Chemistry of Natural Compounds, Vol. 41, No. 1, 2005

OXIDATION OF HYDROLYZED LIGNIN FROM COTTON-SEED HUSKS BY HYDROGEN PEROXIDE

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UDC 547.99.992

The functional composition and structural porosity of hydrolyzed lignin from cotton-seed husks was altered by oxidation with hydrogen peroxide.

Key words: hydrolyzed lignin, oxidation, hydrogen peroxide, capillary-porous structure, modification, functional composition, IR spectra.

A study of the oxidation of lignin by hydrogen peroxide (H_2O_2), which is the active agent for bleaching cellulose [1], has shown that such treatment is one of the possible methods for modifying industrial lignins [2]. The reaction of H_2O_2 with both isolated and natural lignins produces final destruction products, mainly lower polycarboxylic acids [3]. However, the insoluble part of the lignin is practially unstudied. Therefore, we oxidized hydrolyzed lignin of cotton-seed husks (HLCSH) with H_2O_2 at 20 and 90°C for 3 and 24 h.

Table 1 lists the elemental and functional composition of the oxidized hydrolyzed lignins (OHL).

It can be seen that increasing the H_2O_2 concentration decreases the product yield at both 20 and 90°C. The amount of carbonyl and carboxyl groups increases whereas that of hydroxyls changes insignificantly. This may indicate cleavage of esters and ethers in the lignin macromolecule.

IR spectra of oxidized HLCSH exhibit broad absorption bands for hydroxyls. This is apparently due to an increase in the number of carboxyl and hydroxyl groups and is confirmed by results of functional analysis (Table 1). Absorption in the range 1600-1700 cm^{-1} strengthens depending on the degree of oxidation of the derivatives. This absorption is characteristic of various types of C=O groups and is also confirmed by results of functional analysis. The appearance of a new absorption band at 1705-1715 cm^{-1} in IR spectra of the oxidized lignins is typical of carboxylate vibrations.

A study of the capillary-porous structural parameters of oxidized HLCSH makes it possible to evaluate their surface stucture. Tables 2 and 3 present results of sorption of water vapor by oxidized lignins.

The study of water-vapor sorption by oxidized derivatives of hydrolyzed lignin has shown that OHL-4 is the most hydrophilic, i.e., lignin treated with H_2O_2 (15%) at 90°C for 3 h. It should be noted that this sample also has the maximum total pore volume (W_o) and submicroscopic capillary radius (r_k).

The results of determining the caillary-porous structure of the lignin derivatives have shown that H_2O_2 oxidation decreases the specific surface area for all samples compared with that of initial HLCSH. For OHL-4, the total pore volume and radius of submicroscopic capillaries increase compared with those of the initial lignin (Table 3).

Isotherms for water-vapor sorption by derivatives OHL-1, OHL-2, and OHL-3 typically give slightly S-shaped curves. This may be indicative of capillary condensation of water vapor (Fig. 1). Isotherms of HLCSH derivatives prepared at elevated temperature, i.e., OHL-4, OHL-5, and OHL-6, give concave curves relative to the abscissa at all relative pressures. The sorption isotherms indicate that the sorbents (OHL-4-6) are perturbed and components probably dissolve beginning at low pressures. Sorption of water vapor by oxidized lignins in this instance depends on the affinity of the sorbate for the sorbent and on the flexibility of its macromolecules. The poorer the solvent in a thermodynamic sense, the lower the sorption isotherm.

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TABLE 1. Oxidation of HLCSH by H_2O_2 and Composition of the Resulting Products, % (ratio 1:10)

Lignin sample	H_2O_2 conc., %	t°, C	Yield, %	Reaction time, h	C	H	N	OH	CO	COOH
OHL-1	15.0	20	88.8	24	50.52	5.15	1.15	11.98	0.037	0.014
OHL-2	25.0	20	87.2	24	49.47	5.22	1.40	10.60	0.043	0.014
OHL-3	40.0	20	82.6	24	49.18	6.41	1.52	10.90	0.037	0.014
OHL-4	15.0	90	62.6	3	49.49	6.27	1.12	10.90	0.071	0.016
OHL-5	25.0	90	45.0	3	52.21	6.36	1.53	11.90	0.043	0.015
OHL-6	40.0	90	33.0	3	47.29	6.95	1.55	10.43	0.043	0.012
HLCSH init.					54.50	5.30	-	10.50	0.027	0.007

