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## **Binding Properties of Lignins Obtained at Oxidative Catalytic Delignification of Wood and Straw**

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*Composition and binding properties of acetic acid lignins obtained at oxidative catalytic delignification of different types of plant biomass (softwood, hardwood, wheat straw) in the medium: acetic acid – hydrogen peroxide – water – sulfuric acid catalyst were compared.*

*Obtained acetic acid lignins have high concentration of reactive oxygen-containing functional groups, therefore they can be used as low-toxic binding agent for production of wood panel materials with good strength characteristics. The influence of lignin nature, its content in lignin/wood blend and conditions of pressing on the bending strength and water-resistance of obtained wood panel materials was studied. Optimal technological parameters for manufacture of strong and water steady wood panels were found.*

*Keywords: acetic acid lignins, composition, binding properties, wood pressed materials.*

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### **Introduction**

At present the development of modern ecology safe composite materials on the basis of available and inexpensive binding agents with low toxicity is a very important task. Some example of the use for producing composite materials with improved characteristics the non-toxic binding agents on the base of wastes of plant raw materials processing are available in literature [1, 2]. The most large-tonnage waste materials of pulp and hydrolysis plants are industrial lignins.

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The content of lignin in wood and in other types of plant biomass can reach 30 % wt. Lignin is a natural nonregular polymer which consists of phenylpropane units connected by ether bonds [3]. Natural lignin contains the –OH–phenol and aliphatic carbonyl and –COOH groups. The concentration of these groups are much lower in industrial lignins, formed in the processes of wood hydrolysis and cellulose productions [4, 5].

Chemical composition of industrial lignins defines the rational ways of their utilization [6]. Hydrolytic lignins differ significantly from lignins of pulp industry (lignosulfonates, alkaline sulphate lignin, tall lignin). Hydrolytic lignin has more condensed structure and less content of reactive groups, with the exception of methoxyl groups which are stable in the process of hydrolysis. Thanks to ability of hydroxyl groups of lignin to participate in reactions of condensation, the method of producing of lignin-aldehydes resins was developed [7]. It was shown the possibility to use lignins for synthesis of low toxic resins where up to 30–40 % of phenol is substituted on lignin [1] and in obtaining wood composites for building industry [2].

At present the novel ecology safe processes of cellulose production are under development. They are based on the use of “green” delignification reagents – molecular oxygen, hydrogen peroxide, ozone and organic or water-organic medium. Lignins of oxidative delignification processes have a high reaction ability thanks to their low molecular mass and high concentration of oxygen-containing groups.

Oxidative delignification of lignocellulosic raw materials (wood, straw, etc.) in the medium “acetic acid – hydrogen peroxide – water – sulfuric acid catalyst” makes possible to obtain high-quality cellulosic products [8]. Acetic acid lignins produced by oxidative delignification have lower molecular mass and higher reaction ability as compared to hydrolytic lignin.

Depending on nature of plant raw materials and on the conditions of oxidative delignification process the acetic acid lignins can differ in degree of condensation and concentration of various functional groups.

In this paper the composition and binding properties of acetic acid lignins obtained at oxidative catalytic delignification of different types of plant biomass (softwood, hardwood, wheat straw) were compared.

### Experimental

Air dry sawdust (fraction < 2,5 mm) of different types of wood species: larch wood (*Larix sibirica*), abies wood (*Abies sibirica*), aspen wood (*Populus tremula*), birch wood (*Betula pendula*) and wheat straw harvested in a suburb of Krasnoyarsk city were used as the initial raw materials. The chemical composition on initial raw materials (% wt.): larch wood – cellulose 34,5, lignin 26,1, hemicellulose 27,2, extractive substances 13,0; abies wood – cellulose 50,5, lignin 37,8, hemicellulose 13,9, extractive substances 4,5; birch wood – cellulose 46,8, lignin 24,7, hemicellulose 23,3, extractive substances 3,5; aspen wood – cellulose 47,3, lignin 22,9, hemicellulose 16,6, extractive substances 6,1; wheat straw – cellulose 48,7, lignin 21,4, hemicellulose 23,2, extractive substances 2,6.

