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OXIDATION OF ACETYLATED ASPEN WOOD

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Acetylation is a promising method for chemical modification of plant polymers to produce biologically stable thermoplastic polymers for plywood and plastics [1].

Herein we report results from a study of the stability toward peracetic-acid oxidation of aspen wood acetylated by a mechanochemical method to introduce various amounts of acetyls.

Treatment of acetylated wood may cleave a part of the acetyls because the solution usually used to isolated holocellulose (polysaccharides) by delignification is a peracetic acid solution (10%) at pH 2.

According to the literature [2], the degree of delignification as a function of pH of the peracetic-acid solution had a maximum delignification with the highest retention of polysaccharides at pH 4. Therefore, acetylated aspen wood was oxidized at pH 4 for 50 min at 90°C by peracetic-acid solution (10%).

The starting material was aspen wood of the following composition: cellulose, 49.6%; lignin, 21.8; hemicellulose, 22.4 (holocellulose, 72%); hydroxyls, 24.8%. Aspen wood with varying degrees of acetylation was prepared as before [3].

The catalyst was ammonium sulfate (20% of wood mass). The duration of mechanochemical treatment was varied (Table 1). A sample of wood acetylated in the presence of magnesium perchlorate was prepared in the same quantity for comparison.

Wood was acetylated as follows. A portion of air-dried aspen wood sawdust (0.5-0.75 mm, 3.0 g) was placed in a vibration grinder (300 cc, IV-98B industrial vibrator, 2800 rpm) with 15 steel rods (10 × 100 mm) and treated with acetic anhydride (calculated for one mole per mole of wood OH groups).

The reaction temperature was 25°C (thermostat). Ammonium sulfate (0.6 g) was placed in the grinder. The reaction mixture was subjected to vigorous mechanical grinding for 0.5-3 h. The resulting products were removed from the grinder, separated from the rods, washed with water to remove acid and catalyst, and dried in a desiccator to constant mass.

The content of bound acetyls was determined by saponification with alcoholic NaOH solution (0.5 N) with subsequent reverse conductometric titration of the excess of base with HCl (0.5 N) by the literature method [4]. The content of acetyls in the oxidized acetylated wood was calculated for starting wood. The solubility of the acetylated wood in $CHCl_3$ was determined by the handbook method [5] for cellulose acetates.

Table 1 shows that increasing the duration of mechanochemical acetylation increased regularly the content of bound acetyls in the resulting high-molecular-weight products and increased their solubility in $CHCl_3$. The degree of hydroxyl conversion in the wood lignocarbohydrate complex varied from 30 to 83%.

The amount of acetyls in the principal aspen wood components was highest after mechanochemical synthesis for 3 h using ammonium sulfate catalyst (20% of wood mass). Using magnesium perchlorate as catalyst for 1 h of mechanochemical acetylation introduced 26.3% acetyls into the wood polymers (Table 1).

The basic components of aspen wood (24.8% OH groups) can theoretically add 38.9% acetyls. According to the literature [6], lignin can bind 7.2% acetyls. With 72% polysaccharides, 31.6% acetyls can be added calculated for cellulose triacetate. Thus, the value 38.8% is close to the theoretical value for the amount of acetyls in the wood.

The acetylation method cannot completely stabilize the lignin toward oxidation. If 32.6% acetyls is added to the aspen wood polymers (degree of wood OH group conversion 83%), 22% of the lignin is oxidized (4.8% of the wood mass). Adding fewer acetyls, but enough to acetylate the lignin hydroxyls during oxidation with peracetic acid, dissolves 45 to 90% of the lignin (10-20% of the wood mass) (Table 2). Acetylated aspen wood samples (1.0 g) were oxidized at pH 2 and 4 for 50 min at 90°C by peracetic-acid solution (10%) (50:1 ratio).

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TABLE 1. Effect of Duration of Mechanochemical Synthesis on Properties of Acetylated Aspen Wood*

Grinding duration, h	Solubility in $CHCl_3$, %	Content of bound acetyls, %	Degree of wood OH group conversion, %
-	-	5.4	-
0.5	13	11.8	30
1.0	26	28.5	73
2.0	51	30.6	79
3.0	65	32.6	83
1.0**	24	26.3	68

*OH:Ac_2O mole ratio 1:1; temperature, 25°C; amount of ammonium sulfate, 20% of wood mass; **catalyst, magnesium perchlorate (20% of wood mass).

TABLE 2. Stability of Acetylated Wood toward Peracetic-Acid Oxidation

Conditions	Content of acetyls												Solid remaining after oxidation, %					
	before oxidation, %						after oxidation (calc. for starting wood), %											
Grinding duration, h	3	2	1	0.5	1	-	3	2	1	0.5	1	-	3	2	1	0.5	1	-
pH 2	32.6	-	-	11.8	-	5.4	26.3	-	-	10.5	-	3.9	84	-	-	72	-	58
pH 4	32.6	30.6	28.5	11.8	26.3*	5.4	32.1	30.2	27.9	11.2	26.1*	5.2	95	90	84	79	82	73

*Catalyst, magnesium perchlorate.

According to the literature [2], completely acetylated lignin loses about 25% of its mass during oxidation. With 32.6% acetyls in the acetylated wood, 22% of the lignin is oxidized, i.e., the wood lignin is slightly more stable to oxidation than isolated lignin.

Acetylated aspen wood is oxidized more extensively at pH 2 than at pH 4. This is accompanied by a larger mass loss and cleavage (11-19%) of acetyls (Table 2). Acetyls that are comparatively unstable toward acid hydrolysis are practically not cleaved at pH 4.

Thus, increasing the content of bound acetyls in aspen wood acetylated mechanochemically in the presence of ammonium sulfate increased its stability toward oxidation by peracetic acid. The maximum stability was observed for 32.6% acetyls, for which the mass loss was 4.8%.

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