

AMINATION OF HYDROLYZED LIGNIN OF COTTON-SEED HUSKS

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Up to 4% nitrogen was incorporated into the HLCSH macromolecule by amination whereas the functional composition of HLCSH was changed by the hydrolytic action of ammonia. Bile acids were absorbed by the studied specimens. The sorptivity of aminated HLCSH derivatives was dependent on mainly their specific surface area.

Key words: hydrolyzed lignin, amination, capillary-porous structure, sorption, bile acids.

Functionalization of N-containing groups, among which amines are highly interesting, is an important method for modifying hydrolyzed lignin. Introducing basic amines into lignin changes radically the properties of the macromolecule by transforming lignin from a polyacid into a polybase or polyampholyte. This creates new possibilities for its utilization [1]. Taking into account the polyfunctionality of hydrolyzed lignin, introduction of amines by the action of aqueous ammonia is entirely possible.

We aminated hydrolyzed lignin of cotton seed husks (HLCSH) at various temperatures and a 1:3 ratio for 6 h (Table 1). We found that amination of HLCSH by aqueous ammonia (12.5%) at elevated temperature reduced the yield. The contents of carbon and carboxyls, mainly carbonyls, also decreased. The loss of carboxyls and carbonyls indicates that substitution reactions involving these groups of hydrolyzed lignin are occurring and that nitrogen may be incorporated into amine or imine groups. The increased content of hydrogen is consistent with this. The gain of hydroxyls indicates that hydrolytic processes may be occurring upon heating lignin with aqueous ammonia (12.5%).

Increasing the concentration of ammonia reacting with HLCSH to 25% increased the content of reaction products. However, increasing the reaction temperature decreased the yield from 93.4 to 88.0%. In this series of experiments, the amount of carbon and carboxyls also decreased, carbonyls partially decreased, and the amount of hydrogen and total hydroxyls increased insignificantly. Analysis of the elemental and functional compositions of aminated HLCSH showed that up to 4.1% nitrogen was incorporated into the hydrolyzed lignin macromolecule under these conditions. Aminodehydroxylation [2] and imination [3] reactions could probably occur.

It should be noted that nitrogen incorporation into the hydrolyzed lignin macromolecule reached the maximal value of 8.2% by treating it under comparatively harsh conditions, i.e., ammonia (25%) at 230°C [4]. Inspection of the IR spectra of the studied specimens of hydrolyzed lignin revealed the stretching vibrations that were most sensitive to the lignin structural features: OH, CO, COOH, and NH₂ (Table 2).

Group theory cannot be used to interpret the IR spectra because of the amorphous nature of the lignins, the complicated structure of the monomers, and the variety of bonds. Therefore, the bands are interpreted empirically. However, the many methods applicable to their interpretation enables a high degree of accuracy to be achieved.

IR spectra of the studied specimens have almost all bands characteristic of lignins. However, certain absorption bands overlapped because of the modification, for example, the band at 3600-3000 cm⁻¹ characteristic of stretching vibrations of hydroxyls involved in H-bonds and the band at 3500-2900 cm⁻¹ for N-H absorption.

Structural information for the aminated lignins was obtained by analyzing the OH stretching vibrations in the 3200-3500 cm⁻¹ range. The reduction in the OH stretching vibrations for all specimens compared with starting HLCSH indicates that the hydroxyls participate in intermolecular coordination to ammonium ions.

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TABLE 1. Amination of HLCSH and Composition of Resulting Products, % (1:3 ratio, 6 h)

AHL sample	NH ₄ OH, %	Temperature, °C	Yield	C	H	N	OH	CO	COOH
1	12.5	20	88.8	48.88	5.17	2.72	8.66	0.25	0.060
2	12.5	50	78.6	47.0	5.71	3.21	6.5	0.28	0.051
3	12.5	100	80.4	45.9	6.59	4.05	14.5	0.23	0.045
4	25.0	20	93.4	45.31	6.10	3.18	40.0	0.26	0.092
5	25.0	50	94.0	46.48	5.99	4.13	7.35	0.25	0.047
6	25.0	100	88.0	43.72	6.22	3.66	12.4	0.28	0.041
HLCSH initial				54.50	5.30	-	10.50	0.027	0.0071

