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TRANSFORMATIONS OF ASPEN WOOD AND ITS PRINCIPAL COMPONENTS BY O-ACYLATION

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The kinetics of O-acylation of aspen wood, mechanochemical treated, lignin, cellulose, and xylan were studied at various reaction temperatures . The reactivity of the principal wood components in the range 80-120°C follows the decreasing order lignin > xylan > cellulose. Lignin, an amorphous intercellular substance in wood, is acylated fastest.

Key words: acylation, wood, lignin, xylan, cellulose.

We previously acylated aspen wood using a mixture of acetic anhydride and butyric acid (AA—BA) and mechanochemical treatment in the presence of $Mg(ClO_4)_2$ [1]. The study of acyl distribution between lignin and polyoses introduced by O-acylation of wood has found that wood components form mixed esters from anhydrides generated in the acylating mixture [2].

We continued the study of extensive chemical modification of wood by acylation. The properties of the resulting products are determined by the properties of the separate components formed during esterfication directly in the wood. Table 1 lists the content of acyls (acetyl and butyryl) in the acylated lignin isolated from the acetic—butyric esters of aspen wood by the literature method [3] that are obtained at various temperatures (80-120°C) and acylation times (2-8 h).

The degree of transformation of wood components by acyls (α) is the percent ratio content of the respective acyls to the theoretically possible content calculated from the content of hydroxyls in them (with complete substitution by every acid).

The total degree of transformation (α) of lignin after 6 h of reaction at 80, 100, and 120°C is 0.61, 0.72, and 0.78, respectively; of xylan, 0.31, 0.39, and 0.43; of cellulose, 0.33, 0.41, and 0.45. It has been found that lignin acylated under the studied conditions directly in wood (100°C) contains 28.4% total acyls. Then, hydroxyls freed by cleavage of ligno—carbohydrate bonds are next acylated.

Analysis of the amount of phenolic hydroxyls in copper-treated lignin from the starting wood and in acylated lignins confirms that ligno—carbohydrate bonds of aspen wood and ester bonds in lignin are cleaved with release of hydroxyls [4].

The starting copper-treated lignin contains 3.5% hydroxyls. Acylated lignin isolated from wood esterified for 8 h contains ~1.0% phenolic hydroxyls. Analogous trends were noted at 80 and 120°C [4].

Transformations of hemicellulose by wood esterification were estimated from the content of bound acyls in acylated xylans isolated by DMSO after oxidative delignification of acylated wood by peracetic acid (10%); cellulose transformations, by the acyl content in cellulose esters isolated by delignification by peracetic acid (15%) (Table 1).

The content of bound acids in the acylated xylan and the cellulose esters increases smoothly with increasing esterification time in the studied temperature range.

The experimental results (Table 1) showed that lignin is acylated more completely than cellulose and xylan. The degree of cellulose transformation by acetyls (α_{acet}) is slightly greater than for xylan at the same duration and esterification temperature. This may be explained by the fact that the content of hydroxyls in cellulose is greater, including the more reactive primary ones that are missing in xylan.

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TABLE 1. Degree of Transformation (α) of Lignin, Xylan, and Cellulose as a Function of Reaction Time and Temperature

Reaction time, h	Temperature, °C					
	80		100		120	
	α_{acet}	α_{butyr}	α_{acet}	α_{butyr}	α_{acet}	α_{butyr}
			Lignin			
2	0.18	0.04	0.22	0.04	0.28	0.06
4	0.4	0.06	0.47	0.07	0.5	0.09
6	0.53	0.08	0.61	0.11	0.66	0.12
8	0.63	0.12	0.68	0.13	0.7	0.15
			Xylan			
2	0.12	0.02	0.15	0.03	0.17	0.04
4	0.18	0.04	0.23	0.07	0.25	0.09
6	0.25	0.06	0.31	0.08	0.32	0.11
8	0.29	0.08	0.33	0.11	0.37	0.12
			Cellulose			
2	0.19	0.01	0.25	0.03	0.26	0.03
4	0.24	0.03	0.29	0.04	0.31	0.05
6	0.3	0.03	0.36	0.05	0.38	0.07
8	0.34	0.05	0.44	0.06	0.49	0.08

Degree of transformation: α_{acet}, by acetyl groups; α_{butyr}, by butyryl groups; grinding for 15 min in a ball mill with $Mg(ClO_4)_2$ (10^{-3} mole); mole ratio WOH:AA:BA = 1:1:1.

Acylated lignin and xylan contain a large number of bound butyryls compared with cellulose esters. This indicates that they are more reactive toward butyric acid owing to the amorphousness and greater steric availability of the hydroxyls of these components for acylating reagents.

