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Composition and Application of Soluble Products of Wheat Straw Catalytic Oxidative Delignification

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Abstract

The composition of the soluble products of wheat straw delignification in the medium acetic acid–hydrogen peroxide–water–sulphuric acid catalyst was studied by means of elemental and chemical analysis, IR spectroscopy and gas chromatography-mass spectrometry. It was established that the vat residue formed in the regeneration of spent alkali liquor contains the products of polysaccharide degradation (4.7 rel. %), esters (19.9 rel. %) and sterols (37.2 rel. %). The acetic lignin precipitated from the alkali liquor contains a substantial amount of oxygen-containing functional groups. A promising character was demonstrated experimentally for the presently unclaimed bio-renewable resource such as wheat straw as a chemical raw material for obtaining sorbents and binders in the production of wood-based panels.

Key words: wheat straw, oxidative delignification, soluble products, composition, application, binders, enterosorbents

INTRODUCTION

Cellulose production represents one of the areas of rational utilization of agricultural wastes (straw and shucks of cereals, cotton plant stems, *etc.*) [1]. Thereby the interest in the use of annual plants for the production of cellulose is permanently growing [2–4].

More than 200 million tons of wheat straw, a large-scale cellulosic waste is accumulated annually in Russia. It is known that the content of cellulose in straw cereals is comparable with its content in the wood. Unbleached cellulose from straw obtained by means of alkaline digestion method is of poor quality; it is used mainly for the production of cardboard.

At the present time, environmentally safe methods are being developed based on the oxidative delignification of plant row materials using "green" delignification agents such as oxygen, hydrogen peroxide, ozone [5]. A method developed by the authors for the catalytic oxidative delignification of wheat straw and oat shuck by hydrogen peroxide in the aqueous acetic acid medium allows to obtain a high yield of cellulose with a low content of residual lignin [6, 7]. Low molecular mass acetic acid lignin formed in this case is chemically active.

The aim of this work consisted in studying the soluble products of wheat straw oxidative delignification in the environment acetic acid-hydrogen peroxide–water–sulphuric acid catalyst, as well as the possibility of using acetic acid lignin to produce binding agents and sorption materials.

EXPERIMENTAL

As a raw material, we used the straw wheat of Novosibirskaya-15 variety grown at the Yemelyanovskiy District of the Krasnoyarsk

Territory. Air-dry wheat straw was ground and fractionated by sieving. For the studies, we used the fraction less than 1 mm in size. The composition of straw was determined by means of standard methods [8]. The batch of wheat straw used was of the following composition, mass %: cellulose 39.2, lignin 20.6, hemicelluloses 30.7, extractive substances 5.5, and inorganic substances 3.6.

The straw delignification procedure was performed using a stainless steel reactor with a volume capacity equal to 300 cm^3 at the temperature of 125 °C, water duty amounting to 10, the process duration 135 min, and with the following composition of the reaction mixture, mass. %: acetic acid 25.8, hydrogen peroxide 4.2 sulphuric acid catalyst 2.0. Under these conditions, a high yield cellulose product can be obtained, with a low content of residual lignin.

After the delignification, the cellulose product obtained was separated from the liquor by means of filtration under vacuum. From the filtrate we distilled acetic acid which was recycled to the delignification process. From the distillation residue, we isolated acetic acid lignin by means of fivefold dilution with water; the substance was separated from the solution by filtration and air dried.

A schematic diagram of studying the composition of soluble delignification products resulted from wheat straw is demonstrated in Fig. 1.

The registration of IR spectra was performed using a Tensor 27 Fourier transform IR spectrometer (Bruker, Germany) within the range of 400–4000 cm^{-1}. The processing of spectral data obtained was performed using software OPUS package, version 5.0. The samples for registering the absorption IR spectra were prepared in the form of pressed tablets containing 2 mg of lignin in KBr matrix.

In order to determine the composition of soluble substances from the distillation residue formed in the course of the regeneration of the spent liquor resulted from the wheat straw delignification, we performed an exhaustive extraction with alcohol/benzene mixture (1 : 1) with the help of a Soxhlet extractor, during 12–18 h.