A mixture of acetic acid, hydrogen peroxide, water and sulfuric acids catalyst was used as delignification agent. Delignification process was carried out in a metal shaking reactor of 200 cm<sup>3</sup> volume at temperature 130 °C, liquid to solid ratio 10, time of treatment 3 h., CH<sub>3</sub>COOH concentration 23.6–25.2 % wt., H<sub>2</sub>O<sub>2</sub> 4.8-6.4 % wt., H<sub>2</sub>SO<sub>4</sub> 2.0 % wt. At these process conditions the high yields of

cellulosic products with low content of residual lignin are reached [8]. Dissolved lignin was precipitated from concentrated spend liquors by their dilution with water.

The elemental analysis of lignin was studied with the use of FLASH<sup>TM</sup> (Thermo Quest Italia) and the concentration of oxygen-containing functional groups – by chemical analysis [9].

Spectra NMR <sup>1</sup>H and <sup>13</sup>C of lignin samples were registered on Bruker DPX-200 in D<sub>2</sub>O and CDCl<sub>3</sub>. IR spectra – on Tensor 27 (Bruker) at 400–4000 cm<sup>-1</sup>.

Wood panel materials were obtained by mechanical mixing at 150 °C the acetic acid lignin (moisture content 12.7–13.2 % wt.) and wood filler (sawdust of pine wood, fraction < 2.5 mm and moisture content 1.2 % wt.) taking in ratios 10–60 : 40–90 with following pressing at 7–16 MPa and temperatures 150–170 °C during 1 min.

Physical-mechanical characteristics of wood panel materials were defined with standard methods according to GOST 10634-88 and GOST 10635-88.

### Results and discussion

Acetic acid lignins obtained from wood and wheat straw are amorphous fine-dispersed powders which colour varies from light brown to dark brown. They have melting point 175–180 °C and low solubility in water and organic solvents. Their yields from initial raw material are near 9.0–9.5 % wt.

Some data about chemical composition of acetic acid lignins are presented in table 1.

The most high concentration of carboxylic groups (3.2 % wt.) was observed for lignin from abies wood, carbonyl groups –C=O (4.3 % wt.) – for lignin from birch wood, phenolic and aliphatic –OH groups (3.4 % wt. and 2.1 % wt., accordingly) – for lignin from aspen wood.

IR spectra of all lignin samples are mainly identical and only slight shift of frequencies of some absorption bands was observed (Fig. 1).

In all spectra the broad absorption band at region 3420–3400 cm<sup>-1</sup> corresponding to –OH groups connected by hydrogen bonds [10] is present. Absorption bands at region 3000–2810 cm<sup>-1</sup> and also peaks at 1440 and 1380 cm<sup>-1</sup> indicate the presence of CH<sub>3</sub> and CH<sub>2</sub> groups in lignins. Peaks at 1600, 1510 and 1455 cm<sup>-1</sup> correspond to vibration of C–C bonds of benzene ring [11]. The presence of intensive peaks at 1720 cm<sup>-1</sup> (ν C=O) and at 1225 cm<sup>-1</sup> (σ C–O) shows on possible availability in lignins esters of carboxylic acids. Absorption bands at region 1170–1000 cm<sup>-1</sup> probably correspond to deformative and valent vibrations of C–H and C–O bonds, correspondingly [11]. Peak at 1270 cm<sup>-1</sup> which is observed in spectra of all lignin samples can be attributed to skeletal vibration of guacyl ring and peak at 1323 cm<sup>-1</sup> in spectrum of birch lignin – to skeletal vibrations of syringyl ring. The presence of intensive peak at

Table 1. Elemental composition of acetic acid lignins and concentration of oxygen-containing functional groups (% wt.)

