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XANTHOGENATION OF PINE WOOD BY MECHANOCHEMICAL ACTION

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The effect of alkaline-activation conditions on xanthogenation of pine wood was studied. It was shown that the degree of wood conversion was affected by the duration of alkaline activation and xanthogenation and the amount of reagents. The resulting high-molecular-weight products are 30-75% soluble in aqueous alkaline solutions and form viscous solutions.

Key words: pine wood, xanthogenation, mechanochemical method, alkaline activation.

Xanthogenation of cellulose in order to produce viscose fibers and films involves the production of esters by reaction of alkaline celllulose with CS_2 [1]. We developed a mechanochemical method for xanthogenation of wood and other lignocarbohydrate materials to produce water-soluble surfactants and fertilizers [2]. The present article contains results from a study of the effect of alkaline treatment on pine-wood xanthogenation by a mechanochemical method.

The effects of xanthogenation time (Table 1), preliminary alkaline treatment (Table 2), and amount of reagents (Tables 3 and 4) on the properties of pine-wood xanthogenation products were studied. In particular, their solubility in 5% NaOH and the specific viscosity of the solutions at 20°C were determined. The degree of wood conversion by xanthogenation was calculated as the ratio of the content of bound S that was determined analytically to its theoretically possible maximum content calculated from the content of hydroxyls (20.5% S).

The experimental results showed that the S content in the products and the degree of wood conversion increase if the xanthogenation time is increased from 10 to 30 min. The product with S content 3.5% has the maximal solubility (Table 1).

For xanthogenation times up to 40-50 min, the content of bound S decreases slightly. This is explained by a disruption of the equilibrium of the xanthogenation reaction by side processes of thio-salt formation and methanochemical destruction of wood xanthogenates that run in parallel.

The content of bound S in the xanthogenation products increases if the time of preliminary alkaline activation increases from 5 to 30 min (Table 2). However, the solubility of the products decreases. This is probably due to alkaline destruction of wood xanthogenates by prolonged mechanochemical action. The degree of wood conversion changes insignificantly and reaches 18% after 30-40 min of alkaline treatment. Therefore, we selected the optimal time of pine-wood alkaline treatment as 10 min for further investigations.

The study of the effect of the amount of NaOH (Table 3) found that increasing the mole ratio from 0.5 to 1.5 increases the content of bound S in the xanthogenation products and the degree of wood conversion. Increasing the amount of NaOH further to 2-3 moles per mole of wood OH groups causes a slight decrease of S content. Increasing the NaOH concentration slows wood xanthogenation. This can be explained by the binding of free NaOH as thio-salts. The optimal OH:NaOH mole ratio is considered to be 1:1.

Increasing the amount of water from 1 to 4 moles added during preliminary alkaline activation increases the content of bound S and the solubility. This is evidently due to more extensive hydration. Above 4 moles, the S content and the solubility of the products decrease slightly. This is probably a result of partial saponification of the wood xanthogenates and formation of thio-salts. The maximal amount of reacted hydroxyls is 34%.

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TABLE 1. Effect of Pine-Wood Xanthogenation Time on Product Properties

Xanthogenation time, min	S content, %	Degree of conversion, α	Solubility in 5% NaOH, %
10	1.1	0.05	32
20	2.1	0.11	34
30	3.5	0.18	40
40	3.5	0.18	40
50	3.0	0.15	39

OH:NaOH:CS_2 = 1:1:1; alkaline activation time, 10 min.

TABLE 2. Effect of Alkaline Activation Time on Properties of Pine-Wood Xanthogenation Products

Alkaline activation time, min	S content, %	Degree of conversion, α	Solubility in 5% NaOH, %
-	2.4	0.12	34
5	2.8	0.14	38
10	3.5	0.18	40
20	3.5	0.18	41
30	3.7	0.18	39
40	3.7	0.18	34

OH:NaOH:CS_2 = 1:1:1; xanthogenation time, 30 min

TABLE 3. Effect of NaOH/OH Ratio on Properties of Pine-Wood Xanthogenation Products

OH:NaOH, mol	S content, %	Degree of conversion, α	Solubility in 5% NaOH, %
-	2.3	0.11	30
1:0.5	2.7	0.14	33
1:1	3.7	0.18	39
1:1.5	3.5	0.17	40
1:2	3.5	0.17	41
1:2.5	2.7	0.14	40
1:3	1.9	0.09	39

OH:CS_2 = 1:1; alkaline activation time, 10 min; xanthogenation time, 30 min.

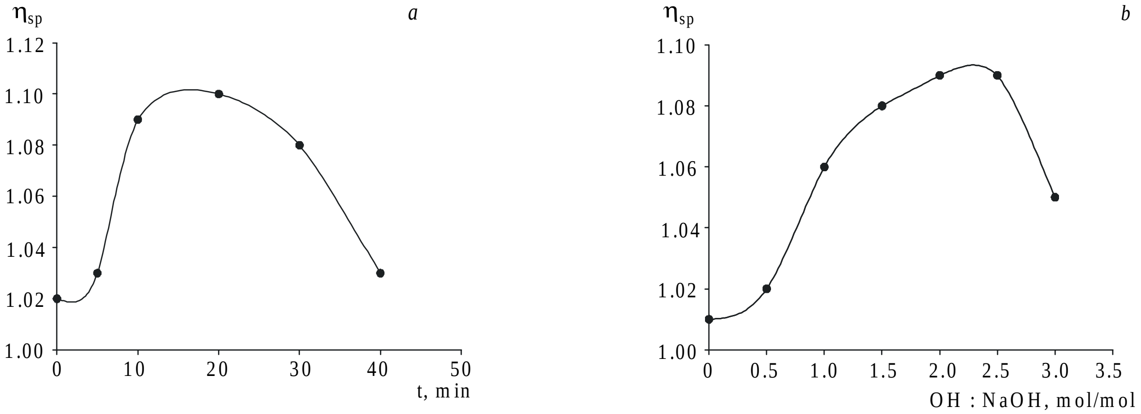

Fig. 1. Specific viscosity of pine-wood xanthogenation products (η_{sp}) as a function of preliminary alkaline activation time (a) and OH:NaOH mole ratio (b).

