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XANTHOGENATION OF LIGNOCARBOHYDRATES BY CARBON DISULFIDE

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High-molecular-weight products containing 4.21-10.4% bound sulfur that are soluble (32-86%) in aqueous alkaline solutions are obtained from xanthogenation of lignocarbohydrates by carbon disulfide in the presence of NaOH in propan-2-ol. The degree of preliminary alkaline activation of the raw material in propan-2-ol has the principal effect on the composition and physicochemical properties of the xanthogenation products.

Key words: xanthogenation, lignocarbohydrates, propan-2-ol.

Xanthogenation of cellulose is widely used in the chemical-fiber industry to produce viscous fibers and films and to prepare cellulose esters by reacting alkaline cellulose and carbon disulfide [1].

Methods for xanthogenating cellulose using activated aqueous alkaline solutions with subsequent pressing and mixing with carbon disulfide are used to produce xanthogenated products [2, 3]. These methods have serious technical deficiencies. Preliminary activation of cellulose is required. The NaOH solutions must be regenerated. The consumption of CS_2 in side reactions is high. This significantly reduces the duration of xanthogenation and causes ecological problems.

The literature contains data on the reaction of individual wood carbohydrates, e.g., cellulose, oligosaccharides, and hemicellulose, with CS_2 in the presence of NaOH [4-6]. However, there is little information on direct xanthogenation of lignin, wood, and other lignocarbohydrates (LCH).

The advantages of using LCH are, first, the cost of the final product is substantially reduced, second, the technology can be made waste-free (the principal LCH components, cellulose, lignin, and hemicellulose, are xanthogenated and then used), third, the LCH do not have to be separated into lignin and carbohydrate parts, and fourth, xanthogenated LCH have a wider spectrum of properties than cellulose xanthogenates.

Our goal was to develop a new method for preparing and studying the properties of LCH xanthogenates that are soluble in water and alkaline solutions and can be used as sorbents with a wide range of application.

Xanthogenation in propan-2-ol leads to deeper penetration of the reagents to wood hydroxyls. A solution of alkali in alcohol can destroy the supermolecular wood structure. This partially destroys LCH bonds and macromolecules of individual wood components and increases the availability of cellulose, lignin, and hemicellulose hydroxyls to the reagent.

Macromolecules of the principal wood components contain free hydroxyls. This increases their reactivity to xanthogenation. Furthermore, performing xanthogenation in isopropanol decreases the consumption of CS_2 in side reactions that form salts (thiocarbonates).

Xanthogenation of LCH consists of activation by NaOH in isopropanol and xanthogenation by CS_2 in isopropanol. We have prepared xanthogenated derivatives of various LCH, the properties of which are listed in Table 1.

We studied the effect of temperature and time of preliminary processing of wood by alkali and the temperature and time of xanthogenation on the properties of the products (Tables 2-5, Fig. 1). The degree of conversion of wood hydroxyls to esterification (xanthogenation) was calculated from the sulfur content.

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TABLE 1. Properties of Xanthogenates of Various Lignocarbohydrates (Alkaline Processing at 20°C for 0.5 h, Xanthogenation at 50°C for 3 h)

Sample	Starting material	Solubility in NaOH (6%)	Sulfur content	Degree of OH conversion
		%		
	Wood:			
1	aspen	32	4.21	21
2	birch	39	4.79	24
3	pine	48	4.98	25
4	Flax pile	53	5.15	26
5	Sunflower husk	54	5.19	26

TABLE 2. Properties of Xanthogenated Aspen Wood Produced under Various Conditions (Alkaline Processing at 20°C, Xanthogenation for 3 h at 50°C)

Aspen wood sample	Alkaline processing time, h	Solubility in NaOH (6%)	Sulfur content	Degree of OH conversion
		%		
1	0.5	32	4.21	21
6	1.0	38	5.53	27
7	2.0	54	7.68	38
8	3.0	68	9.45	47
9	4.0	69	8.76	44
10	5.0	69	8.32	41
11	6.0	63	8.11	40

TABLE 3. Properties of Xanthogenated Aspen Wood Produced under Various Conditions (Alkaline Processing for 3 h, Xanthogenation for 3 h at 50°C)

Aspen wood sample	Alkaline processing temperature, °C	Solubility in NaOH (6%)	Sulfur content	Degree of OH conversion
		%		
8	20	68	9.45	47
12	40	73	9.87	49
13	60	86	10.3	51
14	80	72	9.29	46
15	100	64	8.48	42

The results indicate that various LCH are xanthogenated to varying degrees. The yield of high-molecular-weight products is 85-96%. Sunflower husk has the highest solubility in 6% alkali and sulfur content because it contains the largest amount of lignin, which is more reactive than cellulose and hemicellulose (Table 1).