Lignin	C	H	O	-COOH	-C=O	-OH <sub>phen.</sub>	-OH <sub>aliph.</sub>
Abies	61.2	5.1	33.0	3.2	3.8	2.6	0.12
Aspen	62.7	5.4	31.4	2.3	3.2	3.4	2.1
Birch	62.8	5.1	31.9	2.4	4.3	3.0	0.2
Wheat straw	61.8	5.4	29.7	2.03	1.7	2.9	1.6

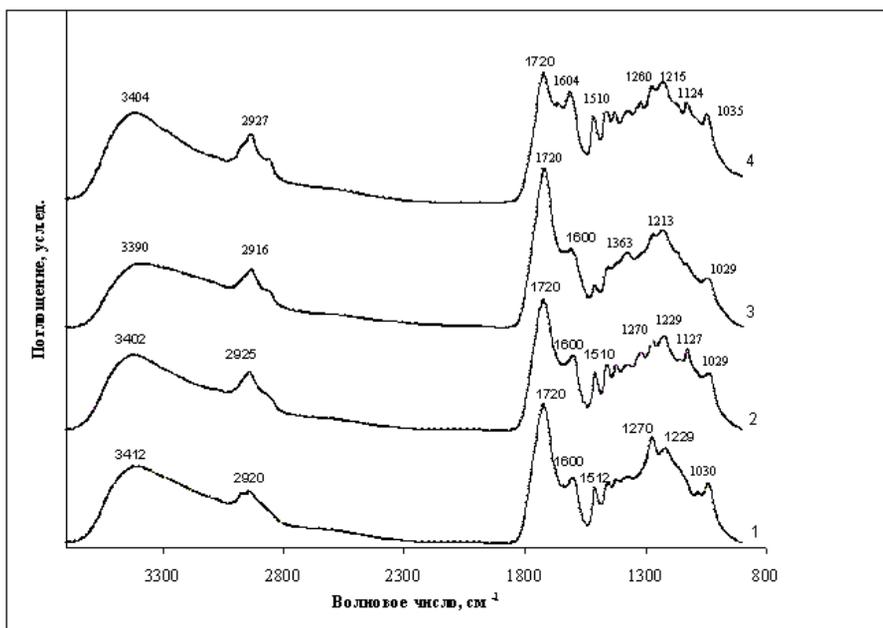
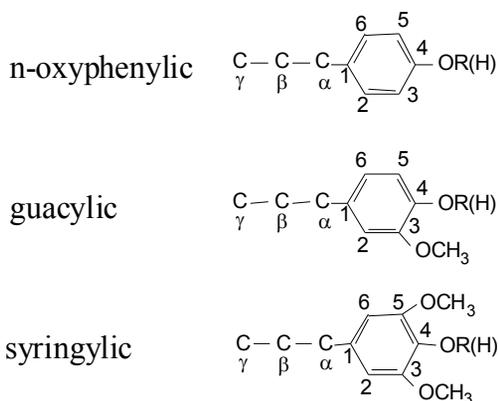


Fig. 1. IR spectra of acetic acid lignins from abies wood (1), birch wood (2), aspen wood (3), wheat straw (4)

1127 in spectrum of birch lignin can indicate on the higher content of simple ether bonds as compared to lignins from abies and aspen wood.

Additional information about structural characteristics of acetic acid lignins was obtained by NMR <sup>1</sup>H and <sup>13</sup>C spectroscopy. The attribution of signals in NMR <sup>1</sup>H spectra was realized in compliance with [12].

The basic structural components of lignin are phenylpropane units of following types:



It is known that n-oxyphenylic units dominate in straw lignins, guacylic – in softwood lignins and syringylic – in deciduous wood. NMR data confirm the presence of all stated structural units in samples of acetic acid lignins.

Intensive signal in region 5.2–4.5 ppm indicates the presence of olefinic groups. Chemical shift (CS) <sup>1</sup>H in the range 4.0–3.0 ppm confirms the existence of olefinic groups connected with aromatic

ring. CS  $^1\text{H}$  in region 2.0–1.0 ppm correspond to hydrogen atoms of  $\beta$ -methyl or  $\beta$ -methylene groups in  $\beta$ -position (or longer) to aromatic ring. CS  $^1\text{H}$  in the range 1.0–0.5 ppm indicates the presence of methyl groups in  $\gamma$ -position (or longer) to aromatic ring.

