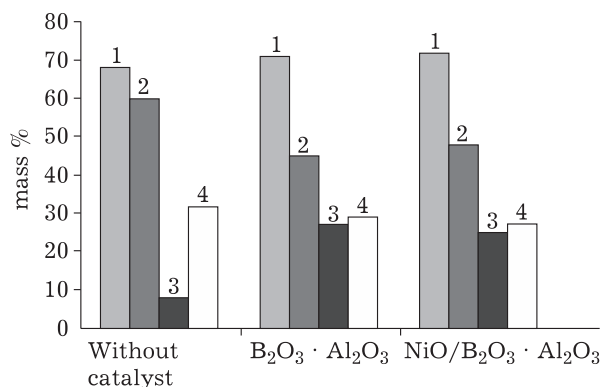


Fig. 3. Effect of catalysts on conversion (1) and yield of liquid fractions boiling above 180 (2) and below 180 °C (3), and solid (4) products of conversion of pine ethanol-lignin in supercritical ethanol at 300 °C.

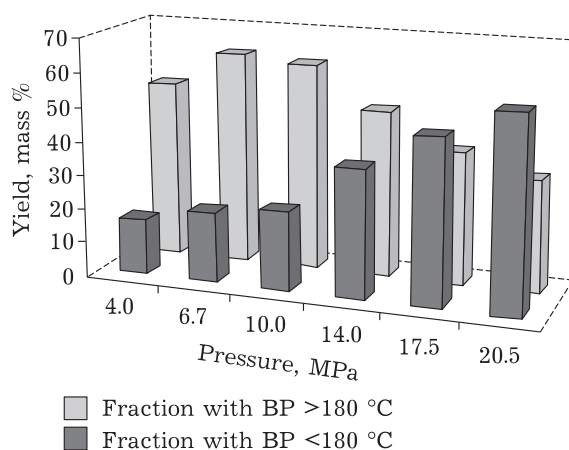


Fig. 4. Effect of ethanol pressure on yields of light-boiling and high-boiling fractions of liquid products formed during aspen wood conversion at 270 °C in the presence of zeolite catalyst with Si/Al ratio of 30.

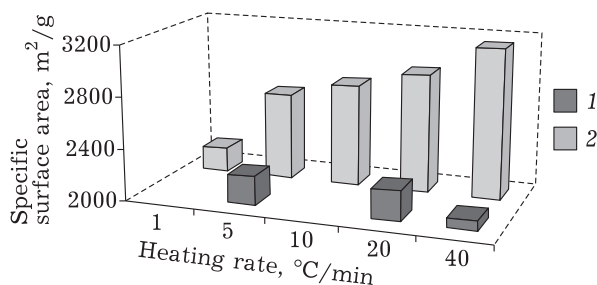


Fig. 5. Effect of heating rate on specific surface area of nanoporous carbon materials (NCM) of alkali lignin and fir ethanol lignin.

ing to their thermochemical properties. The specific surface area of NPCM from ethanol lignin increases from 2191 to 3157 m²/g, and pore volume – from 1.04 to 1.92 cm³/g with heating rate increase during carbonization from 1.04 to 1.92 cm³/g. The specific surface area and pore volume of the resulting NCM for alkali lignin are weakly dependent on heating rate during carbonization (Fig. 5).

For samples of NPCM made of alkaline lignin and ethanol lignin, the regions of micropores and ultramicropores are characterized by a single peak with a maximum of 0.78 nm. However, the region referring to thin micropores (from 2.0 to 4.0 nm) is characterised by the maximum differences. Heating rate increase during carbonization for NCM produced from alkali lignin results in developing wide pore size distribution with a maximum near 2.5 nm.

The heating rate increase for NPCM obtained from ethanol-lignin is accompanied by the formation of mesopores with three apparent maxima that correspond to widths of 2.15, 2.51, and 3.31 nm. Moreover, with the heating rate increase, there is a shift of maxima of the resulting mesopores towards increasing their size.

The sorptive capacity for benzene (in 1.41 g/g) of lignin-derived NCM is several times higher than the capacitance of industrial carbon sorbents.

Synthesis of porous aerogels using lignin

Lignin has good prospects in preparation of aerogels, i.e. a new class of porous materials, with a wide potential for the use in various fields [51, 52]. Aerogel-type materials are usually obtained by sol-gel resin polymerization followed by the solvent exchange in gel pores and drying to obtain the final porous product. Upon preparation of aerogels, phenol resins, such as resorcinol-formaldehyde ones are widely used [53].

