

OXIDATIVE AMMONOLYSIS OF BIRCH WOOD

M. V. Efanov, D. V. Dudkin, and A. I. Galochkin

UDC 634.0.813.16

The functional composition of oxidative ammonolysis products obtained from treatment of birch wood with ammoniacal ammonium persulfate using a mechanochemical method was studied.

Key words: oxidative ammonolysis, birch wood, mechanochemical method.

Complex utilization of plant raw material is currently a very urgent issue. Extensive chemical processing of biomass from lignocarbhydrate plant material is most optimal for producing various polymeric materials.

Of particular interest are N-containing derivatives of lignin, which have been recommended for application as nitrogenous organo-mineral fertilizers and sorbents [1-4]. The principal method for preparing them is oxidative ammonolysis, which consists of treatment of lignin-containing raw material with oxygen in ammoniacal media at 120-250°C in autoclaves at 5-50 atm [5, 6]. These methods have serious drawbacks including the complexity and duration of the process and the low product yield with significant consumption of oxidant and ammonia.

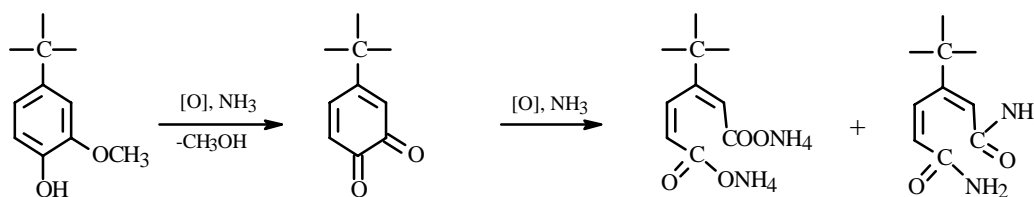
A new method for preparing N-containing lignin derivatives under mild conditions from various lignin preparations by ammoniacal ammonium persulfate at 20°C over 1-5 days has been proposed [7, 8]. Persulfates are widely used as oxidants of organic compounds, in particular, cellulose and its esters [9]. However, the chemistry of the reaction of persulfate on wood and other lignocarbhydrates has been little studied [10, 11]. Only surface physicochemical modification of wood to give it a stable shape has been carried out.

Our goal was to investigate how the functional groups change during the reaction of ammonium persulfate with birch wood in ammonia in order to modify it extensively. Table 1 shows that the content of bound nitrogen increases with increasing processing time with a simultaneous increase of the amount of carboxyl groups formed upon wood oxidation.

The higher content of carboxyls than the amount of nitrogen in the resulting products indicates that groups with organically tightly bound nitrogen were formed. This may also be due to a shortage of ammonia in the reaction mixture.

The content of nitrogen, carboxyls, and methoxyls in the products after reacting for 70-180 min becomes practically constant and then does not change. Demethoxylation with loss of about 5-60% of the starting methoxyls occurs in parallel to the oxidation (Table 1). After reacting for 180 min, the birch wood contains up to 5.3% total nitrogen.

Figures 1 and 2 show the contents of nitrogen, methoxyls, and carboxyls in the products of birch-wood oxidative ammonolysis as functions of the amount of reagents used (ammonium persulfate and ammonia). It can be seen that the amount of nitrogen is inversely proportional to the methoxy content. This can be explained by the fact that wood binds nitrogen mainly via oxidative destruction of its methoxyls and reaction of ammonia with the resulting carbonyls and carboxyls. Scheme 1 shows a possible route for this process in a structural fragment [8].



Scheme 1

Altai State University, 656099, Russia, Barnaul, ul. Dimitrova, 66, fax (83852) 22 54 51, e-mail: efanov@chemwood.dcn-asu.ru. Translated from *Khimiya Prirodnykh Soedinenii*, No. 1, pp. 30-32, January-February, 2003. Original article submitted April 29, 2002.

TABLE 1. Effect of Processing Time on Functional Composition of Products of Birch Wood Oxidative Ammonolysis

Time, min	Yield,* %	Content, %		
		N	COOH	OCH ₃
Starting wood		0.5	2.2	5.6
10	99	1.8	3.6	5.1
20	95	2.2	4.0	4.3
30	95	2.4	4.1	3.5
40	93	2.9	4.5	3.2
50	91	3.1	5.5	3.2
60	90	3.5	7.1	2.9
70	89	5.1	11.5	2.7
80	86	5.2	16.1	2.6
90	85	5.3	16.1	2.6
100	84	5.3	16.3	2.0
180	83	5.3	16.2	2.0

Amount: wood, 5.0 g; ammonium persulfate, 0.2 g/g raw material; ammonia (25% solution), 1.0 g/g raw material; synthesis temperature 30°C.

*% of starting wood mass.

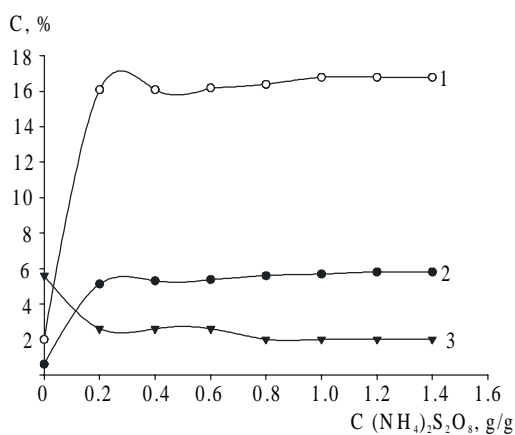


Fig. 1

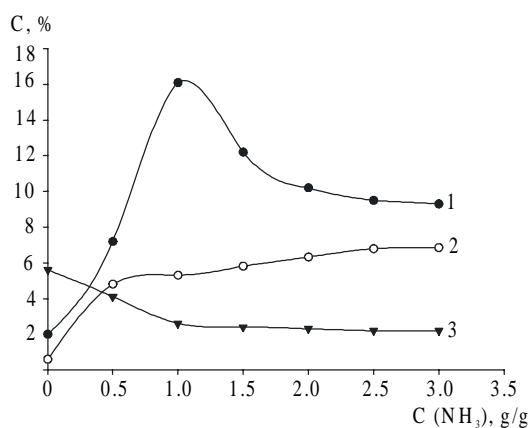


Fig. 2

Fig. 1. Effect of ammonium persulfate on functional composition of birch wood during oxidative ammonolysis ($T = 25^{\circ}\text{C}$, reaction time 30 min). Content, %: COOH (1), N (2), OCH₃ (3).