Chemical shifts  $^{13}\text{C}$  at 192–108 ppm correspond to structural groups, connected with carbon atoms in aromatic ring and at 4.5–5.0 ppm – with carbon atoms in aliphatic chains. Chemical shifts  $^{13}\text{C}$  at 108–130 ppm show the existence of syringyl fragments, which dominate in lignins of deciduous wood.

The high content of reactive functional groups in acetic acid lignins allows to use these lignins as binder agents for manufacture of wood panel materials.

The influence of lignin nature, its content in lignin/wood blend and condition of pressing on the mechanical strength and water-resistance of obtained wood panel materials was studied. Industrial wood panel materials with thickness to 20 mm have bending strength 18–22 MPa and water absorption 14–20 % wt. [13].

Fig. 2 shows that pressed panels obtained at lignin content 10–20 % wt. have low bending strength (9–17 MPa). But the bending strength of pressed materials increases with the growth of lignin content in the blend to 40 % wt.

Pressed materials with abies lignin and birch lignin have the higher bending strength (23–28 MPa) Their characteristics satisfy the specifications on the heat-insulating wood panels with thickness to 50 mm [13].

Some correlations between the nature and content of functional groups in acetic acid lignins and the physical-mechanical characteristics of obtained pressed materials were observed. The growth of concentration of carboxyl and carbonyl groups in lignins increases the strength of wood pressed material. But the increased content of alcohol hydroxyl groups in lignin decreases the water resistance

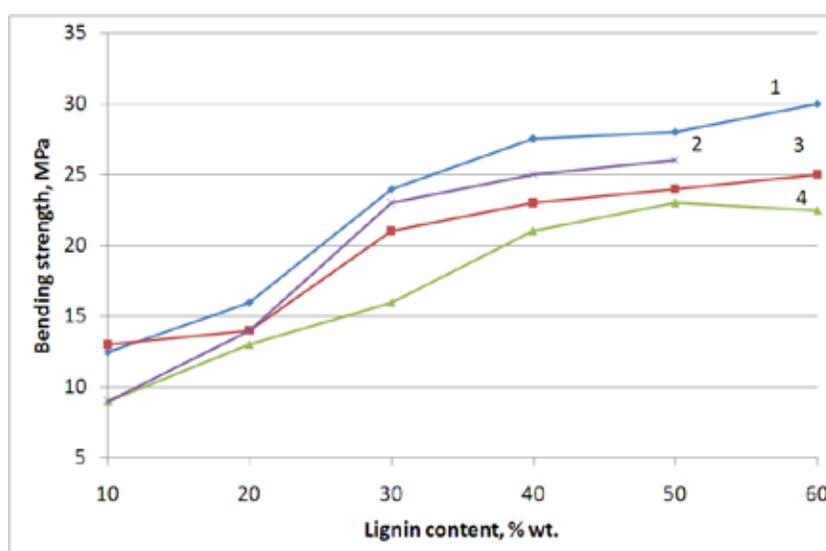


Fig. 2. Influence of acetic acid lignin content in the blend on the bending strength of wood panel materials obtained by pressing at 165 °C and 10 MPa: 1 – abies lignin, 2 – wheat straw lignin, 3 – birch lignin, 4 – aspen lignin

