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Effect of Different Activation Methods on the Composition, Structure and Reactivity of Aspen Wood

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Abstract

An effect of different methods for aspen wood activation (grinding in the mills of different types, explosive autohydrolysis, catalytic oxidation by hydrogen peroxide and the combination of these methods) exerted on the structure, chemical composition and reactivity of activated wood was studied. It has been found that all the methods of aspen wood mechanical pretreatment result in changing the supramolecular structure, chemical composition and reactivity thereof: activated samples exhibit increasing the content of readily hydrolysable polysaccharides, with reducing the concentration of polysaccharides difficult to hydrolyze and of residual lignin, as well as with increasing the rate of polysaccharide acidic hydrolysis into monosaccharides and the rate of lignin oxidation by hydrogen peroxide.

Key words: aspen wood, mechanical activation, explosive autohydrolysis, catalytic oxidation, structure, composition, reactivity

INTRODUCTION

Permanently renewable resources of lignocellulose biomass in the form of wood, a variety of wood and agricultural wastes represent an almost inexhaustible source of raw materials for the production of demanded chemicals, materials and biofuels [1, 2].

In Russia, the most common type of plant raw material is presented by wood, whereof at the present time one obtains a fairly limited range of products at the pulp and paper mills, hydrolytic and wood-chemical enterprises.

Available industrial technologies for delignification, hydrolysis, extraction, pyrolysis and gasification of wood raw material do not meet modern requirements for energy efficiency and environmental safety.

Improving the processes of deep processing the lignocellulose biomass is being performed *via* different directions [3, 4]. The productivity of technologies for deep processing solid organic materials is usually limited by the processes of mass transfer, whose negative impact could be minimized *via* finely grinding the wood in the mills of various design [5, 6].

Improving the efficiency of deep processing the lignocellulose biomass could be achieved by means of mechanical and chemical activation thereof. This causes increasing the reactivity of biomass to facilitate its separation into such components as polysaccharides and lignin. In the latter case, of particular interest is the use of so-called green reagents those are safe for the environment.

As the reagents, one applies steam, oxygen, hydrogen peroxide, etc. In particular, a short-term activation of lignocellulose biomass with superheated steam and the subsequent rapid decrease of steam pressure (so-called explosion autohydrolysis) facilitates the separation of the activated wood into cellulose and low-molecular lignin [7, 8]. A more efficient separation of wood into cellulose and low-molecular lignin can be achieved by means catalytic oxidation thereof with hydrogen peroxide in the environment of acetic acid-water [9].

The aim of this work to study the influence of different methods of activation aspen wood structure, chemical composition and reactivity of activated wood.

EXPERIMENTAL

As a raw material we used aspen wood. Wood samples were cut from the middle part (in length) of five trunks of mature trees harvested in the vicinity of Krasnoyarsk. The samples were ground down to a size less than 10 mm, paddled thoroughly and dried at 100 °C to obtain the moisture content of less than 1 mass %. The tests performed according to standard methods [10] demonstrated that the wood has the following composition (in % as calculated for the mass of solid dry wood): cellulose 46.3, lignin 20.4, hemicellulose 24.1, water-soluble substances 3.6, resins 0.9, extractive substances 4.3, ash 0.5.

Mechanical wood processing

Before mechanical treatment by different methods the wood under investigation was additionally grinded to obtain the particle size less than 0.5 mm. The resulting sample was mixed with distilled water in the proportions required immediately before the treatment.

The cutter grinding was carried out using a LDM-74 disk-type mill for 30 min at the concentration of wood in aqueous suspension amounting to 1.8 mass %.

The jet grinding was performed using a laboratory-scale set-up, wherein the aqueous suspension containing 1.8 mass % of wood under a pressure of 16 MPa was fed during 15 min through a nozzle of 2 mm in diameter to a milling cutter with the velocity amounting up to 145 m/s.

The mechanical activation was carried out in an AGO-2 centrifugal activator at the acceleration value of 60*g* with the process duration of 30 min. The concentration of the wood aqueous suspension was equal to 8 mass %.

The vibration grinding was carried out using a VCA-2 vibration-type stand for 15 min, the aqueous suspension concentration was equal to 8 mass %.

After the completion of mechanical treatment, the products obtained were filtered. The filter residue was washed with distilled water, dried, with further determining the yield thereof. In the solid product we determined the content of readily hydrolyzed polysaccharides (RHPS), difficultly hydrolyzed polysaccharides (DHPS) and the Klasson lignin by means of standard methods described in [10, 11]. For the aqueous fraction obtained after the filtration of the wood suspension resulting from mechanical treatment, we determined the content of reducing substances [11].

