Chemistry of Natural Compounds, Vol. 42, No. 1, 2006

MODIFICATION OF HYDROLYZED LIGNIN IN ACIDIC AND BASIC MEDIA

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UDC 547.99.992

The content of reactive groups such as OH, CO, and COOH was increased by modifying hydrolyzed lignin with sulfuric acid and sodium hydroxide. The increase was confirmed by IR spectral analysis. The sorptive capacity of the resulting hydrolyzed lignin derivatives was increased sharply by base activation.

Key words: hydrolyzed lignin, modification, acid and base activation, sorption isotherm, polymolecular adsorption, IR spectra, functional composition.

Hydrolysis of lignin in acidic and basic media has been well studied. This is due to the fact that hydrolytic processes are used to establish the structure of lignin, to prepare its derivatives, and to destroy polymeric lignin molecules in order to delignify plant materials. Acidic and basic treatment of hydrolyzed lignin frees it of ballast substances and results in the formation of a large internal surface area.

We carried out acidic and basic hydrolysis of hydrolyzed lignin of cotton-seed husks (HLCSH) in order to improve the sorptive properties (Table 1).

Table 1 shows that treatment of HLCSH with weak H_2SO_4 and base solutions decreased the amount of C. This may indicate the occurrence of hydrolytic processes, which is consistent with the increase in the amount of H with increasing concentration of acid and base. Treatment with H_2SO_4 solutions decreases the total amount of hydroxyls and increases the amount of carbonyl and carboxylic groups. Acid hydrolysis probably cleaves ester bonds of the lignin macromolecule. This increases the amount of carbonyl and carboxylic groups.

Like for acid hydrolysis, weak NaOH solutions decreased the amount of hydroxyls and increased the amount of carbonyl and carboxylic groups. This also is consistent with the cleavage of esters in the lignin macromolecule.

Hydrolysis in acidic medium probably leads to HLCSH condensation because the IR spectra of the corresponding derivatives obtained after acid hydrolysis of starting lignin showed a weakened absorption band at 3600-3000 cm^{-1}, which is characteristic of hydroxyl absorption. This agrees with an analysis of the functionality of HLCSH derivatives, where the total amount of hydroxyls decreases compared with starting lignin (Table 1). An increase in the strength of bands at 1707-1716 and 1615-1620 cm^{-1}, which are characteristic of carbonyl absorption, indicates that ester and ether bonds between lignin structural units were cleaved. As a result, the amount of carbonyl and carboxylic groups in the HLCSH derivatives increased (Table 1). Thus, modification of HLCSH by acid hydrolysis increases the amount of carbonyl and carboxylic groups. These changes may have a substantial effect on the reactivity of the studied HLCSH derivatives that will determine their usefulness in industry.

The absorption band at 3650-3000 cm^{-1} in IR spectra of HLCSH derivatives that corresponds to hydroxyl vibrations is broadened. This indicates that condensation may have occurred during base treatment. Lignin condensation during base treatment is known to be ionic in nature [1]. Cleavage of β-*O*-4- or α-*O*-4-ester bonds should form electrophilic carbonium-ion centers and facilitate the generation of nucleophilic centers needed to form secondary C–C bonds. Cleavage of ester bonds in the HLCSH derivatives treated with base probably complicates the hydroxyl absorption bands because carboxylic OH groups vibrate in this region (3550 cm^{-1}). This is especially evident in the IR spectra of GL-B3, GL-B4, and GL-B5. According to functional analysis (Table 1), the amount of carbonyl and carboxylic groups in the HLCSH derivatives from base hydrolysis increased significantly. This experimental fact was confirmed by the IR spectra of the studied samples.

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TABLE 1. Composition of Hydrolyzed Derivatives of Lignin from Cotton-Seed Husks after Acid and Base Hydrolysis at 100°C (0.5 h), %

Lignin	Acid and base concentration	Yield	C	H	OH	CO	COOH
HL-A1	0.1% H_2SO_4	98.67	50.68	5.25	2.40	0.30	0.102
HL-A2	0.5% H_2SO_4	92.84	49.78	6.08	1.70	0.32	0.141
HL-A3	1.0% H_2SO_4	91.70	48.37	7.26	2.50	0.33	0.146
HL-A4	2.0% H_2SO_4	90.30	45.31	7.98	2.13	0.30	0.153
HL-A5	5.0% H_2SO_4	89.65	54.33	8.15	3.63	032	0.154
HL-B1	0.1% NaOH	93.65	49.87	6.06	3.45	0.23	0.085
HL-B2	0.5% NaOH	89.40	49.67	7.37	3.05	0.23	0.047
HL-B3	1.0% NaOH	86.40	44.30	7.64	1.40	0.25	0.018
HL-B4	2.0% NaOH	80.10	42.84	7.71	1.18	0.27	0.019
HL-B5	5.0% NaOH	74.04	41.09	8.02	1.60	0.25	0.087
Starting HLCSH			**54.50**	**5.30**	**10.5**	**0.027**	**0.007**