The componential composition of the extract obtained was examined by means of gas chromatography-mass spectrometry employing an Agilent Technologies 7890 A gas chromatograph (USA) with an Agilent Technologies 5975 C quadrupole mass spectrometer as the detector. We used HP-5 silica column 30 m long with the inner diameter equal to 0.25 mm and the stationary phase film thickness amounting to 0.25 mm. Helium was used as a carrier gas with a constant flow rate equal to 1 mL/min. The evaporator temperature amounted to 280 °C. The temperature program of the column was as it follows: 4 °C/min heating up to 270 °C followed by 25 min hold. The temperature of interface between the gas chromatograph and the mass selective detector was equal to 280 °C; the temperature of the flame ionization detector was

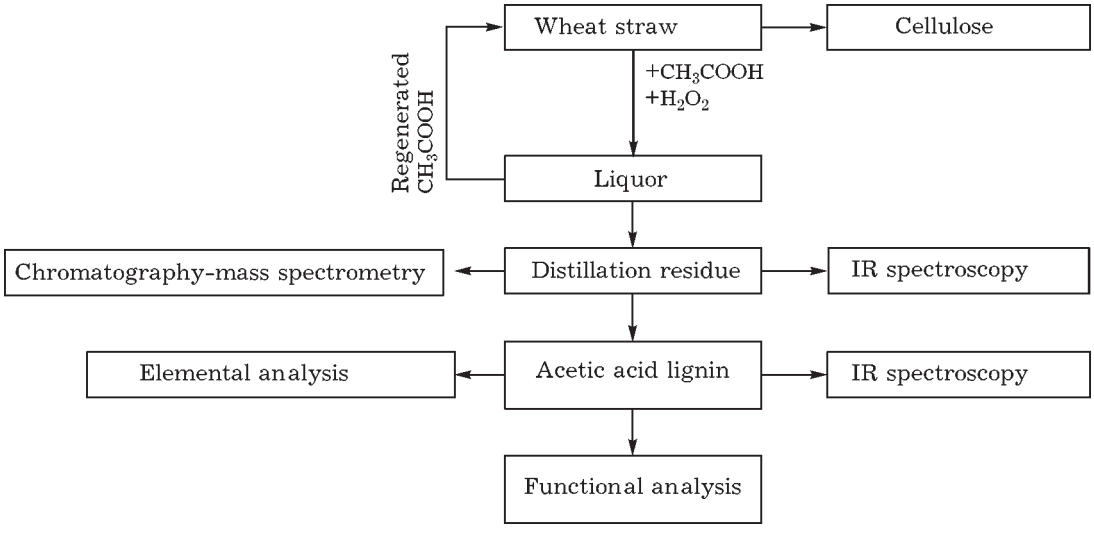

Fig. 1. Scheme of studying the soluble products of wheat straw oxidative delignification.

equal to 173 °C. The energy of ionizing electrons was equal to 70 eV. The sample volume injected into the chromatograph amounted to 1 μL. The identification of the compounds under determination was performed basing on the comparative analysis of the retention time values and their complete mass spectra with the corresponding data from the mass spectra library Wiley 275, as well as from electronic mass spectra atlases.

The elemental analysis of the lignin samples were carried out using a Termo Quest FlashEA 1112 elemental analyzer (Italy).

The content of phenolic hydroxyl groups and carboxyl in the wheat straw acetic acid lignin was determined using the method of chemisorption, that of alcoholic hydroxyl groups was determined by means of the phthalation method, and that of carbonyl groups was determined using the oximation method [9].

The wood-based panel materials were prepared by mechanical mixing wheat straw acetic acid lignin (moisture content 13.2 mass %) and wood filling agent (pine sawdust fraction of less than 2.5 mm with the moisture content of 1.2 mass %) taken at a ratio of (10–50) : (50–90) at the temperature of 150 °C, with subsequent pressing at a pressure of 10 MPa and temperature of 165 °C during 1 min.

The obtained samples of wood-based panel materials were evaluated by the density change, water absorption, thickness swelling and the static bending strength.