Wood activation by explosive autohydrolysis

Activation of grinded aspen wood (5–10 mm fraction) by means of explosion autohydrolysis was carried out using a set-up operating in a periodic mode described in [12, 7], within the temperature range of 180–240 °C, at the saturated vapor pressure ranging within 1.0–3.3 MPa. To a reactor with the capacity of 0.8 L preliminary heated to a predetermined temperature, was loaded grinded wood. The reactor was sealed to feed with heated water vapor from a vapor storage unit. After holding for 3–4 min, we performed rapid depressurization with a "shot" of autohydrolyzed wood from the reactor through an opened ball valve into a receptacle. Then the autohydrolyzed wood was extracted with hot water at a temperature of 100 °C, at the water duty value equal to 50 during 3 h in order to remove water-soluble substances.

Obtaining the microcrystalline cellulose from autohydrolyzed wood

For obtaining microcrystalline cellulose (MCC) we exposed the autohydrolyzed wood to oxidative delignification in an environment of the system such as acetic acid, sulphuric acid, hydrogen peroxide water, sulphuric acid catalyst in a stainless steel reactor as described in [13]. The resulting MCC was separated from the solution by means of filtration, washed with distilled water until obtaining neutral pH of washing waters, dried at 103 °C.

The content of residual lignin in the MCC obtained as well as the moisture and ash content were determined by means standard methods described in [11].

The MCC polymerization level (PL) was determined with the use of sodium iron tartrate complex in accordance with the State Standard GOST 25438-82 by means of a VPZh-3 capillary viscometer as described in [11].

Studying the structure of wood and cellulose products obtained

The structure of the original and activated wood and cellulose products obtained was examined using the methods of XRD, IR and scanning electron microscopy (a Hitachi TM-1000 electron microscope).

XRD profiles were obtained using a DRON-3M diffractometer, CuK_α radiation, within the range of angles $2\theta = 5-55°$. Processing the profiles of diffraction peaks was performed using a New-Profile software package. The crystallinity index was calculated in accordance with the procedure described in [14].

IR spectra were registered using a Bruker Vector 22 FT-IR spectrometer. The processing of spectral information was carried using an OPUS/YR software package (version 2.2). Solid samples for analysis (3 mg) were prepared in the form of pellets in KBr matrix.

RESULTS AND DISCUSSION

Effect of aspen wood mechanical treatment on the properties thereof

According to scanning electron microscopy, the mechanical pre-treatment of aspen wood in the devices of cutter, jet and vibratory grinding as well as mechanical activation in an aqueous medium is accompanied by the deformation and partial destruction of the main mechanical wood tissue with simultaneous dispersing the substructure components. The most significant changes were observed in the course of mechanical activation in an AGO-2 centrifugal activator: cell wall deformation, splitting and disruption occurs, with a partial fibrillation of fiber bundles.

According to XRD data (Fig. 1), the mechanical activation of aspen wood results in a decrease in the intensity and peak width increase for the peaks with the index equal to 002. The width X-ray diffraction lines depends on the size of the crystallinity regions (areas of coherent scattering): the larger the size of these areas, the narrower is the peak in the XRD profile. The quantitative indicator is the ratio between the peak intensity and the half-width thereof.

The crystallinity index of original aspen wood calculated from the XRD profiles is equal to 0.50, the average crystallite size being of 4.69 nm. The activation of wood samples in AGO-2 at the water duty value equal to 12.5 is accompanied by increasing the crystallinity index up to 0.68 and the crystallite size up to 4.71 nm (as calculated according to Scherrer).