TABLE 2. Porous Structure Properties of HLCSH Derivatives Activated by H_2SO_4

Porous structure property	Starting HLCSH	HL-A1	HL-A2	HL-A3	HL-A4	HL-A5
X_m, g/g	0.0256	0.0257	0.0117	0.0125	0.0102	0.0104
S_{sp}, m^2/g	89.98	90.54	41.13	43.94	36.03	36.65
W_O, cm^3/g	0.108	0.083	0.071	0.064	0.043	0.086
r_c, Å	24.0	18.3	34.5	29.1	23.8	46.9

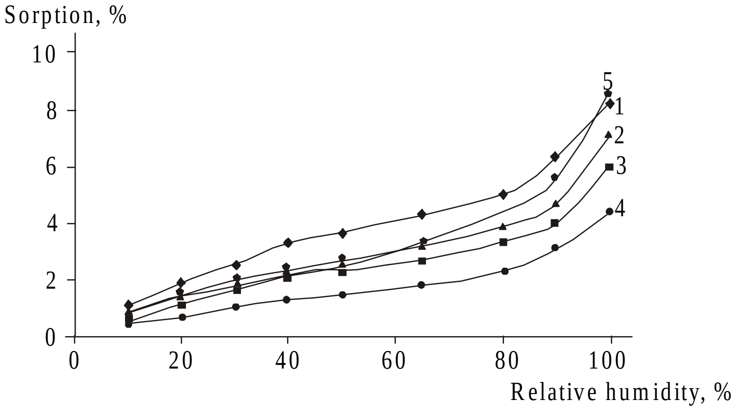

Fig. 1. Sorption isotherms for water vapor of HLCSH derivatives prepared using H_2SO_4 solution: HL-A1 (1), HL-A2 (2), HL-A3 (3), HL-A4 (4), HL-A5 (5).

Table 2 lists the capillary-porous properties of the derivatives prepared by treatment of HLCSH with weak H_2SO_4 solutions.

The most hydrophilic of the HLCSH derivatives that were activated by H_2SO_4 was HL-A1. The equilibrium moisture content in HL-A1 and that at low (10-30%) relative pressures, where water vapor binds mainly to the internal surface of the lignin as a monolayer, and at high (80-100%) pressures, where mainly capillary condensation occurs, were greater than for the other derivatives. Sample HL-A1 also had the maximum specific surface area (S_{sp}), which agrees well with the results for sorption of water vapor by this sample.

TABLE 3. Capillary-Porous Structure Properties of HLCSH Derivatives Activated by NaOH

Property	Starting HLCSH	HL-B1	HL-B2	HL-B3	HL-B4	HL-B5
X_m, g/g	0.0256	0.0191	0.0243	0.0258	0.0274	0.0290
S_{sp}, m^2/g	89.98	67.14	85.52	90.77	96.38	102.03
W_O, cm^3/g	0.108	0.085	0.155	0.165	0.227	0.300
r_c, Å	24.0	25.3	36.2	36.3	47.1	58.8

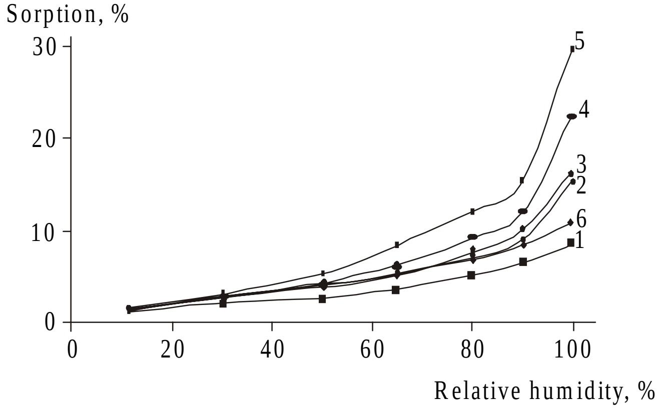

Fig. 2. Sorption isotherms for water vapor of HLCSH derivatives prepared using NaOH: HL-B1 (1), HL-B2 (2), HL-B3 (3), HL-B4 (4), HL-B5 (5), HLCSH (6).