We used aspen wood in further investigations (Tables 2-5, samples 6-24) because it is an inexpensive wood that is widely distributed in Russia. Furthermore, aspen wood is known to be easily esterified by chemical processing [7].

We studied the effect of the following factors on the properties of xanthogenated aspen wood: temperature and time of preliminary alkali processing and temperature and time of xanthogenation. The sulfur content in the products was determined by the Schoeniger method [8]; the solubility, in NaOH solution (6%); the relative viscosity, in the same solvent.

TABLE 4. Properties of Xanthogenated Aspen Wood Produced under Various Conditions (Alkaline Processing for 3 h at 60°C, Xanthogenation for 3 h)

Aspen wood sample	Xanthogenation temperature, °C	Solubility in NaOH (6%)	Sulfur content	Degree of OH conversion
		%		
13	50	86	10.3	51
16	20	60	6.88	34
17	30	67	7.46	37
18	40	75	9.57	47
19	60	82	10.1	50

TABLE 5. Properties of Xanthogenated Aspen Wood Produced under Various Conditions (Alkaline Processing for 3 h at 60°C, Xanthogenation at 50°C)

Aspen wood sample	Xanthogenation time, h	Solubility in NaOH (6%)	Sulfur content	Degree of OH conversion
		%		
13	3.0	86	10.3	51
20	0.5	44	5.69	28
21	1.0	57	7.37	37
22	2.0	71	9.16	46
23	4.0	79	10.4	52
24	5.0	76	10.4	52

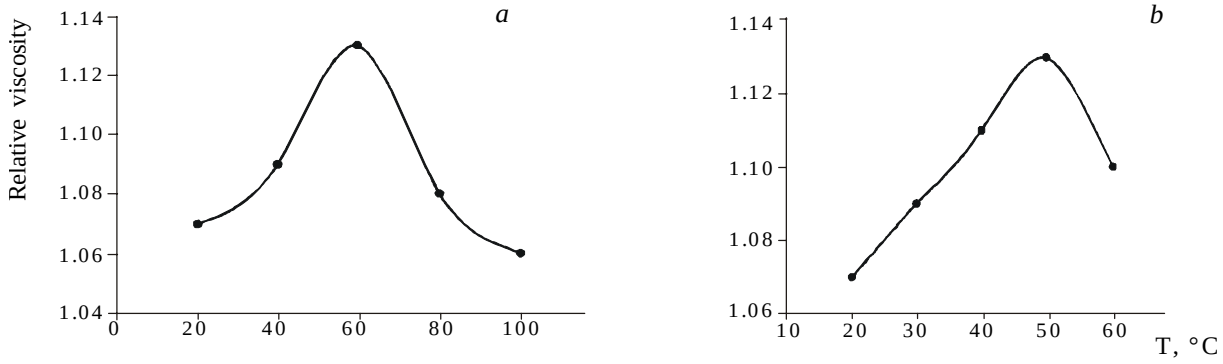

Fig. 1. Relative viscosity of aspen-wood xanthogenation products as a function of alkaline processing temperature (a) and xanthogenation temperature (b).

Table 2 presents data on the effect of time of preliminary alkali processing of aspen wood in isopropanol at 20°C on the properties of its xanthogenation products.

Increasing the duration of alkali processing from 0.5 to 3 h increases the solubility of its xanthogenation products in 6% alkali. The sulfur content is maximal (9.45%) in product 8 (3 h). Increasing the duration of alkali processing to 4-5 h does not further increase the solubility and decreases the sulfur content (Table 2).

Thus, we selected an alkali processing time of 3 h for further investigations. The decreased solubility and sulfur content in product 11, which was obtained after 6 h of alkali activation, is apparently due to more extensive alkaline destruction.