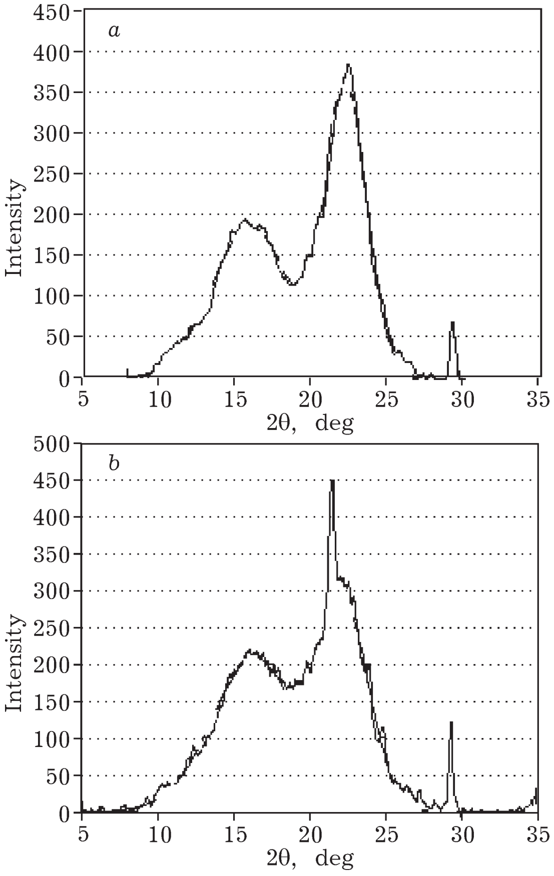

Fig. 1. XRD profiles of original (*a*) aspen wood and mechanically treated one in an AGO-2 mill for 30 min at water duty value equal to 6 (*b*).

The observed changes could be, to all appearance, connected with the dissolution of a part of amorphous wood component in water in the course of activation.

The mechanical wood processing has a significant impact on the chemical composition thereof. All the methods of mechanical activation used result in increasing the content of RHPS in the samples as well as in reducing the content of DHPS and residual lignin therein. The character of changing the chemical composition of mechanically activated aspen wood due to acidic hydrolysis is demonstrated in Fig. 2.

At the same time, the yield of water-soluble and reducing substances exhibits an increase. Thus, the content of water-soluble products in the wood mechanically activated with the use of AGO-2 2 exhibits a 3.6-fold increase (up to 12.8 mass %), whereas the content of reducing substances exhibits a 19-fold increase (up to 5.7 mass %) as to compare with the original wood.

The mechanical activation wood promotes both increasing the RHPS level, and increasing the rate of acidic hydrolysis thereof. As it follows from Table 1, the greatest effect is observed for aspen wood mechanically activated with the help of an AGO-2 centrifugal activator.

Effect of explosive wood autohydrolysis on the properties thereof

According to XRD data, changing the structure of the wood occur already after the treatment by steam at the temperature of 200 °C. In this case the XRD profiles demonstrate an abrupt decrease in the peak intensity with the maximum at 2θ = 18.5° degrees; decreasing the intensity of the peak at 2θ = 22° deg exhibits a decrease.

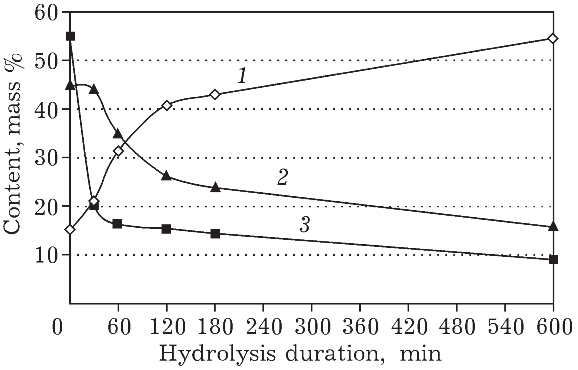

Fig. 2. Changing the chemical composition of aspen wood activated in AGO-2 apparatus at water duty value 12.5 in the course of hydrolysis by 2 % HCl at 96–100 °C: *1* – RHPS, *2* – residual lignin, *3* – DHPS.

TABLE 1

Effect of preliminary mechanical treatment on the rate of sugar formation in the course of aspen wood hydrolysis in 2 % HCl during 1 h

Treatment methods	Sugar formation rate, g/(L · h)
Original wood	0.07
Jet grinding	0.11
Vibratory grinding	0.18
Cutter grinding	0.23
Activation in AGO-2	0.33

The activation treatment results in decreasing absorption band intensity at 1600 cm^{-1} in the IR spectra, corresponding to the vibrations of the aromatic C=C bonds, and in increasing the intensity of the absorption band at 1720 cm^{-1} that can be attributed to the vibrations of the C=O bond in the carboxyl group. The changes observed are connected, to all appearance, with disordering the supramolecular structure of wood and with a partial depolymerization of lignin and hemicellulose [7, 8]. With increasing the temperature and the duration of wood treatment by steam one observes increasing the intensity of depolymerization. At temperature values above 240 °C, the reactions of wood thermal decomposition are intensified with releasing volatile substances and resins.

The fraction of hemicellulose in the original aspen wood is two times greater as to compare with pine wood amounting to 24.4 %. However, after the treatment at the temperature of 187 °C for 5 min, in the autohydrolyzed aspen wood, there remains 7 % of hemicellulose. Increasing the temperature of the explosive autohydrolysis process up to 220 °C, results in further reducing the content of hemicellulose in the autohydrolyzed aspen wood down to 0.5 %. At the temperature of autohydrolysis equal to 240 °C, there is almost no hemicellulose in autohydrolyzed aspen wood.