The S-shape of the sorption isotherms of the studied lignins is consistent with capillary condensation of the sorbate molecules and polymolecular adsorption (Fig. 1). However, the sorption isotherms give only a qualitative characterization of the hydrophilicity of the samples. The quantitative hydrophilicity of the lignin samples can be evaluated from the specific surface areas [2]. Table 2 shows that HL-A1 had the greatest values for the monolayer capacity (X_m) and specific surface area (S_{sp}). Sample HL-A1 also had the greatest total pore volume (W_O). Increasing the H_2SO_4 concentration probably led to condensation that decreased sharply the specific surface area and total pore volume starting with sample HL-A2 (treatment of HLCSH with 0.5% H_2SO_4).

Increasing the amount of ionizable groups such as C=O and COOH increases the sorptivity of the HLCSH derivatives treated with H_2SO_4. However, the capillary-porous parameters of these derivatives are inferior to those of aminated HLCSH derivatives [3].

Table 3 gives the capillary-porous parameters of HLCSH derivatives prepared by treatment with NaOH solutions. Activating hydrolyzed lignin with base improved its physicochemical properties and increased the content of reactive centers such as carbonyl and carboxylic groups.

Activation with base increased the hydrophilicity of all HLCSH samples. Thus, HL-B5 was the most hydrophilic of the studied HLCSH derivatives. The equilibrium moisture content in HL-B5 at low relative pressures where water vapor binds mainly to the internal surface of lignin as a monolayer and at high pressures where mainly capillary condensation occurs was greater than for the other derivatives. All capillary-porous parameters of HL-B5 were better than those of the other samples. It should be noted that activation with base improved all parameters of the porous structure and increased the hydrophilicity of the prepared derivatives (Table 3). The sorption isotherms for water vapor of the HLCSH samples activated by base were S-shaped. This is consistent with capillary condensation of sorbate molecules and polymolecular sorption (Fig. 2).

Thus, activation wth base sharply improved the capillary-porous structure of HLCSH when compared with other types of modification (amination, H_2O_2 oxidation, activation with H_2SO_4, phosphorylation). The specific surface area increased by 13.5%; the pore radius, by almost 2.5 times; the total pore volume, by almost 3 times compared with those of starting HLCSH.

The capillary-porous parameters and the nature of the sorption isotherms lead to the conclusion that the studied HLCSH derivatives are sorbents with connected pores [4]. Therefore, they can absorb large quantities of sorbate. This is definitely of practical value.

EXPERIMENTAL

Raw Material Preparation. HLCSH was prepared at Yangiyul′ Biochemical Plant and was purified of traces of mineral acids by washing with hot distilled water until the washings were neutral.

Functional Analysis. The content of hydroxyls was determined by acetylation; of carbonyls, by oximation; of carboxylic groups, by a previously described chemosorption method [5].

IR spectra of starting HLCSH and their derivatives were recorded on a Perkin—Elmer System 2000 Fourier IR spectrometer (Sweden) at resolution 4 cm^{-1}, scan rate 0.2 cm/s, and 500 scans. Samples were prepared as pressed KBr disks.

Acid hydrolysis of HLCSH was carried out using H_2SO_4 solutions (0.1, 0.5, 1.0, 2.0, and 5.0%). A weighed portion of HLCSH was treated with the appropriate H_2SO_4 solution at 100°C for 30 min at a 1:10 ratio. Then the lignins were separated by filtration, washed with water until the washings were neutral, dried, and used for further analyses.

Base hydrolysis of HLCSH was carried out using NaOH solutions (0.1, 0.5, 1.0, 2.0, and 5.0%). A weighed portion of HLCSH was boiled with base solution (100°C) for 30 min at a 1:10 ratio. Then the lignins were separated by filtration, washed with water until the washings were neutral, dried, and used for further analyses.

Capillary-porous structures of HLCSH and its derivatives were studied using a gravimetric version of the static sorption method that enables simultaneous measurement of the amount of vapor absorbed by the lignin samples and the equilibrium pressure of this vapor over the resulting solution on a high-vacuum sorption apparatus with a McBain quartz microbalance.

The experiments on water-vapor sorption by lignin samples were performed at 298 K and residual air pressure 10^{-3} Pa. The specific surface area (S_{sp}), total pore volume (W_o), and average radius of submicroscopic capillaries (r_c) were calculated using sorption isotherms and the BET method.

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