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PEROXIDE-AMMONIA DELIGNIFICATION OF PINE WOOD

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Oxidative delignification of pine wood by hydrogen peroxide in aqueous ammonia was studied. A new method for producing cellulose and N-containing organic fertilizers was developed. It was demonstrated that a solution of hydrogen peroxide (3-9%) in aqueous ammonia delignified extensively wood to produce cellulose in yields up to 54.6% with a residual lignin content up to 1.1%. The process of pine-wood delignification by hydrogen peroxide in aqueous ammonia was described satisfactorily by a first-order kinetic equation.

Key words: wood, oxyammonolysis, hydrogen peroxide, cellulose, N-containing derivatives.

Peroxide delignification of wood in alkaline medium is an effective ecologically pure method of producing cellulose and is rather promising economically and technically [1]. Hydrogen peroxide has advantages as a digesting agent over gases that contain oxygen. It occupies the same phase as the reaction medium, freely diffuses within wood fibers, and, therefore, does not require elevated pressures and temperatures [2].

The new surfactant (lyoxide) obtained from peroxide oxidation of hydrolyzed lignin was recommended for use in certain economic applications [3, 4]. A method was developed [5] for producing cellulose from plant materials in two steps using peroxide-soda. Studies of peroxide delignification of wood in acidic and alkaline media have been reviewed [5, 6].

However, systematic studies of delignification of plant material by H_2O_2 in aqueous NH_3 have not been published. Therefore, we studied the conditions for oxidation of wood by H_2O_2 in aqueous ammonia in order to develop a method for its delignification to produce cellulose and N-containing organic fertilizers.

The experiments showed that an increase in the duration of wood delignification by 3% H_2O_2 in 10% NH_3 at 90°C is accompanied by a reduction in the yield of solid residue and the mass fraction of lignin in the cellulose. The degree of lignin conversion (α) increases, i.e., the delignification is rather extensive ($\tau = 3$ h, $\alpha = 84\%$).

Figure 1 shows experimental results as a semilogarithmic plot of the dynamics of the change of degree of lignin conversion during delignification. The linearity of this graph indicates that the observed kinetic order is close to unity (slope of the line). Table 1 gives the rate constants and reaction order calculated using these data. A heating time of 3 h should be considered the most optimal.

If the temperature is increased from 60 to 100°C, the yield of solid residue and lignin content decrease smoothly owing to more extensive oxidative destruction of lignin and polyose (Table 2). The delignification can be carried out at atmospheric pressure and temperatures up to 100°C if H_2O_2 is used as the digesting agent.

The study of the effect of H_2O_2 concentration on yield and composition of cellulose mass found that increasing the H_2O_2 concentration from 3 to 9% leads to a regular drop in the yield of solid residue and mass fraction of lignin in cellulose owing to more extensive oxidative destruction of lignin and polysaccharides. The resulting solid residues contain 1.1-4.2% residual lignin (Table 3).

The content of α-cellulose was determined according to the literature [7] in order to characterize the composition of hemicellulose in certain samples of solid residues. It was found that the peroxide—ammonia method of delignification preserves much of the hemicellulose. As a result, the yield of technical cellulose is comparatively high and the content of α-cellulose is low (Table 3).

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TABLE 1. Effect of Pine-Wood Delignification Time on Yield and Composition of Solid Residue

Time, h	Solid residue, %	Lignin, %	Degree of lignin conversion, α, %
0.5	81.5	17.2	34
1	74.5	12.5	52
1.5	71.3	10.3	61
2	69.5	8.4	68
2.5	67.3	6.3	76
3	64.5	4.2	84
4	60.7	2.9	89

Temperature, 90°C; ratio, 20; H_2O_2 concentration, 3%; NH_3 concentration, 10%; $K \cdot 10^3 = 4.5$ min^{-1}, n = 1.05.

TABLE 2. Effect of Process Temperature on Yield and Composition of Solid Residue

Temperature, °C	Solid residue, %	Lignin content, %	Degree of lignin conversion, α, %
60	74.8	12.7	51
70	70.4	9.3	64
80	68.2	6.9	73
90	64.5	4.2	84
100	57.3	1.5	93

Ratio, 20; H_2O_2 concentration, 3%; NH_3 concentration, 10%; heating time, 3h.

TABLE 3. Effect of Amount of H_2O_2 on Yield and Composition of Solid Residue

H_2O_2 concentration, %	Solid residue, %	Lignin content, %	Degree of lignin conversion, α, %
3 (a)	64.5	4.2	84
5	60.4	2.9	89
7	56.7	1.7	93
9 (b)	54.6	1.1	96

Ratio, 20; NH_3 concentration, 10%; temperature, 90°C; heating time, 3 h; α-cellulose content, %: 69.7 (a) and 85.3 (b).

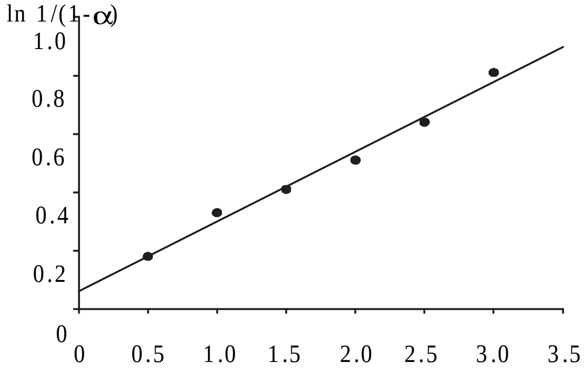

Fig. 1. Semilogarithmic plot of the dynamics of the change of degree of lignin conversion during heating.