TABLE 2. Sorption of Water Vapor by Oxidized HLCSH Derivatives at 25°C, %

Relative humidity, %	OHL-1	OHL-2	OHL-3	OHL-4	OHL-5	OHL-6
10	0.90	0.60	0.50	0.90	0.75	0.70
30	1.90	1.40	1.10	1.80	1.65	1.50
50	2.40	1.90	1.60	2.60	2.40	2.15
65	3.00	2.40	1.90	3.60	3.20	2.70
80	3.80	3.25	2.50	4.90	4.35	3.80
90	4.90	4.30	3.20	6.10	5.45	4.70
100	6.80	5.90	4.40	8.30	6.90	6.30

TABLE 3. Capillary-Porous Structure of Oxidized HLCSH Derivatives

Lignin sample	OHL-1	OHL-2	OHL-3	OHL-4	OHL-5	OHL-6	HLCSH init.
X_m, g/g	**0.0171**	0.0132	0.0103	0.0156	0.0154	0.0137	
S_{sp}, m^2/g	**60.12**	46.40	36.20	54.98	54.13	48.16	63.08
W_o, cm^3/g	0.068	0.059	0.044	**0.083**	0.069	0.063	0.076
r_k, Å	22.6	25.4	24.3	**30.2**	25.5	26.2	24

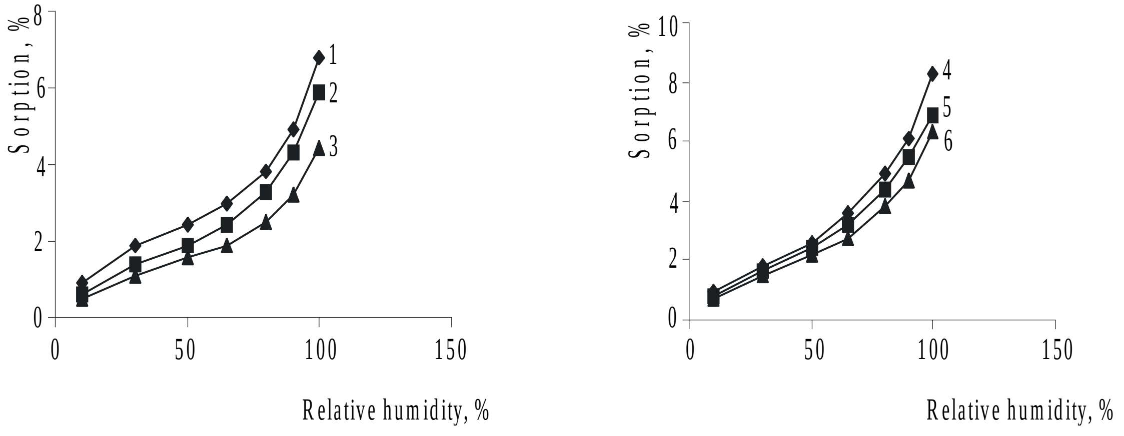

Fig. 1. Sorption isotherms: OHL-1 (1), OHL-2 (2), OHL-3 (3), OHL-4 (4), OHL-5 (5), OHL-6 (6).

Thus, the mechanism for water-vapor sorption by oxidized HLCSH derivatives varies. In our instance, it depends on the preparation conditions of the derivatives. Those prepared at room temperature by the action of H_2O_2 on HLCSH (OHL-1-3) exhibit S-shaped isotherms typical of polymolecular adsorption [4].

EXPERIMENTAL

HLCSH prepared at the Yangiyul′ biochemical plant was purified from traces of mineral acids by washing with hot distilled water until the washings were neutral.

Oxidation of HLCSH by H_2O_2. Weighed portions of lignin were oxidized by H_2O_2 of varying concentration (15, 25, and 40%) for 3 and 24 h at 20 and 90°C. The product was separated by filtration after the reaction. The ratio was 1:10.

Functional Analysis. The content of hydroxyls was determined by acetylation; of carbonyls, by oximation; of carboxyls, by chemisorption as described previously [5].

Capillary-porous structure of initial HLCSH and its oxidized derivatives was studied using a gravimetric variant of a static sorption method that enables simultaneous measurement of the amount of vapor absorbed by the samples and the equilibrium pressure over the resulting solution in a high-vacuum sorption apparatus with a quartz McBain balance. Experiments on water-vapor sorption by lignin samples were performed at 298°K with a residual atmospheric pressure of 10^{-3} Pa.

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