In order to obtain enterosorbents based on wheat straw acetic acid lignin, we modified the latter via alkaline treatment [10]. Lignin with 65–70 % moisture was treated by 0.4 % NaOH solution under continuous stirring for 15 min at a room temperature. The modified lignin washed out from alkali-soluble substances to obtain a neutral pH value of cleansing water. Under the same conditions we modified wheat straw acetic acid lignin using 0.4 % $NaHCO_3$ solution and hot water.

The quality of enterosorbents obtained by modifying acetic acid lignin was assessed from the ability to absorb marker substances used in the most of medical sorbents. Iodine and methylene blue (MB) simulate low molecular mass toxicants. Gelatine was used to assess the sorption activity of pathogenic substances of protein nature.

The determination of sorption activity with respect to iodine was carried out according to Russian State standard GOST 6217–74. The sorption activity of lignin-based sorbents with respect to MB was determined by means of colorimetric method according to Russian State standard GOST 4453–74. The sorption of gelatine was determined colorimetrically *via* a colour reaction with biuret-based reagent [11].

RESULTS AND DISCUSSION

Studying the composition of the distillation residue after delignification

The assignment of the absorption bands in the infrared spectrum of the after distillation residue wheat straw delignification in acetic acid–hydrogen peroxide–water environment was performed basing on data from [12–14].

The IR spectrum of the distillation residue (Fig. 2) is characterized by a broad absorption band having a maximum at 3240 cm^{-1}, which indicates the presence of hydroxyl groups involved in hydrogen bonding. The absorption in the region of 3000–2800 cm^{-1} and the band with the maximum at 1370 cm^{-1} indicate the presence of CH_2 and CH_3.

The absorption band with the maximum at 1506 cm^{-1} is caused by skeletal vibrations of C=C bonds of benzene rings with a guayacyl type of substitution. An intense band at 1714 (ν C=O) and the band at 1225 cm^{-1} (σ C–O) indicate the presence large number of carboxylic acid esters in the sample under investigation. Stretching vibrations of C–O bonds, inherent in

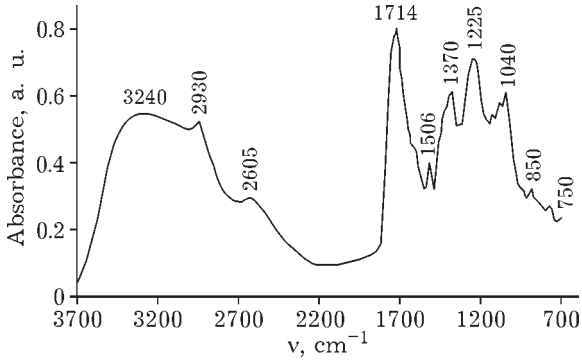

Fig. 2. IR spectrum of the distillation residue formed after the regeneration of spent liquor resulted from wheat straw oxidative delignification.

TABLE 1

Content of components in the alcohol/benzene extract of the distillation residue from wheat straw delignification (according to gas chromatography-mass spectrometry)

Components	Retention time, min	Molecular mass	Relative content, %
Acetic acid	6.53	60	11.04
Furfurol	6.98	96	3.59
5-Methylfurfurol	9.97	110	1.06
Butanedioic acid, ethyl ester	11.48	146	1.08
Butyllevulenate	12.38	157	0.70
Ethyl *n*-hydroxybenzoate	15.47	166	7.63
3-(*p*-Methoxyphenyl)propionic acid	15.67	180	1.96
p-(Hydroxyphenyl)pyruvic acid	12.67	180	4.42
Acetosyringone	18.38	196	9.73
Ethyl vanilate	23.48	196	0.75
Stigmasthane-3,5-diene	33.19	396	21.72
5-Stigmasthene-3-β-ol	47.78	414	15.52
Not identified			19.80

primary alcoholic hydroxyl groups are exhibited in the form of an absorption band at 1040 cm^{-1}.

The analysis of spectral data for distillation residue demonstrated that wheat straw delignification products contain a wide variety of oxygen functional groups. It is known [15] that for the extraction of hydrolytic lignin extractives one commonly uses an alcohol/benzene mixture.