Table 4 shows that increasing the NH_3 concentration decreases the yield of solid residue and its lignin content. The higher yield of hemicellulose (62.8-64.5%) compared with that from other methods of oxygen—alkaline delignification and oxyammonolysis (52-55%) indicates that part of the hemicellulose is preserved from destruction in the ammonia solution.

TABLE 4. Effect of NH_3 Concentration on Yield and Composition of Solid Residue

NH_3 concentration, %	Solid residue, %	Lignin content, %	Degree of lignin conversion, α, %
3	70.4	8.4	68
5	69.2	7.5	71
7	68.4	6.3	76
9	66.8	5.1	80
10	64.5	4.2	84
11	62.8	3.1	88

Ratio, 20; H_2O_2 concentration, 3%; temperature, 90°C; heating time, 3 h.

TABLE 5. Effect of Ratio on Yield and Composition of Solid Residue

Ratio	Solid residue, %	Lignin content, %	Degree of lignin conversion, α, %	Dry substances from liquor, % of wood mass
20	64.5	4.2	84	21.2
40	57.8	2.1	92	30.4
60	54.7	1.2	95	36.5

Temperature, 90°C; heating time, 3 h; H_2O_2 concentration, 3%; NH_3 concentration, 10%.

TABLE 6. Effect of N-containing Liquor on Vegetative Indices of Sugar Pea Plants

Sample	Plant height, cm	Additive, % to control	Absolute dry mass, g	Additive, % to control
Control	18	-	0.81	-
Liquor, h:				
1	23	25	1.25	54
4	24	30	1.32	63

The effect of the ratio on the yield and composition of solid residue (Table 5) indicates that the yield of solid residue and its lignin content decreases smoothly with increasing ratio from 20 to 60. This is apparently due to more extensive oxidative destruction and higher solubility of the lignin decomposition products.

Spent liquor contained less dry substances than starting wood after digestion at a low ratio. This is explained by a faster rate of oxidation of dissolved wood substances. The rate is proportional to their concentration and that of H_2O_2 in the digestion solution. As a result, dissolved substances are more extensively oxidized if the ratio is reduced.

The properties of lignins isolated from liquors by acidification with H_2SO_4 by the literature method [8] showed that the yield of water-soluble lignin was 3.8% of the starting wood and the N content was 4.5% at 90°C, a ratio of 20, H_2O_2 concentration 3%, NH_3 concentration 10%, and delignification time 1 h; for a delignification time of 4 h, the amounts are 10.6 and 7.6%, respectively. The low yield of water-soluble high-molecular-weight lignins indicates that the wood lignin was substantially decomposed to low-molecular-weight soluble products.

Table 6 presents results of agrochemical tests of the liquors by a vegetative experiment [10] as organic fertilizers for Sugar peas.

It can be seen that N-containing liquor from peroxide—ammonia delignification of pine wood stimulated pea-plant growth by 25-30%.

Thus, N-containing liquors produced by oxyammonolysis of wood chips can be used as effective N-containing organo-mineral fertilizers.

The experimental results lead to the conclusion that delignification of pine wood by H_2O_2 in aqueous ammonia produces technical cellulose in yields up to 54.6% with a residual lignin content up to 1.1% and N-containing liquors with a N content in the lignin up to 7.6%. Delignification of pine wood by H_2O_2 in aqueous ammonia is described satisfactorily by a first-order kinetic equation. The reaction rate constant and order are $4.5 \cdot 10^{-3}$ and 1.05, respectively. The optimum conditions for wood delignification are 3 h, 90°C, 9% H_2O_2, and 10% NH_3.

EXPERIMENTAL

Starting material was analyzed by handbook methods [7]. The pine-wood composition was: Kuerschner cellulose, 53.8%; Komarov lignin, 26.1%; Wise holocellulose, 69.3%. Air-dried wood chips (0.4-0.75 mm, 2.0 g) were placed in a round-bottom flask with a reflux condenser. The flask was placed on a water bath (thermostatted at 60-100°C). H_2O_2 (3-9%) in aqueous ammonia (3-11%) was added (ratio 20). Sodium silicate (2% of the wood mass) was added as a stabilizer. The flask was stirred every 0.5-4 h. Then the mixture was filtered through a previously weighed glass filter (160 pore). The solid on the filter was washed with hot water until neutral and dried to constant mass in a drying chamber at 100-105°C. The yield was determined (as mass % of starting wood).

The lignin content in the solid residues was determined by the Komarov method; α-cellulose, by solubility in NaOH solution (18%) [7]. Water-soluble lignin was isolated from liquors by acidification first with H_2SO_4 to pH 3 and then HCl to pH 1, washed with ether to remove traces of acid and water, and dried in a desiccator as before [8]. The N content in the lignin was found by the Kjeldahl method [9]. Vegetative experiments of liquors as fertilizers were performed by handbook methods [10] by determining the biomass increase.

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