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Integrated transformations of plant biomass to valuable chemicals, biodegradable polymers and nanoporous carbons

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Abstract
Integrated transformations of wood biomass to valuable chemicals and materials are described. They include the main biomass components separation, the conversion of cellulose to glucose, levulinic acid, biodegradable polymers and lignin – to nanoporous carbons. For wood fractionation on pure cellulose and low molecular mass lignin the methods of catalytic oxidation and exploded autohydrolysis are used. The processes of acid-catalysed hydrolysis of cellulose to glucose and levulinic acid were optimized. New methods of biodegradable polymers synthesis from lactone of levulinic acid and nanoporous carbons from lignin were suggested.

1. Introduction
Plant biomass annual stock addition significantly exceeds the yearly demands of a mankind in the fuels and chemical products [1].

Russia has around 23 % of world forest resources which can serve as a relevant source of raw material for production of a big variety of needed chemicals, materials and alternative fuels.

Wood biomass contains 40–50 % of cellulose, 15–30 % of hemicelluloses and up to 30 % of lignin [2]. Cellulose is a linear polymer, constructed from C6H10O5 units. Hemicelluloses are branched polysaccharides, containing C5–units with shorter chains as compared to cellulose. Lignin is non-regular polymer of aromatic nature composed of phenylpropane fragments.

Traditional industrial technologies of wood deep processing are inefficient and dangerous for the environment and they give only the limited range of products. Perspective directions in the development of innovative technologies of plant biomass processing to valuable products are connected with a design of integrated processes which ensure the total utilization of all main components of a biomass.

In this paper some results of study the integrated transformations of wood components to valuable chemicals, biodegradable polymers and nanoporous carbon materials are presented.
2. Experimental

Air–dry sawdust (fraction 2–5 mm) of Siberian origin wood: aspen (Populus tremula L.), birch (Betula pendula Roth.), abies (Abies sibirica Ledeb.), larch (Larix sibirica Ledeb.) were used as the initial raw materials. The chemical composition (% wt. on abs. dry wood) of aspen wood: 46.3 cellulose, 21.8 lignin, 24.5 hemicelluloses, 7.8 extractive substances; birch wood: 41.3 cellulose, 19.9 lignin, 30.3 hemicelluloses, 8.4 extractive substances; abies wood: 50.3 cellulose, 27.7 lignin, 15.4 hemicelluloses, 6.8 extractive substances; larch wood: 34.5 cellulose, 26.1 lignin, 27.2 hemicelluloses, 13.0 extractive substances.

Method of catalytic oxidation by hydrogen peroxide was used for the fractionation of wood biomass on cellulose and low molecular mass lignin. The delignification medium was composed of acetic acid, hydrogen peroxide, sulphuric acid catalyst and distilled water.

Oxidative delignification of wood sawdust with 2 % mas. of H$_2$SO$_4$ catalyst was carried out in metal shaking reactor of 200 cm$^3$ volume at variation of temperature, process time, liquid/wood ratios, concentrations of CH$_3$COOH, H$_2$O$_2$ and catalyst. Such parameter as a residual lignin content in cellulosic product of wood delignification was used to evaluate the delignification activity of catalyst. The yield of cellulosic product was estimated by weight method.

The exploded autohydrolysis of wood by overheated steam was carried out in experimental installation with stainless reactor of 800 cm$^3$ volume at temperatures 187 –240 °C, pressure 1.2 –3.4 MPa [3]. Wood sawdust were heated at 105 °C and then loaded in the heated reactor. The overheated steam was injected into the sealed reactor. The duration of steam treatment was 1–5 min. and then the pressure was dropped through a spherical stopcock. This treatment resulted in transformation of initial wood cheaps to fibrous material.

The contents of cellulose and lignin in cellulosis products were determined by standard chemical analysis. The structural characteristics of cellulose were studied by FTIR (Vector–22, Bruker) and γ–ray (Dron–4) methods.

Nanoporous carbon materials were synthesized by alkaline thermal activation of lignin and cellulose. The mixture of air–dried raw material (fraction 0.25–1.0 mm) was placed into a horizontal reactor made from stainless steel and was subjected to pyrolysis in argon atmosphere. The procedure of a thermal treatment included the nonisothermic heating of sample up to 800 °C with the rate 5 °C/min and the isothermic soaking at final temperature during 1 hour. Thermally treated samples were washed by water, then treated by 0.5 M HCl, washed again by water at 50 °C and dried at 100-105 °C up to the constant weight.