In the course of the extracting the distillation residue after wheat straw delignification we used an alcohol/benzene mixture with a componential ratio equal to 1 : 1. The chemical composition of the extract was investigated by means of gas chromatography-mass spectrometry. The identification of organic compounds was carried out with the coinsiding probability of mass spectra with respect to database equal to more than 80 %. Data concerning the content of the components in the alcohol/benzene extract of the distillation residue are presented in Table 1.

It can be seen that the alcohol/benzene of the distillation residue from of wheat straw delignification contains the degradation products of polysaccharides (4.65 rel. %), esters (19.89 rel. %), aromatic acids (6.38 rel. %), acetic acid (11.04 rel. %) and sterols (37.24 rel. %). Unidentified compound presented, to all appearance, by lignin oxidation products are amounting to 19.80 rel. %.

Composition and properties of acetic acid lignin

Wheat straw acetic acid lignin was obtained via delignification under the conditions those provide a high yield of cellulose product with a low residual lignin content [6]. The substance represents a fine amorphous powder of light brown colour with the density of 1.23 g/cm^3 and the softening point equal to 148 °C. The lignin has the following elemental composition, mass %: C 61.83, N 5.37, O 29.69.

The IR spectrum of wheat straw lignin is characterized by a broad absorption band having a maximum at 3385 cm^{-1}, which indicates the presence of hydroxyl groups bound by hydrogen bonds. The band of medium intensity at 1215 cm^{-1} and a weak band at 1348 cm^{-1} correspond to the stretching vibrations of the C–OH phenolic groups [12, 13]. The absorption band at 2940 cm^{-1} corresponds to the vibrations of CH_2 and CH_3, whereas the band at 1712 cm^{-1} indicates C=O bonds in carboxylic and carbonyl groups [12, 13]. The vibrations of C=C aromatic ring bonds are exhibited as intense absorption bands at 1605 and 1506 cm^{-1}. The presence of alcoholic hydroxyl groups in the wheat straw acetic acid lignin is indicated by absorption bands at 1035 and 1120 cm^{-1} corresponding to the bending vibrations of the C–

OH group in primary and secondary alcohols, respectively [14].

The presence of these absorption bands in the IR spectrum indicates that the wheat straw acetic acid lignin contains a great amount of oxygen-containing functional groups.

Using chemical analysis methods [8], we determined at a quantitative level the content of oxygen-containing functional groups in the wheat straw lignin, mass. %: −COOH 2.0, $-OH_{phen}$ 2.9, $-OH_{prim}$ 0.4, $-OH_{sec}$ 1.2, −C=O 1.7. These data support the conclusion that there is a high content of reactive groups in the acetic acid lignin.

Owing to a great amount of oxygen-containing groups, the acetic acid lignin could be used as a binding agent in the manufacture of wood composites and as an efficient sorption material.

Binding properties of acetic acid lignin

An influence of the content of acetic acid lignin and wood filler was studied concerning the physicomechanical characteristics of plate materials, obtained by pressing at the temperature of 165 °C and pressure of 10 MPa during 1 min.

Figure 3 presents data on the effect of the wheat straw acetic acid lignin content on the mechanical strength and water resistance of wood-based panels produced. It can be seen that when the mass fraction of acetic acid lignin ranges within 10−20 %, the tensile strength of plate materials under static bending is equal to 9−14 MPa being less than the physicomechanical parameters of commercially produced wood-based panels: 18−22 MPa for plate thickness of 20 mm, water absorption level equal to 20−14 % [16]. The maximum density (781 kg/m^3) and flexural strength (26 MPa) are exhibited by plate materials with the mass fraction of lignin in the pressed mixture equal to 50 mass %.

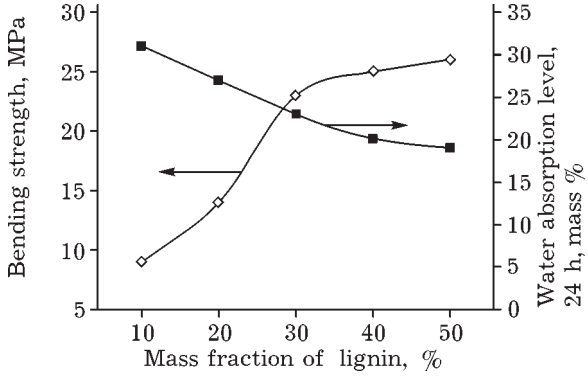

Fig. 3. Influence of the content of acetic acid lignin for strength and water absorption of wood-based panels.