1-6, aminated hydrolyzed lignin (AHL)

TABLE 2. Properties of Capillary-Porous Structure of Aminated Derivatives of HLCSH

Property	AHL-1	AHL-2	AHL-3	AHL-4	AHL-5	AHL-6
x_{mp} , g/g	0.0241	0.0224	0.0178	0.0239	0.0256	0.0161
S_{sp} , m ² /g	84.76	78.94	62.71	84.09	90.08	56.77
w_o , cm ³ /g	0.093	0.083	0.105	0.083	0.092	0.096
r_c , Å	21.9	21.0	35.5	19.7	20.4	33.8

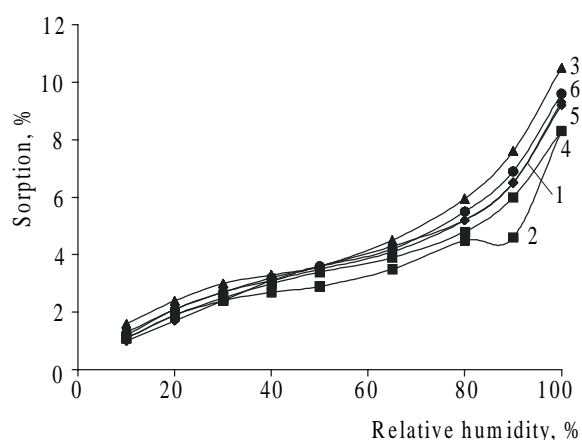


Fig. 1. Sorption isotherms of water vapor by aminated derivatives: AHL-1 (1), AHL-2 (2), AHL-3 (3), AHL-4 (4), AHL-5 (5), AHL-6 (6).

Bands at 1600 and 1510 cm⁻¹ in lignin chemistry refer unambiguously to skeletal vibrations of aromatic rings. However, carboxylates can increase the intensity of the band at 1600 cm⁻¹. This fact is confirmed by the absence in the IR spectra of the studied specimens of an absorption band at 1750 cm⁻¹, which corresponds to carboxyl vibrations. This experimental fact is consistent with the formation of complexes with predominantly ionic ammonium—ligand bonds.

Vibrations near 1115 cm⁻¹ are due to ether absorptions, in particular, C—O—C stretches in lignins. This band shifts slightly to low frequency in the IR spectra.

Thus, analysis of characteristic bands in the IR spectra of HLCSH and its aminated derivatives indicated that lignin macromolecules may be coordinated intermolecularly with ammonium ions through “ionic ammonium—ligand” bonds. The main lignin reaction centers are carboxyls and hydroxyls.

TABLE 3. Sorptivity of Aminated Derivatives of HLCSH as a Function of Specific Surface Area

Property	HLCSH	AHL-1	AHL-2	AHL-3	AHL-4	AHL-5	AHL-6
Sorptivity, %	38.0	42.0	37.0	35.0	40.0	36.0	37.0
S_{sp} , m ² /g	63.08	84.76	78.94	62.71	84.09	90.08	56.77

The surface structure in swelled lignin can be estimated by studying the properties of the capillary-porous structure of aminated HLCSH. This has definite value for sorption processes of certain classes of compounds. Determination of the amount of sorbed water vapor showed that AHL-3 was the most hydrophilic of HLCSH derivatives treated with aqueous ammonia (12.5%, samples AHL-1, -2, and -3) (Fig. 1). It should be noted that this sample also had the maximal total pore volume and radii of submicroscopic capillaries (Table 2). Determination of the amount of water vapor sorbed in HLCSH derivatives treated with aqueous ammonia (25%, samples AHL-4, -5, and -6) showed that AHL-6 is the most hydrophilic (Fig. 1) and also had the maximal total pore volume and radii of submicroscopic capillaries (Table 2). This experimental result correlates with those for water-vapor sorption. Thus, certain parameters of the capillary-porous structure of the derivatives improve as the temperature at which HLCSH is treated with aqueous ammonia increases.