TABLE 4. Effect of Water Content on Properties of Pine-Wood Xanthogenation Products

$OH:H_2O$, mol	S content, %	Degree of conversion, α	Solubility in 5% NaOH, %
-	3.7	0.18	39
1:1	4.1	0.21	41
1:2	4.5	0.22	49
1:3	5.9	0.30	56
1:4	6.9	0.34	60
1:5	6.0	0.30	57
1:6	6.0	0.30	55

$OH:NaOH:CS_2$ = 1:1:1; alkaline activation time, 10 min; xanthogenation time, 30 min.

TABLE 5. Effect of CS_2 Content on Properties of Pine-Wood Xanthogenation Products

$OH:CS_2$, mol	S content, %	Degree of conversion, α	Solubility in 5% NaOH, %
1:1	6.9	0.34	60
1:1.5	7.0	0.35	65
1:2	7.8	0.39	69
1:2.5	8.7	0.44	74
1:3	8.7	0.44	75
1:3.5	8.8	0.44	70
1:4	8.8	0.44	68

$OH:NaOH:H_2O$ = 1:1:4; alkaline activation time, 10 min; xanthogenation time, 30 min.

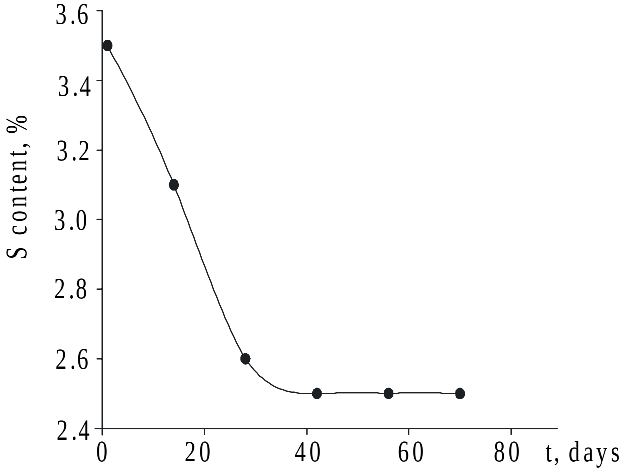

Fig. 2. Pine-wood xanthogenate decomposition (initial S content, 3.5%).

Increasing CS_2 from 1 to 2.5 moles increases the content of bound S in the wood xanthogenation products. Increasing it to 3-4 moles/mole does not change the S content. The degree of wood conversion by xanthogenation calculated based on S content indicates that 5-44% of the wood hydroxyls reacted under the studied conditions (Tables 1-5).

The effects of the various process conditions on the macromolecular reactions can be evaluated from the change of specific viscosity of the wood xanthogenation products. The specific viscosity decreases with prolonged alkaline activation and high reagent ratios (Fig. 1). This is due predominantly to alkaline and mechanochemical destruction of the principal wood components. The specific viscosity of alkaline solutions of wood xanthogenate as a function of principal alkaline-activation parameters exhibits a peak that is probably due to competition of two parallel processes occurring during wood xanthogenation. These are xanthogenate formation and their destruction with partial dissolution of the principal wood components in the reaction medium as the process conditions change.

The resistance of the products to decomposition was investigated in order to determine the possibility of using wood xanthogenates as nitrification—denitrification inhibitors because the released CS_2 (inhibitor) plays the main role in this instance. Figure 2 shows the S content as a function of product storage time in an open vessel at 25°C.

The results indicate that wood xanthogenates are relatively stable. The xanthogenate is completely decomposed after 40 days (Fig. 2). This period coincides with the time of vigorous growth of agricultural cultures, which indicates that wood xanthogenates may have practical applications as nitrification inhibitors.

Thus, high-molecular-weight products containing up to 8.8% bound S that are soluble up to 75% in aqueous alkaline solutions are produced by xanthogenation of pine wood using mechanochemical action. It was found that preliminary alkaline activation of the raw material determines the effect on the wood xanthogenation process and the properties of the products. Up to 44% of the wood hydroxyls react with CS_2 after 30 min of xanthogenation.

EXPERIMENTAL

Air-dried pine-wood chips (0.5 mm fraction) were used as starting material, the composition of which was: Komarov lignin, 26.1%; Kuerschner cellulose, 53.8%; Wise hemicellulose, 17.6%. The content of hydroxyls determined by Verley acetylation in the presence of pyridine by the handbook method [4] was 23.5%.

The S content in the resulting products was analyzed by the Schoeniger method as before [5].

We have previously described the xanthogenation method [3]. Wood xanthogenation consists of mechanochemical activation in the presence of NaOH with or without added water and xanthogenation itself. The reaction products were purified of thio-salts by washing with acetic acid in ethanol (5%, 50-100 mL) until the pH was 3-4 and then with ethanol until the reaction for S^{2-} using lead(II) nitrate was negative. The solubility of the products in 5% NaOH solution and the specific viscosity of the resulting solutions at 20°C were determined in an Ubbelohde viscosimeter as before [6].

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