With increasing the content of lignin from 10 to 40 mass % the water absorption level and the thickness swelling of the samples of plate materials are reduced from 31 to 20 % and from 22 to 17 %, respectively. The water resistance of wood-based panels obtained under these conditions is less than the value required by the standard regulations [17].

In order to improve the water resistance of wood-based panels we performed modifying the mixture of wood filler and a binding agent by 0.5 % aqueous solution of sulphuric acid, whose consumption was equal to 8 % from the mass of a dry mixture of acetic acid lignin and pine sawdust. The modification procedure was carried out at 85 °C during 60 min, where after the composition was subjected to pressing. As the result of the modifying treatment the water resistance of the samples of wood-based panels became doubled (water absorption was equal to 10 %).

Sorption properties of wheat straw acetic acid lignin

In order to enhance the sorption capacity of wheat straw acetic acid lignin, we performed washing-out with hot water and modifying by alkali treatment.

Table 2 demonstrates data concerning an effect of processing method employed with respect to wheat straw acetic acid lignin on the yield of the sorbent obtained and its sorption properties.

For comparison, we used enterosorbent "Polyphepan" (St. Petersburg) as a reference sample.

We revealed that the sorption capacity of sorbent samples with respect to iodine is almost independent of the processing conditions to be comparable with the activity of commercial enterosorbent "Polyphepan".

The sorption activity with respect to MB depends on the conditions of acetic acid lignin treatment. The maximum value of the adsorption level with respect to the MB (89 mg/g) is exhibited by a sample of lignin treated with

TABLE 2

Yield and properties of sorbents from wheat straw acetic acid lignin

Processing methods	Sorbent yield, %	Sorption activity, with respect to		
		iodine, %	MB, mg/g	gelatine, mg/g
0.4 % NaOH, 25 °C	47	35.7	79	142.8
0.4 % $NaHCO_3$, 25 °C	74	34.7	86	74.8
H_2O, 85 °C	83	34.2	89	73.6
Commercial enterosorbent «Polyphepan» *	–	38.7	44	140.9

*Obtained from hydrolytic lignin.

hot water. The reduced adsorption of with respect to MB inherent in the sample of lignin treated with 0.4 % NaOH solution could be explained by an increase in pore size and a decrease of pore number resulting from the alkali degradation of the lignin straw. However, all the sorbents obtained from acetic acid lignin, exhibit 1.5–2 times increased sorption activity with respect to MB comparing to the commercial enterosorbent "Polyphepan".

The maximum sorption with respect to gelatine is exhibited by the sample of acetic acid lignin modified by 0.4 % NaOH solution. This value is about two times greater as compared to the samples treated with 0.4 % $NaHCO_3$ solution, or with hot water. To all appearance, in this case the sorption capacity is determined both by the porous structure of the sorbent, and by the nature and concentration of the surface functional groups.

CONCLUSION

The composition of the soluble products of wheat straw oxidative delignification in the medium of dilute acetic acid in the presence of sulphuric acid catalyst was investigated.

It was found that the extractive substances of the distillation residue forming after the distillation of acetic acid from the spent liquor of wheat straw delignification are presented by degradation products of polysaccharides such as esters and sterols.

Acetic acid lignin isolated from the spent liquor of wheat straw delignification process contains a significant amount of reactive functional groups: –COOH, $-OH_{phen}$, $-OH_{prim}$, $-OH_{sec}$, –C=O.

It is proposed to use wheat straw acetic acid lignin as a binder with reduced toxicity for manufacturing wood-based panels with improved strength characteristics. Modifying the wheat straw lignin and the wood filler with 0.5 % aqueous sulphuric acid solution at 85 °C and subsequent hot pressing results in two-fold enhancing the water resistance of wood-based panels obtained.

It is demonstrated that the modified sorbent prepared via treating the wheat straw acetic acid lignin by 0.4 % NaOH solution, exhibits a high sorption activity with respect to the markers used in the pharmacopoeia and could be recommended for obtaining "Polyphepan" type enterosorbents.

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