Natural polymers from renewable resources containing phenolic monomers may be used as a substitute for resorcinol and phenol. Lignin is regarded to be a potential source of phenols and may be used as a substitute for toxic and expensive raw materials to prepare organic and carbon aerogels.

In previous works, performed with the participation of the authors [54, 55], for the first time, there were synthesized aerogels with lignin content in 90 mass %. There was determined a significant effect of lignin content and drying method (extraction by supercritical CO₂ and sublimation drying) on physical and structural properties of lignin-phenol-formaldehyde aerogels. It was found that lignin content increase in the reaction mixture led to a decrease in density and an increase in the porosity of aerogels. Aerogel samples dried under supercritical conditions have a lower density and higher porosity than those dried by lyophilic drying (Fig. 6).

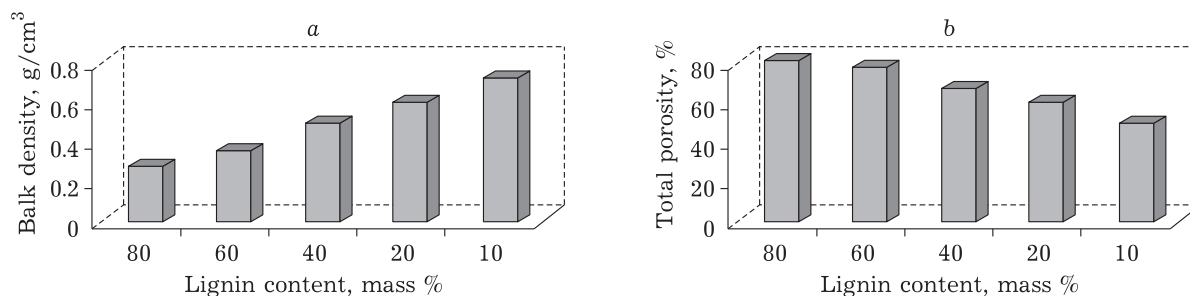


Fig. 6. Density (a) and total porosity (b) of lignin-phenol-formaldehyde aerogels with different lignin contents.