Unlike hemicellulose, the cellulose content in autohydrolyzed aspen wood changes to an

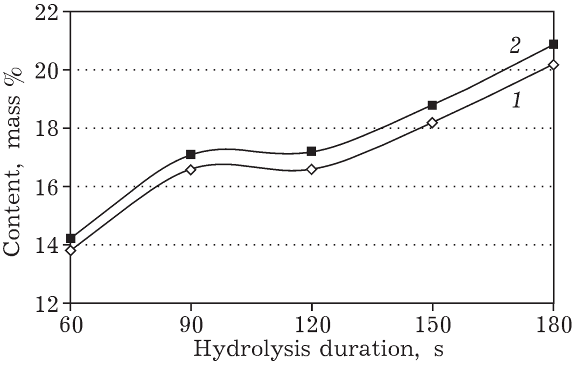

Fig. 3. Data concerning the extraction of low molecular lignin (LML) from aspen wood autohydrolyzed at 220 °C (% with respect to dry solid autohydrolyzed wood): *1* – extraction by rom 0.25 M Na_2CO_3 soln., *2* – extraction by 0.1 M NaOH soln.

insignificant extent with varying the temperature the duration of steam processing.

Lignin under the conditions of explosive autohydrolysis could be subjected to partial depolymerisation with the formation of low molecular fragments those are capable to dissolve in organic solvents and aqueous alkali solutions in a similar manner of native lignin.

It has been found that low-molecular mass lignin can be extracted from autohydrolyzed aspen wood by 0.1 M NaOH and 0.25 M Na_2CO_3 solutions (Fig. 3).

The amount of low molecular lignin formed in the course of explosion wood autohydrolysis is determined both by the process temperature and by the duration of the treatment. At a fixed temperature of autohydrolysis, the amount of low molecular lignin increases with increasing the duration of the activation process (see Fig. 3).

By means of removing the soluble substances and low molecular lignin from autohydrolyzed wood of pine, spruce and aspen there were fiber products containing up to 85 % of cellulose obtained with the yield ranging within 57–68 %.

Earlier [9, 13], the authors demonstrated that a significant intensification of oxidative wood delignification by hydrogen peroxide in the medium of dilute acetic acid at 120–130 °C takes place in the presence of sulphuric acid catalytic additives. Under such conditions, alongside with the oxidative degradation of lignin and hemicellulose, there occurs also the hydrolysis of an amorphous part of cellulose, thereby allowing one to realize a one-stage method for producing the microcrystalline cellulose (MCC) from the wood.

In the present work there has been a choice of optimal regimes performed for the stages of aspen wood autohydrolysis and of the oxidative delignification of autohydrolyzed wood by hydrogen peroxide, in order to provide a high yield of high-quality MCC at the expense of decreasing the temperature of oxidation and the consumption of hydrogen peroxide.

TABLE 2

Effect of the conditions of MCC obtaining from autohydrolyzed aspen wood exerted on the MCC yield and the consumption of hydrogen peroxide

Parameters of wood autohydrolysis stages			Parameters of delignifying stages for autohydrolysed wood (T = 110 °C, WD = 10, τ = 3 h)			MCC content, mass %	Residual lignin content in MCC, mass %	H_2O_2 consumption, g/g of MCC
			Composition of the solution, mass %					
T, °C	P, MPa	τ, min	CH_3COOH	H_2O_2	H_2SO_4			
180	1.0	2	23.6	6.4	2	32.3	1.2	2.0
190	1.2	2	23.6	6.4	2	31.7	1	2.0
210	1.9	2	21.8	8.2	2	31.9	<1	2.5
220	2.3	2	22.7	7.3	2	31.0	<1	2.3
230	2.8	2	23.6	6.4	2	30.2	<1	2.1
240	3.3	2	23.6	6.4	2	30.4	<1	2.1
210	1.9	3	20.0	10.2	2	29.2	<1	3.5
220	2.3	3	26.0	4.2	2	30.5	<1	1.4
230	2.8	3	23.6	6.4	2	29.2	<1	2.2
240	3.3	3	23.6	6.4	2	29.8	<1	2.1

TABLE 3

Effect of autohydrolysis and delignification conditions on the MCC polymerization level and crystallinity index

Process parameters						MCC characteristics	
for wood autohydrolysis			for autohydrolyzed wood delignification*			PL	K_p
T, °C	P, MPa	τ, min	Composition of the solution, mass %				
			CH_3COOH	H_2O_2	H_2SO_4		
180	1.0	2	23.6	6.4	2	187	0.60
190	1.2	2	23.6	6.4	2	165	0.64
210	1.9	2	21.8	8.2	2	170	0.64
220	1.9	2	22.7	7.3	2	108	0.65
230	2.8	2	23.6	6.4	2	83	0.60
240	3.3	2	23.6	6.4	2	90	0.63

Note. τ is process duration, PL is polymerization level, WD is water duty value, K_p is crystallinity index

*T = 110 °C, WD – 10, τ = 3 h.

