Chemistry of Natural Compounds, Vol. 40, No. 3, 2004

OXYAMMONOLYSIS PRODUCTS OF BIRCH WOOD AND ITS PRINCIPAL COMPONENTS

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UDC 634.0.861.16

The composition of products from oxidative ammonolysis of the principal components of birch wood by mechanochemical treatment with atmospheric oxygen and ammonium persulfate in aqueous ammonia was studied.

Key words: oxyammonolysis, birch wood, lignin, holocellulose, cellulose.

We developed mechanochemical methods for preparing N-containing derivatives of lignocarbohydrate materials from plant raw material using ammonium persulfate [1] or atmospheric oxygen [2] in aqueous ammonia. Herein we present results from studies of the elemental composition of oxyammonolysis products of birch wood and its principal components that were prepared by these methods. The principal polymeric components persist in the birch wood. The oxidation products contain the same amount of lignin (~19.4 mass %). This indicates that delignification processes occurred only minimally. Wood polysaccharides underwent the greatest destruction.

Elemental analysis of oxidation products of birch wood and its macrocomponents by atmospheric oxygen and ammonium persulfate showed that they contain up to 3.3 and 6.9%, respectively, of bound N, an increased amount of C, and a lower amount of O compared with the starting wood.

Treatment with ammonium persulfate decreased the amount of holocellulose from 73.1 to 51.3% compared with starting wood.

Elemental analysis of starting holocellulose and that isolated from the wood oxidation products indicates that its polysaccharides contain 1.4% (atmospheric oxygen) and 0.9% (ammonium persulfate) N. Therefore, the N is bound by oxidation products of birch-wood polysaccharides. The increased content of O and reduced content of C in birch-wood holocellulose after oxyammonolysis indicates that wood polysaccharides were extensively oxidized. This is confirmed by the increased content of carboxylic acids in them (Table 1).

The elemental composition of lignin isolated from the product of birch-wood oxyammonolysis by atmospheric oxygen differs substantially from that of dioxanlignin from starting wood. Thus, lignin isolated from the oxyammonolysis product typically has a higher C content and a significant number of COOH groups. The lignin contains more N and carboxylic acids than polysaccharides (Table 1).

The elemental composition of lignin isolated from birch wood after treatment with ammonium persulfate differs significantly from that of dioxanlignin from starting wood and lignin isolated from wood oxidized with atmospheric oxygen. Lignin treated with ammonium persulfate has a noticeably lower C content, increased O content, and higher N (6.3%) and carboxylic acid (16.7%) contents. Obviously, ammonium persulfate is a strong oxidant and additional source of free-radical formation. It in combination with mechanical cracking leads to more extensive oxidation of lignin whereas the lignin aromatic system helps stabilize the radicals [3].

The degree of polymerization (DP) was measured by viscosimetry for starting birch-wood cellulose (1250) and that isolated from the products of oxyammonolysis by atmospheric oxygen (230) and ammonium persulfate (150).

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Translated from Khimiya Prirodnykh Soedinenii, No. 3, pp. 235-236, May-June, 2004. Original article submitted December 30, 2003.

0009-3130/04/4003-0280

TABLE 1. Elemental Composition of Oxyammonolysis Products of Birch Wood and Its Principal Components from Treatment with Atmospheric Oxygen (a) and Ammonium Persulfate (b) in Aqueous Ammonia

Sample	Content, %									
	C		H		N		O		COOH	
	a	b	a	b	a	b	a	b	a	b
Starting birch wood	47.3	47.3	6.1	6.1	0.5	0.5	46.0	46.0	2.3	2.3
Birch-wood oxyammonolysis product	49.9	48.9	3.9	7.6	3.0	6.9	43.1	36.7	9.5	12.2
Dioxanlignin from starting birch wood	60.4	60.4	6.1	6.1	0.1	0.1	33.3	33.3	0.7	0.7
Dioxanlignin isolated from oxyammonolysis product of birch wood	67.4	52.3	5.5	6.6	3.3	6.3	23.8	35.2	12.5	16.7
Holocellulose from starting birch wood	42.7	42.7	6.1	6.1	-	-	51.2	51.2	3.6	3.6
Holocellulose isolated from oxyammonolysis product of birch wood	37.7	38.5	6.0	5.9	1.4	0.9	54.9	54.6	10.3	11.2

The length of the cellulose macromolecules decreases during oxyammonolysis. Cellulose isolated from the product of oxidation by persulfate gave the lowest yield and DP. The reason for such a drop in the DP is mechanical cracking and oxidation and basic hydrolysis of the polysaccharide chain from the reacting end.

Thus, mechanochemical oxyammonolysis of birch wood by atmospheric oxygen and ammonium persulfate in aqueous ammonia leads to oxidation of the lignin and polyoses, condensation of lignin, and oxidative-mechanochemical destruction of wood polysaccharides. This gives different N contents in them. Lignin is more reactive than polyoses to oxyammonolysis.

EXPERIMENTAL

The compositions of the starting material and oxyammonolysis products were determined using handbook methods [4]: holocellulose, by Wise; cellulose, by Kuerschner; lignin, by Komarov. Starting birch wood has the following composition: cellulose, 49.3%; holocellulose, 73.4%; lignin, 19.7%. Oxyammonolysis of birch wood by atmospheric oxygen and ammonium persulfate was carried out by the literature methods [1, 2, 5]. The C and H contents were determined gravimetrically by combustion in a stream of oxygen (O content was calculated by difference); N content, by the published Kjeldahl method [6]. The content of COOH groups was calculated by conductometric titration [7]. Dioxanlignin was isolated by the Pepper method as modified by Chudakov in a N_2 atmosphere according to the published procedure [8]. The DP of cellulose was found from the characteristic viscosity of its Cu—ammonia solutions (0.1%) in a Ubellohde viscosimeter at 20°C [4].

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