The texture characteristics of porous carbons were measured by BET method (N$_2$ adsorption at 77 K) using ASAP 2420 V2.02J and Soptometer–M.

Hydrolysis of cellulose to glucose was carried out with 60–80 % sulfuric acid at 25 °C, liquid to solid ratio 3–5 and time 1–2 hours, with following inversion of hydrolyzate at 100 °C, liquid to solid ratio 30–40 during 1–2 hours. Then the solution of glucose was neutralized by Ca(OH)$_2$ and purified by active carbon. The content of C$_6$– and C$_5$–sugars in hydrolyzates was measured by photocolorimetric method with o–toluidine blue at 355, 460, 630 nm.

The conversion of cellulose to levulinic acid (LA) was accomplished at autoclave conditions at temperature 200–250 °C. The cellulose was impregnated by sulfuric acid catalyst (5 % mas.). Synthesis of LA from glucose, fructose and sucrose was carried out at 98 °C and atmospheric pressure in the presence of acid catalysts HCl, H$_2$SO$_4$, H$_3$PO$_4$.

Angelicalactone was obtained from levulinic acid in vacuum still at 67–72 °C, 3.3 Pa and was purified by fractional melt crystallization.

Polyesterification of angelicalactone was carried out in the presence of sodium butylate and sodium hydroxide at temperatures 25–122 °C. Molecular weights of the obtained polymers were estimated by
viscosimetry method. The chain–length distribution was determined by phase–reversal chromatography with the use Nova-Pak CIS column, octadecyl–coupled silica gel sorbent; vaporizing light scattering detection device, model 500 (Alltech Corporation, USA). 1H NMR spectroscopy was also used for study the polymers structure.

Biodegradation ability of the obtained polymers was estimated by liveweight gain of cultures of microorganisms Sacharomices cerevisae, Streptomyces chrysomallus and Streptomyces lividans and by detection of polymers mass decreasing.

3. Results and discussion

The study of integrated transformation of wood sawdust to cellulose, glucose, levulinic acid, biodegradable polymers and nanoporous carbons was accomplished according to the scheme, presented in figure 1.

![Figure 1. Scheme of integrated transformations of wood to valuable chemicals and materials](image)

The first stage of studied integrated transformations is the wood separation on cellulose and low molecular mass lignin. The following methods of wood separation were compared: catalytic oxidation by hydrogen peroxide in acetic acid–water medium and exploded autohydrolysis with overheated water steam.

The complete separation of wood biomass on cellulose and soluble lignin was realized by catalytic oxidation with hydrogen peroxide in acetic acid–water medium in the presence sulfuric acid catalyst.

It was found that the growth of oxidation process temperature from 110 to 140 °C increases the cellulose content and degreases the lignin concentration in cellulosic product. At the same time, the yield of cellulosic product decreases because the oxidative destructions of lignin and polysaccharides are accelerated with temperature. Similar effects were observed when the initial hydrogen peroxide concentration is increased from 2.0 to 10.2%. The optimal conditions of aspen–wood and birch–wood oxidation were found, which supply the rather high yield of cellulose (48–50 % relative to a. d. wood) with very low content of residual lignin (0.3–0.4 % mas.): temperature 120–130 °C, H₂O₂ concentration 4–6 % mas., H₂SO₄ concentration 2 % mas. In order to obtain high–quality cellulose from abies or larch wood, which contain more lignin than aspen or birch wood, it is necessary to use the more active catalysts, such as TiO₂ and H₂MoO₄ [4].
The process of high temperature hydrolysis of wood cellulose by diluted mineral acids is used in industry and it demands the low expenses of acid catalyst. But the low-temperature hydrolysis of cellulose by concentrated acids has its own advantages: higher yield of glucose and possibility to carry out the hydrolysis process at atmospheric pressure.

The data on hydrolysis of cellulose from aspen wood with concentrated sulfuric acid are presented in table 1.

**Table 1.** Influence the conditions of aspen cellulose hydrolysis and inversion stages on the yield of glucose.

<table>
<thead>
<tr>
<th>Concentration of H₂SO₄, %</th>
<th>Hydrolysis</th>
<th>Inversion*</th>
<th>Yield of glucose, % **</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Liquid to solid ratio</td>
<td>Temperature, °C</td>
<td>Time, h</td>
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<tr>
<td>80</td>
<td>5</td>
<td>20</td>
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</table>

* hydrolysis of oligosaccharides obtained at the first stage of cellulose hydrolysis, ** from mass of a.d. cellulose

Obtained solutions have no C₅-sugars, which inhibit the fermentation of glucose to alcohols, lactic acid, polyhydroxyalcanoates etc.

