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MECHANOCHEMICAL ACETYLATION OF ASPEN WOOD

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Known methods for producing wood esters using ordinary esterification reagents employ acetic anhydride with H_2SO_4 as a catalyst. The resulting acylated derivatives retain the outward appearance of the starting wood and are poorly soluble in organic solvents. This is the principal drawback of this method because the products are of little industrial use [1].

The goal of the present investigation was to develop a new effective method for acetylating aspen wood by mechanochemical treatment with acetic anhydride in the presence of ammonium sulfate as a catalyst.

According to the published equation [2], the amount of acetylated OH groups $C_{OH(ac)}$ will follow the expression:

$$C_{OH(ac)} = (17C_{ac}/43)/(1 - 42C_{ac}/4300),\%$$

where C_{ac} is the content of bound acetyls, %.

Knowing the content of OH groups in the starting aspen wood (24.8%), this formula determines the theoretically maximum possible content of acetyls that can be introduced into the wood by exhaustive acetylation (38.9%).

Thus, the degree of conversion of wood OH groups by acetylation is determined as the ratio of the content of bound acetyls determined analytically and theoretically to the maximum possible acetyl content.

We studied the effect of the duration of mechanochemical synthesis with equimolar amounts of acetic anhydride and wood OH groups on the content of bound acetyls and the $CHCl_3$ solubility of the resulting acetylation products. As the time of mechanochemical acetylation increased from 0.5 to 3.0 h, the content of bound acetyls in the products and their solubility in $CHCl_3$ (from 13 to 65%) increased regularly. The degree of wood OH group conversion changed from 30 to 83%.

The lower solubility of the aspen wood acetylation products from the mechanochemical method than those produced after preliminary mechanochemical activation and subsequent esterification at increased temperature [3] is probably due to the irregular substitution and condensation processes in the solid phase in the presence of released acetic acid, which slightly decrease the solubility.

Table 1 shows the effect of the amount of acetic anhydride per mole of wood OH groups on the content of bound acetyls and the $CHCl_3$ solubility of the resulting acetylation products.

Table 1 shows that the content of bound acetyls in the resulting products increased from 21.2 to 36.2% and the $CHCl_3$ solubility increased as the amount of acetic anhydride per mole of wood OH groups increased from 0.5 to 3 moles. The degree of wood OH group conversion changed from 54 to 93%.

Table 2 shows the effect of the amount of catalyst (ammonium sulfate) on the content of bound acetyls and the solubility in $CHCl_3$ of the resulting acetylation products.

The content of bound acetyls in the resulting products and their solubility in $CHCl_3$ increased as the amount of catalyst increased. The degree of conversion of the wood OH groups changed from 32% (without catalyst) to 83% with catalyst (30% of the wood mass). An acetylation product with 68% conversion and 25% solubility in $CHCl_3$ was obtained using magnesium perchlorate as catalyst (20% of the wood mass) [4] (Table 2).

The degree of conversion (73%) is rather high for the acetylation product obtained with 20% ammonium sulfate (% of wood mass), which was used in further syntheses.

Using mechanochemical activation during acetylation of wood with acetic anhydride in the presence of ammonium sulfate catalyst could reduce the time for the process from 4-6 h to 1-3 h, reduce the consumption of acetic anhydride from 3-10 to 1-3 moles per mole of OH groups, and decrease the reaction temperature from 100 to 25°C, i.e., intensify the process.

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TABLE 1. Effect of Amount of Acetic Anhydride on Properties of Aspen Wood Acetates*

Amount of Ac_2O and wood OH groups (mol/mol)	Solubility in $CHCl_3$, %	Content of bound acetates, %	Degree of wood OH group conversion, %
0.5	18	21.2	54
1.0	26	28.5	73
1.5	37	33.8	87
2.0	45	34.5	89
2.5	56	35.7	92
3.0	68	36.2	93

*Duration of acetylation, 1 h; temperature, 25°C; amount of ammonium sulfate, 20% of wood mass.

TABLE 2. Effect of Amount of Ammonium Sulfate on Properties of Aspen Wood Acetates*

Amount of catalyst, g	Solubility in $CHCl_3$, %	Content of bound acetates, %	Degree of wood OH group conversion, %
Without catalyst	13	12.5	32
0.1	13	14.0	36
0.2	20	23.7	61
0.4	26	28.5	73
0.6	29	32.1	83
0.4**	25	26.3	68

*Duration of acetylation, 1 h, mole ratio OH to Ac_2O, 1:1; temperature, 25°C.

**Catalyst, magnesium perchlorate.

Thus, the products obtained from mechanochemical acetylation of aspen wood are 68% soluble in $CHCl_3$ and can be recommended for use as thermoplastic binders for plywood and for isolation of cellulose acetates.

Wood Acetylation. A portion of air-dried aspen wood sawdust (0.5-0.75 mm, 2.0 g) was placed in a vibration grinder (300 cc, IV-98B industrial vibrator, 2800 cm^{-1} frequency) with 15 steel rods (10 × 100 mm) and treated with acetic anhydride (calculated for 0.5-3 moles per mole of wood OH groups). The temperature was 25°C (thermostat). Ammonium sulfate (0.1-0.6 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.

Content of bound acetyls was determined by saponification with alcoholic NaOH (0.5 N) with subsequent reverse conductometric titration of the excess of base with HCl (0.5 N) by the literature method [5]. The solubility of the wood acetylation products in $CHCl_3$ was determined by the published method [6] for cellulose acetates.

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