Table 3 presents results for the effect of temperature of alkali processing on the properties of wood xanthogenation products. The solubility in alkali (86%) and sulfur content (10.3%) are maximal for the product obtained at an alkali-processing

temperature of 60°C under otherwise equal conditions. Increasing the activation temperature to 80-100°C significantly decreases the sulfur content and the solubility in alkali.

It has been found that the time and temperature of preliminary alkali processing have the main effect on the properties of the xanthogenation products.

The study of the effect of wood xanthogenation time at 50°C on the product properties indicates that product 13 has the maximal solubility and sulfur content. It was xanthogenated for 3 h (Table 4). Increasing the xanthogenation time to 4-5 h does not increase the sulfur content in the products and slightly decreases their solubility in alkali.

Data for the effect of xanthogenation temperature on the properties of the products are also presented. The optimal xanthogenation temperature should be considered 50°C.

The degree of wood conversion by xanthogenation that was calculated from the sulfur content shows that 20-52% of the wood hydroxyls reacted under the studied conditions (Tables 1-5).

Thus, the principal effect on wood xanthogenation and the properties of the products comes from the preliminary alkali activation of the raw material in isopropanol. About 20-52% of the wood hydroxyls react with CS_2 after 3-5 h of xanthogenation. IR spectra were obtained for the products with the highest sulfur content (samples 8, 13, 19, 23). The spectra exhibit S–H absorption bands at 2500 cm^{-1}; C=S, 1250 cm^{-1}. This confirms that bound sulfur is present.

Therefore, wood xanthogenation products are 32-86% soluble in aqueous alkali and form highly viscous solutions. The time and temperature of preliminary alkali processing have the main effect on the xanthogenation products.

The effect of various process conditions on the macromolecular reactions can be estimated from the change of relative viscosity of the xanthogenation products. The relative viscosity decreases upon prolonged alkali activation and xanthogenation of wood at high temperatures (Fig. 1). This is due to the predominance under these conditions of alkali and solvolytic destruction of the principal wood components. We noted analogous functions by varying the duration of alkali processing at 20°C and xanthogenation at 50°C.

Figure 1 shows that the relative viscosity of alkaline solutions of wood xanthogenate as a function of the temperature of alkali processing and xanthogenation is typically bell-shaped. This is explained by the competition of two parallel processes occurring during wood xanthogenation, i.e., condensation and destruction of the principal components as the time and temperature of the process change.

Depending on the xanthogenation conditions, the physicochemical properties of the products are determined by the competition of two parallel processes, destruction and condensation of the principal wood components. The aspen wood xanthogenation products form highly viscous aqueous solutions and can be used as surfactants.

EXPERIMENTAL

Xanthogenation products of LCH were prepared by the following method. A portion (5.0 g) of air-dried chips (0.5-0.75 mm fraction) was vigorously stirred in isopropanol (100 mL). Aqueous NaOH (40 mL, 30%) was added over 30 min with constant stirring at 20-100°C (calculated one mole NaOH per one mole OH). Then, the mixture was stirred for another 0.5 h at the same temperature (alkali activation stage). The time of alkali activation varied from 0.5 to 6 h. The mixture was decanted and washed with isopropanol (50 mL).

The reaction mixture was treated over 30 min with CS_2 (12 g, one mole CS_2 per one mole OH) dissolved in isopropanol (50 mL). The vessel with the reaction mixture was placed in a thermostat at 20-50°C for 0.5-5 h. The resulting product was separated by decantation and mixed with ethanol (96%), adding glacial acetic acid to neutralize the excess of base and to destroy thio salts. Then, the product was filtered, washed with ethanol until the washings were neutral, and dried in a desiccator (xanthogenation stage).

The content of bound sulfur in the products was determined by the Schoniger flask method as previously described [8]. The solubility of the products was found in NaOH solution (6%) by preparing a solution (0.5%) of the polymer in the solvent used. The relative viscosity of aqueous alkaline solutions of the LCH xanthogenation products was determined in an Ubbelohde viscometer (d 0.65 mm) at 20°C by the method for cellulose xanthogenates given in a handbook [9].

IR spectra of the LCH xanthogenation products were recorded in pressed KBr pellets (2% mixture with products) on a Specord M-80 spectrophotometer with air background.

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