Chemistry of Natural Compounds, Vol. 37, No. 2, 2001

CAPILLARY—PORE STRUCTURE OF HYDROLYZED LIGNIN DERIVATIVES

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UDC 547.99.992

The polymolecular nature of sorption by various samples of hydrolyzed lignin is studied by water-vapor sorption.

Keywords: hydrolyzed lignin, sorption, sorption—desorption isotherms.

In continuation of the study of the capillary—pore structure of hydrolyzed lignin derivatives by water-vapor sorption, we present results from the investigation of the following derivatives of hydrolyzed lignin from cotton-seed husks (HLCH): piperidinomethylated hydrolyzed lignin (PMHL), phosphorylated piperidonomethylated dioxanelignin from cotton stems (PPDL), phosphorylated hydrolyzed lignin (PHL), and oxidized hydrolyzed lignin (OHL).

We determined the specific surface area (S_{sp}), total pore volume (W_t), and dimensions of submicroscopic capillaries (r_c) (Tables 1 and 2). Sorption isotherms for water vapor were S-shaped for the studied hydrolyzed lignins. This is characteristic of loosely packed and highly cross-linked polymers [1]. Furthermore, the S-shaped sorption isotherms for these lignins is consistent with capillary condensation of sorbate molecules and polymolecular adsorption. However, the sorption isotherms give only a qualitative picture of the sample hydrophilicity. The quantitative hydrophilicity of the lignin samples can be estimated from the specific surface areas. Table 2 shows that the monolayer capacity (X_m), specific surface area, and total pore volume are greatest for PMHL. The ionic groups that are responsible for adsorptivity, e.g., carboxylate, aliphatic hydroxyl, amino-, nitro- and sulfo-groups, probably increase in number if electronegative elements such as N and S are present [2]. Ionized groups of sorbents are known to facilitate polymolecular adsorption of water vapor on the sorbent surface through van-der-Waals forces [3]. Therefore, the best absorption of water vapor by PMHL, like for neutral and sulfolignins [4], can be explained by the presence of ionized groups in these samples. Phosphorylation of HLCH decreases the total pore volume and specific surface area and increases the radii of capillaries (PHL). Phosphorylation of HLCH may produce a more densely packed lignin that makes water-vapor sorption by this sample the lowest (Table 1).

OHL was prepared by oxidation with H_2O_2 of starting HLCH. It has a specific surface area equal to that of PMHL but a total pore volume lower than it (Table 2). Oxidation of HLCH is known to destroy some of the lignin active functional groups and probably decrease the sorptivity.

Thus, water-vapor sorption is used to determine the pore structure of certain hydrolyzed-lignin derivatives. Analysis of the radii of submicroscopic capillaries, sorption isotherms, and sorption hysteresis indicates that the studied HLCH derivatives are sorbents with transitional pores [5]. This suggests that they can absorb large amounts of sorbate, which has definite practical value.

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 0009-3130/01/3702-0188$25.00

TABLE 1. Sorption and Desorption of Water Vapor by Hydrolyzed Lignin Derivatives

Rel. hum., %	PMHL, %		PPDL, %		PHL, %		OHL, %	
	sorption	desorption	sorption	desorption	sorption	desorption	sorption	desorption
10	0.6	0.6	0.9	0.9	0.3	0.3	0.6	0.6
20	1.1	1.4	1.3	1.3	0.55	0.55	1.1	1.1
30	1.5	2.1	1.5	1.6	0.75	0.75	1.5	1.55
40	1.85	2.75	1.6	1.8	0.85	0.9	1.7	1.9
50	2.1	3.3	1.7	2	0.95	1.2	1.9	2.3
65	2.4	3.9	1.85	2.2	1.4	1.75	2.3	3.05
80	3.4	4.8	2.35	3	2.35	2.7	3.35	3.9
90	4.65	6	3.25	3.9	3.25	3.5	4.3	4.65
100	7.7	7.7	5.2	5.2	4.3	4.3	5.6	5.6

TABLE 2. Capillary—Pore Structure of Hydrolyzed Lignin Derivatives

Sample	X_m, g/g	S_{sp}, m^2/g	W_t, cm^3/g	r_c, Å
PMHL	0.0157	55.185	0.077	28
PPDL	0.0117	41.177	0.052	25
PHL	0.0078	27.585	0.043	31
OHL	0.0157	55.185	0.056	20
HLCH	0.0179	63.08	0.076	24

EXPERIMENTAL

Water-vapor sorption was studied using a McBain quartz balance of sensitivity 2·10 m/kg at 298 K and residual air pressure 10^{-3}-10^{-4} Pa. A KM-8 cathetometer was used to measure the mass change upon sorption of water vapor. The vapor pressure was measured when the amount of sorbed water was at equilibrium. Sorption isotherms were constructed.

Purification of Hydrolyzed Lignin. HLCH from Yangiyulsk biochemical plant was purified from traces of sulfuric acid by washing with distilled water until the washings were neutral, filtered, and dried at room temperature.

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