Data concerning the effect of the conditions (temperature, duration, concentration of the components in the reaction mixture) of autohydrolysis processes and of catalytic delignifying the autohydrolyzed aspen wood by the mixture of acetic acid and hydrogen peroxide exerted on the MCC yield, on the content of residual lignin therein and on hydrogen peroxide consumption are presented in Table 2.

The maximum yield of MCC from the autohydrolyzed aspen wood is equal to 32.3 % as calculated for the mass of absolutely dry raw material, with the residual lignin content in MCC amounting to 1.2 mass %. The minimum amount of residual lignin (less than 1 mass %) is present in MCC samples derived from wood autohydrolyzed at 210–240 °C for 2–3 min. In this case, the yield of MCC remains at a level of 29.2–30.4 mass %.

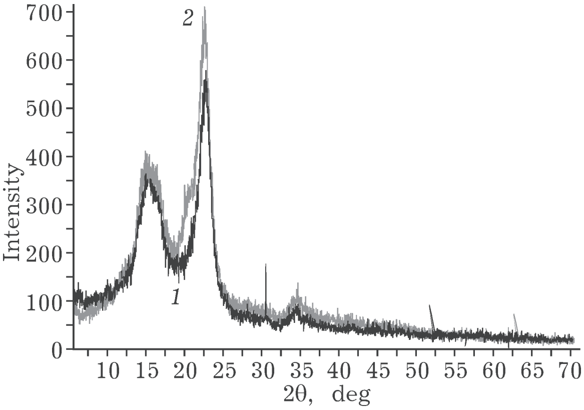

Fig. 4. XRD profiles of industrial Ankir-B grade MCC (*1*) and MCC resulted from autohydrolyzed aspen (*2*).

The consumption of hydrogen peroxide in the course of the MCC preparation is twice less than that with the use of a known method for its preparation [17].

With increasing the of aspen wood autohydrolysis temperature from 180 to 240 °C, the polymerization level of the MCC obtained exhibits an increase from 187 to 83. It should be noted that the PL value ranging within 83–187 corresponds to the PL inherent in industrial MCC samples (PL < 250) [19]. Table 3 presents data concerning the effect of autohydrolysis and delignification stage parameters exerted on the PL value and on the crystallinity index of the MCC samples (K_p).

The K_p values for calculated the MCC samples amount to 0.60–0.65 (see Table 3), which is comparable with the crystallinity indices inherent in the MCC obtained from sulphate and sulphite wood cellulose (0.65–0.67) [19].

According XRD data (Fig. 4), the crystallinity level of MCC obtained from autohydrolyzed aspen is quite comparable with Ankir-B grade industrial MCC, produced by the Evalar Co. (Russia).

CONCLUSION

An effect of different methods of aspen wood activation (grinding in the mills of various types, explosive autohydrolysis, catalytic oxidation with hydrogen peroxide and the combination of these methods) exerted on the structure, chemical composition and reactivity of activated wood was investigated.

It has been found that all the methods of aspen wood mechanical pretreatment used result in changing the supramolecular structure of lignocellulose matrix. According to XRD and electron microscopy data, the most significant changes occur in the case of aspen wood mechanical activation in an AGO-2 apparatus. In this case, an intense fibrillation of wood fiber large bunches occurs, as well as destruction and deformation of the walls of the large vessels are observed. At the same time there occurs a change in the chemical composition and reactivity of activated wood manifested in increasing the content of readily hydrolyzed polysaccharides in activated samples, in reducing the concentration of DHPS and residual lignin, in increasing the rate of the acidic hydrolysis of polysaccharides into monosaccharides and lignin oxidation by hydrogen peroxide.

An ecologically safe method is proposed for obtaining MCC that combines the stages of aspen wood activation by means of explosive autohydrolysis and catalytic oxidation of autohydrolyzed wood by hydrogen peroxide. Choosing the optimum modes has been performed for aspen wood autohydrolysis stages as well as for the oxidative delignification of autohydrolyzed wood by hydrogen peroxide, providing a high yield of the MCC almost free from residual lignin. The advantage of the novel method for obtaining MCC in comparison with known one consists in reducing the temperature of oxidative delignification and the consumption of hydrogen peroxide.

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