Fig. 2. Effect of ammonia on functional composition of birch wood during oxidative ammonolysis ($T = 25^{\circ}\text{C}$, reaction time 30 min). Content, %: COOH (1), N (2), OCH₃ (3).

Comparison of the plots for the change of carboxyl content in wood during oxidative ammonolysis and the content of nitrogen and methoxyls in the wood oxidation products (Figs. 1 and 2) showed that there are more carboxyls than bound nitrogen. This may be due to a low amount of ammonia in the reaction mixture and the oxidation of not only the aromatic ring of lignin but also the alkyl side chain of the phenylpropane group in addition to hemicellulose and cellulose polysaccharides. The maximum in the plot for the change of carboxyl content as a function of amount of ammonium persulfate and ammonia (Figs. 1 and 2) is evidently due to the decomposition of the hydroperoxide derivatives formed during the oxidation.

Thus, birch wood is oxidized by ammoniacal ammonium persulfate to give N-containing derivatives. Mechanochemical processing can decrease the consumption of ammonia and oxidant by 1.5-2 times. The N-containing products contain (based on birch wood): 1.8-6.8% total nitrogen, 3.6-16.2% carboxyls, and 2.0-5.1% methoxyls. They can be used as organic fertilizers and sorbents [12].

EXPERIMENTAL

Air-dried birch-wood dust (0.4-0.75 mm) was used as starting material. The cellulose content was determined by the Kirsner method; lignin content, by the Komarov method; hemicellulose content, by the Wise method according to methodology given in a handbook [13]. The raw-material composition was (%): cellulose 52.3, lignin 20.7, hemicellulose 21.2; nitrogen 0.5, methoxyls 5.6.

Wood was treated mechanochemically as follows. A weighed portion of raw material (5.0 g) was placed in the cylindrical reactor (500 cm³ volume) of a vibratory grinder (IV-98B-2 vibrator, 2800 min⁻¹ frequency) with 15 steel rods (10×110 mm). The amount of ammonium persulfate was 0.2-1.4; ammonia (25% solution), 0.5-3.0 g/g of raw material. The temperature in the reaction chamber was 30±1°C (thermostat). The reaction mixture was vigorously ground mechanically for 10-180 min. Then, the products were unloaded from the grinder, separated from the grinders, washed with distilled water until the reaction was negative for sulfate, and dried in a desiccator to constant mass.

The nitrogen content was determined by a semimicro Kjeldahl method [14]; the amount of carboxyls, by reverse conductometric titration [15]; the methoxyl content, by the Zeisel method using GC analysis as described previously [16].

The sorptivity of the products was studied by establishing equilibrium after 24 h for sorption by a weighed quantity of substance of certain heavy-metal cations (Cd²⁺, Cu²⁺, Zn²⁺) from their nitrate solutions (0.1 N) by the literature method [8].

REFERENCES

1. A. M. Kazarnovskii and M. I. Chudakov, *Products of Wood Processing - Agriculture* [in Russian], Riga (1973), Vol. 2, p. 155.
2. M. S. Dudkin, N. G. Shkantova, and N. A. Lemle, *Khim. Sel'sk. Khoz.*, 50 (1967).
3. V. R. Yaunzems and V. N. Sergeeva, *Khim. Drev.*, No. 2, 115 (1968).
4. USSR Pat. No. 486033; *Byull. Izobret.*, No. 36 (1975).
5. USSR Pat. No. 635104; *Byull. Izobret.*, No. 4 (1978).
6. A. M. Kazarnovskii and M. I. Chudakov, *Gidrolyz. Lesokhim. Promst.*, 8 (1973).
7. USSR Pat. No. 363710; *Byull. Izobret.*, No. 4 (1973).
8. G. F. Zakis, B. Ya. Neiberte, and V. N. Sergeeva, *Khim. Drev.*, 85 (1973).
9. V. N. Kislenco and A. A. Berlin, *Zh. Prikl. Khim.*, **53**, 2069 (1980).
10. W. E. Sohs, *Forest Prod. J.*, **27**, 17 (1977).
11. E. E. Kluge and Yu. A. Zoldners, *Khim. Drev.*, No.6, 91 (1984).
12. M. V. Efanov, *Scientific Principles and Methods of Complex Usage of Siberian Plant Resources* [in Russian], Krasnoyarsk (2002), p. 42.
13. A. V. Obolenskaya, in: *Practical Studies in Wood and Cellulose Chemistry* [in Russian], V. M. Nikitin, ed., Lesnaya Prom'st, Moscow (1965).
14. V. A. Klimova, *Basic Micromethods in Organic Analysis* [in Russian], Khimiya, Moscow (1975).
15. G. F. Zakis and B. Ya. Neiberte, *Izv. Akad. Nauk Latv. SSR*, 377 (1977).
16. D. B. Bolotin and A. G. Chernykh, *Khim. Drev.*, No. 5, 109 (1982).