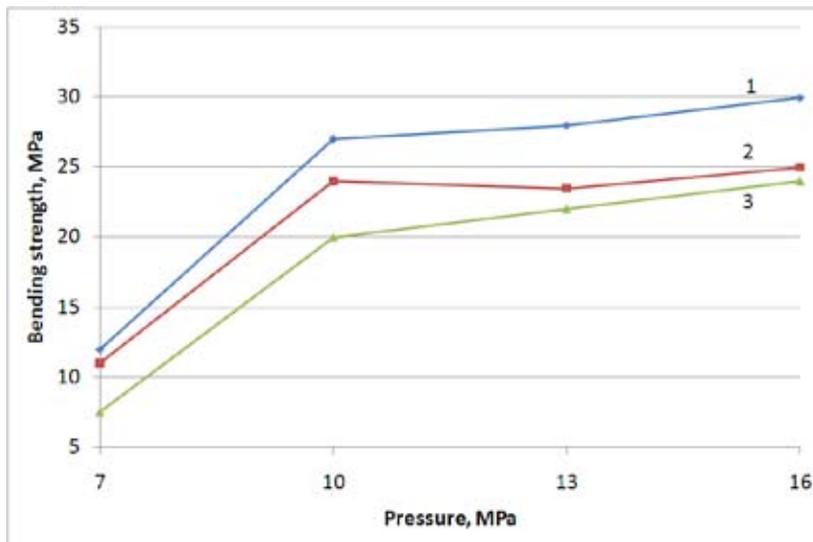


Fig. 3. Influence of pressure of lignin/wood blend (40:60) pressing at 165 °C on the bending strength and water-resistance of obtained panel materials: 1 – abies lignin, 2 – birch lignin, 3 – aspen lignin

of pressed material. Their strength and water-resistance increase with growth of pressing temperature from 150 to 165 °C. Higher temperature promotes the chemical interaction between oxygen-containing functional groups of acetic acid lignin and wood filler, resulting in improvement of physical-mechanical characteristics of obtained pressed materials.

Fig. 3 illustrates the influence of pressure of blend pressing on the strength and water-resistance of produced panel materials.

The growth of pressure of blend pressing from 7 to 10 MPa significantly increases the strength of wood panels and their water-resistance. Further growth of pressure to 16 MPa only slightly increases the strength of pressed material. Wood panel materials obtained with the use of birch lignin have the highest water-resistance as compared to abies lignin, aspen lignin and wheat straw lignin.

In order to increase the water-resistance of wood panel materials the treatment of lignin/wood blend with 0.5 % water solution of H<sub>2</sub>SO<sub>4</sub> at 85 °C during 1 h before pressing was used. Chemical modification of blend with sulfuric acid allow to increase by 2.5–3 times the water resistance of the wood panel materials. Wood pressed materials obtained from pre-treated blend absorb 8, 7 and 10 % of water, accordingly when acetic acid lignins from aspen wood, abies wood and wheat straw were used.

Results of the accomplished study show that acetic acid lignin – side products of cellulose obtaining by oxidative delignification of wood and straw can be used as low-toxic binding agents in production of wood panel materials.

### Conclusion

Elemental and functional composition of acetic acid lignins-side products of oxidative delignification of wood (larch, abies, birch, aspen) and wheat straw in the medium of diluted acetic acid with sulfuric acid catalysts was studied. According to obtained results the acetic acid lignins have

high concentration of reactive oxygen-containing functional groups. It was suggested to use acetic acid lignins as low-toxic binding agent for production of wood panel materials with good strength characteristics. The influence of lignin nature, its content in lignin/wood blend and conditions of pressing on the bending strength and water-resistance of obtained wood panel materials was studied. Optimal technological parameters for manufacture of wood panel materials were found; lignin content near 40 % wt., pressing temperature 160–165 °C, pressure 10–13 MPa. Chemical modification of blend lignin/wood with 0.5 % solution of sulfuric acid at 85 °C before pressing increases by 2.5–3 times the water resistance of obtained wood panel materials.

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## **Связующие свойства лигнинов, полученных при окислительной каталитической делигнификации древесины и соломы**

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*Сопоставлены состав и связующие свойства лигнинов, полученных в качестве побочных продуктов при окислительной каталитической делигнификации различных видов растительной биомассы (хвойная и лиственная древесина, солома пшеницы) в среде уксусная кислота – пероксид водорода – вода – серно-кислотный катализатор.*

*Получаемые уксусно-кислотные лигнины имеют высокую концентрацию реакционных кислород-содержащих групп, что позволят их использовать в качестве низкотоксичных связующих веществ для производства древесных плитных материалов с хорошими прочностными характеристиками. Изучено влияние природы лигнина, его содержания в смеси лигнин/древесина и условий прессования на прочность и водостойкость получаемых древесных панелей. Установлены оптимальные технологические параметры для производства прочных и устойчивых к действию влаги древесных плитных материалов.*

*Ключевые слова: уксусно-кислотные лигнины, состав, связующие свойства, древесные прессованные материалы.*

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