It should be mentioned that the specific surface area, total pore volume, and radius of submicroscopic capillaries of starting HLCSH are 63.08 m²/g, 0.076 cm³/g, and 24 Å, respectively [5]. The analytical results indicate that the specific surface area of the lignin derivatives increases upon treatment of HLCSH with ammonia solution (12.5%) compared with that of untreated HLCSH. However, its value decreases to that of starting HLCSH (samples AHL-1, -2, and -3) if the reaction temperature is raised from 20 to 100°C. About the same trend is observed for derivatives prepared by treatment with ammonia solution (25%, samples AHL-4, -5, and -6, Fig. 2).

Sorption isotherms for water vapor by the studied HLCSH derivatives are S-shaped (Fig. 1). This is consistent with capillary condensation of sorbate vapor. The S-shaped isotherms are typical of polymolecular adsorption [6]. Therefore, such sorption of water vapor can be assumed for the aminated lignin derivatives. The presence of such an electronegative element as nitrogen probably increases the amount of ionizable groups, in particular, carboxyls, aliphatic hydroxyls, and amines that control the adsorptivity of the lignins.

Ionizable groups of sorbents are known to be capable of polymolecular adsorption of water vapor on the sorbent surface through Van-der-waals forces. Therefore, better capabilities of AHL-3 and AHL-6 to adsorb water vapor can be explained by the higher content of such ionizable groups as OH and C=O in these samples than in the others (Table 1).

We also studied the sorptivity of aminated HLCSH derivatives *in vitro* experiments using human bile obtained through operative intervention. The bile:HLCSH derivative ratio was 1:10; temperature, thermostatted at 37°C; time, 2 h. The content of bile acids in the supernatant liquid of experimental and control specimens was determined by the Pettenkofer reaction [7] (Table 3).

It can be seen that HLCSH derivatives treated with ammonia solutions (12.5 and 25.0%) at 20°C have sorptivities greater than the control and other samples. This is probably due to the fact that AHL-1 and AHL-4 have similar parameters for the capillary-porous structure such as the monolayer volume and specific surface area, total pore volume, and dimensions of submicroscopic capillaries (Table 3).

A study of the sorptivity of the derivatives as a function of certain parameters of their capillary-porous structure found a relatively weak dependence of the sorptivity on the specific surface area. Analysis of other parameters of the capillary-porous structure on the sorptivity of aminated HLCSH derivatives indicates that it is independent of the dimensions of submicroscopic capillaries and total pore volume.

The total pore volume w_0 does not reflect its true value because it is the limiting volume of adsorption space that depends on the molecular size of the sorbate. Therefore, this explains why they are not correlated.

Thus, pharmacological tests of aminated HLCSH derivatives showed that these substances can absorb bile acids. Comparison of the sorptivities of the aminated HLCSH derivatives showed that they depend relatively weakly on the specific surface area of the studied substances.

EXPERIMENTAL

HLCSH was prepared in the Yangiul Biochemical Plant and purified from traces of mineral acids by washing with hot distilled water until the washings were neutral.

The content of hydroxyls was determined by acetylation; of carbonyls, by oximation; of carboxyls, by chemisorption as described in the literature [8].

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

Preparation of Aminated HLCSH. HLCSH samples were treated with aqueous ammonia (12.5 and 25.0%) at 20, 50, and 100°C in a 1:3 ratio. After the reaction time expired (6 h), lignin was separated by filtration and washed with water until neutral.

Capillary-porous structures of HLCSH and its derivatives were studied using a gravimetric variation of static sorption that enables the amount of vapor absorbed by the lignin samples and the equilibrium pressure of this vapor over the resulting solution to be measured on a high-vacuum sorption apparatus with a quartz Mack—Ben balance. Experiments on water-vapor sorption by lignin samples were performed at 298 K and residual air pressure 10^{-3} Pa . The specific surface area was calculated based on the sorption isotherm by the BET method using the equation:

$$S_{\text{sp}} = (X_{\text{m}}/M)N_{\text{A}}a_{\text{m}}10,$$

the total pore volume, $w_0 = X/m$.

The average radius of submicroscopic capillaries was determined using the equation $r_c = (2w_0/S_{\text{sp}})10$; the concentration of bile acids after sorption on lignin samples, by the Pettenkofer reaction [7].

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