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FUNCTIONAL COMPOSITION OF OXYAMMONOLYSIS PRODUCTS OF BIRCH WOOD

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Oxidative ammonolysis of lignocarbohydrate materials was studied in order to produce their N-containing derivatives, which can be used as organic fertilizers and cation exchangers [1, 2]. We developed methods to produce N-containing derivatives of lignocarbohydrate materials using ammonium persulfate [1] or atmospheric oxygen [3] in aqueous ammonia with mechanochemical treatment. The functional composition of the bound N in the oxyammonolysis products of birch wood that were produced by these methods was investigated.

The total N content was determined by the Kjeldahl method as before [4]; the content of bound-N forms, by differential H_2SO_4 hydrolysis by solutions of increasing concentration (from 0.5 to 5 N) using the literature method [5] and analyzing the content of residual N in the hydrolyzed samples. The total content of hydroxyls was established by Verlei acetylation [4]; of carbonyls, by oximation [4]. The amount of carboxylic acids was analyzed by reverse conductometric titration using the literature method [6]. The content of methoxyls was calculated by the Zeisel method using GC analysis and a handbook method [7].

Table 1 shows that birch wood ammonized by ammonium persulfate in aqueous ammonia contains a very large amount of difficultly hydrolyzed forms of N. Evidently this is due to its high oxidizing capability, which leads to a more extensive transformation of the easily hydrolyzed forms of N into difficultly hydrolyzed and unhydrolyzed ones. The products of birch wood oxyammonolysis by atmospheric oxygen contain 40% easily cleaved N and 60% difficultly hydrolyzed whereas wood ammonized by persulfate contains 35% easily cleaved and 65% difficultly hydrolyzed N (Table 1).

The content of bound N forms in the oxyammonolysis products of pine wood and sunflower shell by atmospheric oxygen in aqueous ammonia are also given for comparison. According to Table 1, the oxyammonolysis products of sunflower shell and pine wood contain primarily N in the easily hydrolyzed forms (63-71%). An analogous phenomenon is observed for oxidation by ammonium persulfate. This is probably due to structural features of the lignocarbohydrate complexes in coniferous wood and the non-woody plant raw material.

Oxidative ammonolysis of birch wood by atmospheric oxygen oxidizes hydroxyls and also removes methoxyls (Table 2). It can be seen that all hydroxyls are oxidized. The content of carbonyls does not significantly change. This group is probably an intermediate functional group for binding N and for further oxidation to carboxylic acids. This keeps their content in dynamic equilibrium.

Table 2 shows that the changes in the functional composition of the oxyammonolysis products of birch wood that are produced by the various oxidants (atmospheric oxygen, ammonium persulfate) are similar. However, the degree of oxidation of the oxyammonolysis product isolated from persulfate is greater. This product contains fewer hydroxyls and methoxyls. This corresponds to a greater N content for oxidation of wood by persulfate (Tables 1 and 2).

Thus, ammonolysis oxidation products of birch wood contain bound N in various forms: ~20-24% in the ammonium form and 15-16% as an easily hydrolyzed form (amide). The rest (55-70%) consists of difficultly hydrolyzed functional groups (amines and heterocycles).

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TABLE 1. Content of Bound-Nitrogen Forms (% of Total Content) in Oxyammonolysis Products of Birch and Pine Wood and Sunflower Shells

Bound N form	Oxyammonolysis product prepared by			
	atmospheric oxygen (3.0% N)	ammonium persulfate (6.9% N)	atmospheric oxygen	
	birch wood		pine wood (3.1% N)	sunflower shell (5.5% N)
Ammonium	24	20	35	45
Easily hydrolyzed	16	15	28	26
Difficultly hydrolyzed	31	39	22	17
Unhydrolyzed	29	26	15	12

TABLE 2. Functional Composition of Birch Wood and Holocellulose Treated with Atmospheric Oxygen in Aqueous Ammonia (Without N Functional Groups)

Products	Functional group content, %				
	$OH_{tot.}$	COOH	CO	OCH_3	N
Oxyammonolysis of birch wood by:					
atmospheric oxygen	13.7	9.5	2.1	3.0	3.0
ammonium persulufate	11.7	12.2	2.3	2.2	6.9
Holocellulose isolated from oxyammonolysis product of birch wood by:					
atmospheric oxygen	8.4	10.3	1.7	-	0.9
ammonium persulufate	5.3	11.2	1.7	-	1.4

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