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STUDY OF THE CAPILLARY-POROUS STRUCTURE OF TECHNICAL LIGNINS

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Differences in the supermolecular structures of various samples of technical lignins have been revealed by studying their water vapor sorption.

It is known that the sorption method is widely used for investigating the porous structures of various materials, including natural and synthetic polymers and compositions based on them [1-3].

In spite of being loaded with residues of organic and mineral acids, carbohydrates, resins, nitrogen bases, etc., technical hydrolysis lignin possesses a developed surface. The area of the internal surface of the moist product amounts to 700 m^2/g and its pore radius to 50-200 Å. which indicates a high sorption activity of hydrolysis lignin.

Our task was to study the parameters of the capillary-porous structure of hydrolysis lignins and their derivatives by the water vapor sorption method. This provides the possibility of evaluating the surface structure of the lignin in the swollen state and has definite practical importance in the sorption of some classes of compounds by technical lignins.

We have investigated the hydrolysis lignins of rice husks (HLRH), of cottonseed hulls (HLCSH), and of sawdust (HLSD), and also the sulfo-, nitro-, and chlorolignins (SL, NL, and CL) obtained in the modification of HLCHS. To determine their capillary-porous structures, we studied the sorption of water vapor by the samples of technical lignins and determined the specific surface (S_{sp}), total pore volume (W_0), and mean, radius of the submicroscopic capillaries (r_c) of each of the samples investigated. The results obtained are presented in Tables 1 and 2 and in Figs. 1 and 2.

A determination of the amounts of water sorbed showed that among the initial hydrolysis lignins (samples 1-3) the most hydrophilic was HLRH, and among the modified lignins (samples 4-6) the SL was the most hydrophilic over almost the whole range of relative humidities. The equilibrium moisture content of SL, both at low values of the relative pressure (5-30%), when water vapor is bound mainly by the internal surface of the lignin in the form of a monomolecular layer, and also in the region of high pressures (75-95%), when the main process is capillary condensation, was greater than for the other samples of HL.

The magnitudes of the specific surface were calculated from the results for the initial stage of sorption by means of the Brunauer–Emmet–Teller equation [3]. Analysis of the figures obtained showed that among the initial lignins the specific surface and the total pore volume were greatest for the HLRH. This is probably connected with a less dense structure or an amorphous nature of the HLRH.

The maximum value of the specific surface and of the total pore volume were found for SL, which correlates with the sorption of water vapor by this material.

The isotherms for the sorption of water vapor by the lignins investigated had sigmoid shapes (Figs. 1 and 2) which shows capillary condensation of the sorbate vapors. Since a sigmoid form of a sorption isotherm is characteristic for polymolecular adsorption [4], it may be assumed that the sorption of water vapor by technical lignins is of this nature.

It is known that hydrophilic sorbents are used for purifying sorbates (petroleum products, oils, etc.) [5]. In view of the hydrophilicity of the materials investigated, it may be concluded that SL and NL can be used for the sorption of hydrophobic sorbates.

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TABLE 1. Sorption of Water Vapor by Technical Lignins, %

Relative humidity	HLRH	HLCSH	HLSD	SL	NL	CL
10	0.70	0.60	0.50	0.80	0.90	0.30
30	1.80	1.60	1.00	2.30	2.20	0.80
50	2.70	2.10	1.50	3.60	3.00	1.30
65	3.50	2.90	2.20	4.50	3.70	2.00
80	4.50	3.90	3.30	5.60	4.90	3.00
90	5.50	5.10	4.60	7.00	6.50	4.00
100	8.10	7.60	7.30	9.60	9.40	5.30

TABLE 2. Parameters of the Capillary-Porous Structure of Samples of Technical Lignins

Sample	S_{sp}, m^2/g	W_0, cm^3/g	r_c
1. HLRH	68.29	0.081	24
2. HLCSH	63.08	0.076	24
3. HLSD	30.54	0.073	48
4. SL	99.74	0.096	19
5. NL	79.07	0.094	24
6. CL	31.54	0.053	34

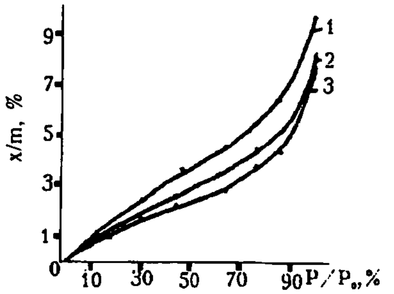

Fig. 1

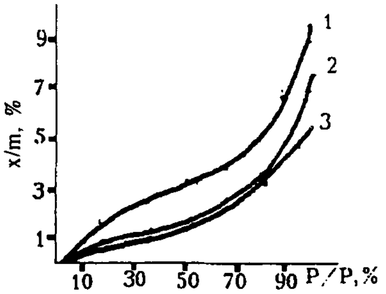

Fig. 2

Fig. 1. Sorption of water vapor by samples of lignin: *1*) SL; *2*) HLRH; *3*) HLCSH.

Fig. 2. Sorption of water vapor by samples of lignin: *1*) NL; *2*) HLSD; *3*) CL.

Thus, a study of the sorption of water vapor by samples of lignins has shown differences in their supermolecular structures.

EXPERIMENTAL

To study the sorption of water vapor by technical lignins, we used a high-vacuum apparatus with mercury valves and a McBain quartz balance. The measurements were conducted at 25°C under a pressure of 10^{-10} mm Hg.

Samples of hydrolysis lignins (HLRH, HLCSH, HLSD) were obtained from the Yangiyul' biochemical factory. Nitro- and sulfolignins were obtained by the method of [5]. Chlorolignin was obtained by passing gaseous chlorine through a suspension of hydrolysis lignin in CCl_4 at 20-22°C for 5 h. After the lapse of this time, the product was filtered off.

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