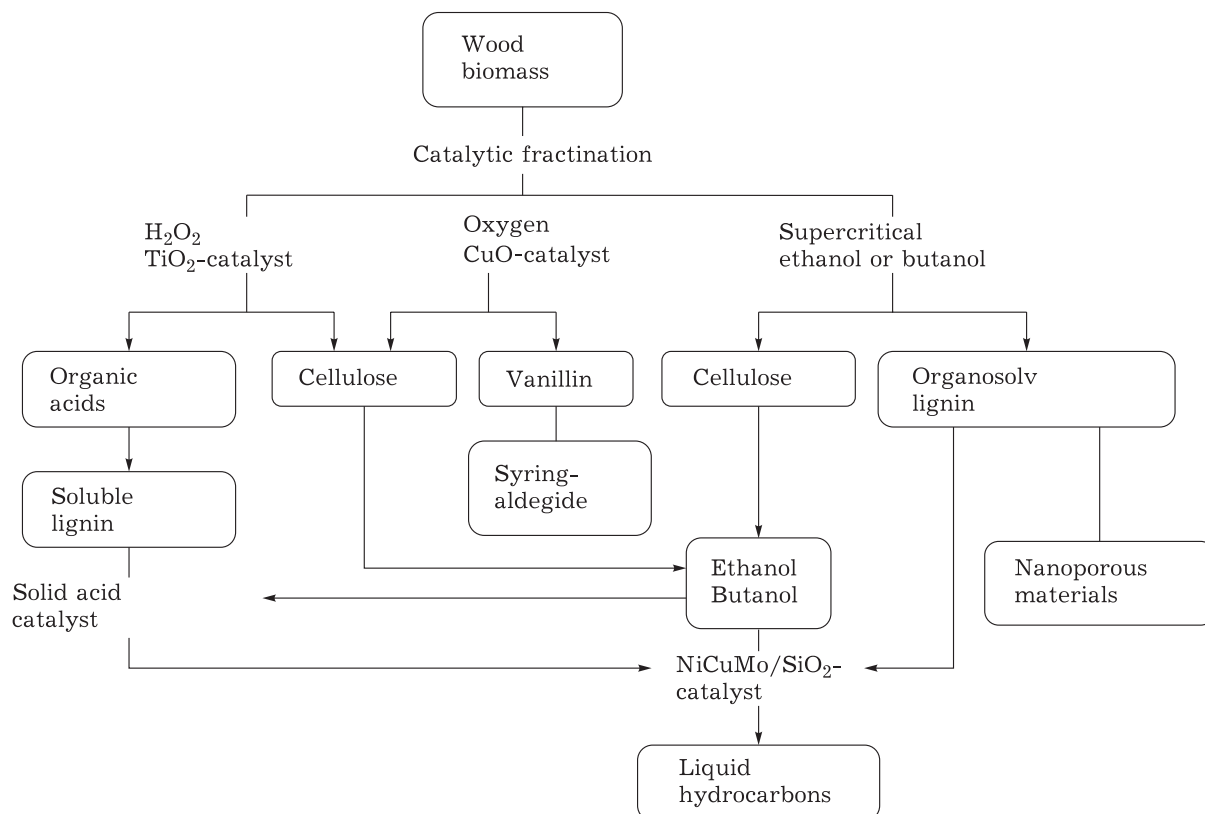


Fig. 7. Scheme for green biorefining of wood biomass based on integrated processing polysaccharides and lignin.

The values of specific pore volume for the organic gels under study vary within 0.4–3.6 cm³/g. Herewith, the specific surface area value is changed in the 120–490 m²/g range. It is found that the area of surfaces of gels passes through a maximum with lignin content increase from 10 to 80 mass %. Moreover, the specific surface area of gels obtained by lyophilisation is higher in all cases than that of samples produced using supercritical drying.

Lignin-derived aerogels have a porosity of about 80 % and thermal conductivity in the 0.040–0.045 W/(m · K) range, close to heat conductivities of thermal insulating materials, such as polystyrene foams.

It is proposed to synthesize organic gels by polycondensation reactions of formaldehyde and polyphenols from larch bark, and also from their mixtures with lignosulphonates [56]. To produce gels, there were used polyphenols isolated by extraction of larch bark with ethanol or 0.5 % water solution of NaOH. Polyphenolic substances in larch bark mainly comprise of condensed pyrocatechin tannins with an average molecular mass of 1680 Da, the content

of which was 11–13 mass % (per absolutely dry bark.) Lignosulphonates produced during the industrial process of sulphite delignification of spruce wood were used as lignin additives. There was used the following composition of lignosulphonates, mass %: S 48.4; H 5.24; S 5.5; N 0.5, an ash content of 15.4, the average molecular mass of 50 kDa. An opportunity to adjust the porous texture of polymer gels based on ethanolic extracts of polyphenols from larch bark has been determined by the variation of the pH of the initial polyphenols/formaldehyde mixture. Conditions for the production of gels with a specific surface area of 477 m²/g and a narrow mesopore size distribution have been determined.

It is found that lignosulfonate additives have an effect on the formation of the porous structure of condensation products of polyphenols with formaldehyde. The introduction of lignin in an amount of 10 mass % to polyphenols from larch bark improves the quality of the resulting organic and carbon gels, namely, increases their specific surface area and total porosity, and enhances elasticity and strength.

However, lignin content increase in the mixture to 20–30 mass % reduces the total porosity and the total volume, and also reduces the strength and adsorption properties of the gels.

Thus, the results of the undertaken research demonstrate opportunities for the successful application of enormous inexpensive resources of lignins and wood bark to produce organic and carbon aerogels with a given set of properties.

CONCLUSION

Currently, there have been intensively explored integrated processes of lignocellulosic biomass complex processing (biorefining) into biofuels (mainly into bioethanol and biobutanol) and chemical products based on the use of catalysts and green reagents [57–62].

The integration of the new methods of conversion of wood lignin and conventional bioalcohol synthesis from the cellulose component of wood described in the paper would allow reaching wood biomass complex processing into valuable chemical products. This is based on the use of green chemicals (water, oxygen, hydrogen peroxide, acetic acid, and alcohols) and non-toxic solid catalysts (TiO_2 , CuO , zeolites, and NiCuMo/SiO_2 (Fig. 7).

Chemicals (cellulose, organic acids, aromatic aldehydes, liquid hydrocarbons, and nanoporous materials) obtained from components of renewable woody biomass may replace various products of industrial petrochemical synthesis in the near future.

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