The effective methods of lignin depolymerization and hemicelluloses removal from wood is the short-time treatment of wood with overheated water steam with following fast drop of the pressure (exploded autohydrolysis) [5].

The significant reduction of hemicelluloses concentration was observed after aspen wood treatment at 220 °C at conditions of exploded autohydrolysis (Figure 2).

**Figure 2.** Content of hemicelluloses in aspen wood, autohydrolyzed at 187 °C (A) and 220 °C (B)

The same results were obtained after treatment of birch wood, abies wood and larch wood. The optimal conditions of wood autohydrolysis were selected (220–230 °C, 3 min) which allow to obtain solution of glucose with concentration of C₅-sugars less 1 %. C₅-sugars are completely absent in solutions of glucose obtained via stages of autohydrolysed wood catalytic oxidation to cellulose and of subsequent cellulose hydrolysis by concentrated H₂SO₄.
The other valuable product of acid-catalyzed conversions of carbohydrates is levulinic acid (LA). The high-temperature and low-temperature methods are used for LA synthesis. In the presence of sulfuric acid catalyst the highest yield of LA from cellulose reaches 35–40 % mas. at 240 °C.

The relative reactivity of different carbohydrates at 98 °C decreases in the order: fructose > sucrose > inulin > glucose > cellulose. Glucose is of 20–40 times less reactive, than fructose, and cellulose is of 30 times less reactive, than glucose.

In glucose conversion to LA the hydrochloric acid is twelve times more active, than sulfuric acid, but the selectivities of the LA formation are practically the same in both cases. In the presence of phosphoric acid catalyst the maximum yield of levulinic acid does not exceed 5 mol. %, and the rate of process is low.

Lacton of LA (α-angelicalactone) is an attractive substance for syntheses the new types of biodegradable polymeric materials.

There are two possible ways of angelicalactone polymerization: – disclosing of an olefinic linkage with formation of a polyfuranone and disclosing of the lactone cycle with formation of a polyester.

Polyesterification of angelicalactone is the most interesting way for producing of new biologically compatible polymers [6].

Polyesters of alpha-angelicalactone were obtained with the use of alkali based catalysts – sodium butylate and NaOH. The obtained polymers are light yellow resins or solids, water-insoluble and soluble in polar organic solvents. Molecular weight of the obtained polymers is up to 2000 amu.

According to 1H NMR spectroscopy data the polymer of alpha-angelicalactone is a polyester having the "head to tail" structure. The part of polyester intermonomeric bonds in the obtained products of polymerization reaches 68–80 %.

The obtained polymers are exposed to full biodegradation by microorganisms Sacharomices cerevisae during 5–15 day, and by Streptomyces lividans and Streptomyces chrysomallus - during 20–30 day.

For producing the nanoporous carbons from various type of carbon-containing raw materials the different methods of alkaline thermal activation are used [7]. It was found that the melted sodium hydroxide and potassium hydroxide promote the significant development of nanoporous structure of carbon materials from lignin and cellulose.

Such characteristics of obtained nanoporous carbons as a specific surface area, the volume and size of pores are depend on the nature of initial raw material and alkali, ratio raw material/alkali and temperature of thermal treatment.

The specific surface area of nanoporous carbons, obtained by alkaline thermal activation of cellulose and lignin in melted KOH goes through a maximum with the increase of ratio KOH/raw material (Fig. 3). Maximal surface area of carbons from cellulose (1170 m²/g) corresponds to the content of KOH in a mixture of 67 % mas. In the case of lignin the maximal surface area (2035 m²/g) of obtained carbons corresponds to KOH content 75 % mas.
Nanoporous carbon materials obtained by alkaline thermal activation of cellulose and lignin have high sorption activity to hydrogen (sorption capacity 3 % mas. at 77 K and 5 MPa H₂), to volatile organic compounds (hexane, CHCl₃, benzol, butanol etc.). Also they are able to separate the mixtures He–CH₄, H₂–CH₄ (separation factor 3.6–3.8).

4. Conclusion
As a result of the accomplished study, the integrated process of wood biomass conversion to cellulose and low molecular mass lignin with their subsequent transformations to glucose, levulinic acid, biodegradable polymers and nanoporous carbons was developed. For the each stage of developed integrated process the optimal reaction conditions were selected which allow to produce the target product with the high yield and with the required characteristics.

5. References