Therefore, the distribution of acyls among the principal wood components during esterification depends on the steric availability and reactivity of their hydroxyls. Lignin is acylated more completely than polyose under all esterification conditions.

Thus, the degree of substitution of the principal wood components by acetyl and butyryl varies for acylation by a mixture of acetic and butyric (1:1) acids. It has been shown using GLC and PMR spectroscopy that the acylating agents during wood esterification by a mixture of acetic anhydride and butyric acid are acetic and a mixed acetic-butyric anhydrides [5]. The comparatively low degree of transformation to butyryls is probably explained by the greater reactivity of acetic anhydride compared with the mixed anhydride, the concentration of which becomes significant only if the reaction is carried out for more than 2 h.

Mechanochemically activated aspen wood is esterfied under heterogeneous conditions at the interface where the starting wood and the acylation product are in the solid state and the acylating reagents and catalyst are in the liquid. Thus, this can be considered a topochemical reaction.

The kinetics of wood esterification were described using the Erofeev—Kolmogorov—Avraami equation [6]:

$$\alpha = 1-\exp(-kt^{n}), \tag{1}$$

where α is the degree of wood transformation, k is the reaction rate constant, t is the reaction time, and n is the reaction order.

The kinetics of wood esterification as a heterogeneous process can be adequately described by using this equation [5].

The logarithmic form of Eq. (1) is:

$$\ln[-\ln(1-\alpha)] = \ln k + \ln t. \tag{2}$$

TABLE 2. Rate Constant and Reaction Order as Functions of Acylation Temperature

T, ºC	Aspen wood	Lignin	Xylan	Cellulose
80	$\frac{5.8\cdot10^{-3}}{1.32}$	$\frac{3.4\cdot10^{-3}}{1.24}$	$\frac{6.67\cdot10^{-4}}{0.82}$	$\frac{3.33\cdot10^{-4}}{0.57}$
100	$\frac{8.81\cdot10^{-3}}{1.48}$	$\frac{4.07\cdot10^{-3}}{1.25}$	$\frac{8.30\cdot10^{-4}}{0.77}$	$\frac{4.61\cdot10^{-4}}{0.52}$
120	$\frac{9.25\cdot10^{-3}}{1.70}$	$\frac{4.07\cdot10^{-3}}{1.10}$	$\frac{9.91\cdot10^{-4}}{0.77}$	$\frac{8.16\cdot10^{-4}}{0.62}$

The reaction rate constant appears in the numerator; the acylation reaction order, in the denominator.

The reaction rate constant is converted to units of min^{-1} using the method proposed by Sakovich [6]:

$$k_p = n\cdot k^{1/n}. \qquad (3)$$

The rate constants and reaction order for acylation of wood and its principal components at various temperatures and a mole ratio WOH:AA:BA = 1:1:1 are listed in Table 2.

The morphological, supramolecular, and electronic state of the principal wood components (lignin, cellulose, hemicellulose) that form the cell wall and intercellular substance of wood tissue are the principal factors that determine the kinetics of acylation in addition to the reaction conditions (temperature, catalyst) and reactivity of the acylating reagent.

The amounts by which the rate constants change, $k_{wood} > k_{lignin} > k_{xylan} > k_{cellulose}$, are the same in the range 80-120ºC. The orders of magnitude for the wood and lignin acylation rate constants are also the same.

The wood and lignin esterification rate constants at 80-120ºC are an order of magnitude greater than those for cellulose. A comparison of the trends in the change of rate constants for acylation of wood and its principal components and the morphological structure and chemical composition of wood tissue has shown that the structure of the intercellular substance consisting mainly of lignin is primarily destroyed. This provides access to hemicellulose and cellulose fibrils oriented parallel to each other.

The order of the topochemical reaction is determined by the number of centers involved in forming the reaction product. The number grows comparatively slowly during acylation of xylan and especially cellulose, probably due to the slow rate of diffusion of the acylating reagents to the cellulose fibrils in the cell wall. The order and rate of wood acylation increase with increasing temperature because the morphological and supramolecular structures forming lignin, xylan, and cellulose are more extensively destroyed. The availability of hydroxyls to acylating reagents also increases.

The higher reaction orders for lignin also indicate that substances located in the intercellular space, i.e., the middle lamina, are acylated first. The wood is digested during the reaction. Lignin is also digested. The mixed lignin esters formed in the first reaction step hinder further penetration of the reagents inside the cell wall.

As the time and temperature of the reaction increase, the acylated lignin disintegrates because of its ligh thermoplasticity and hinders less the penetration of acylating reagents into polyose fibrils where the xylan and cellulose are acylated [7]. According to x-ray diffraction [8], the amount of the amorphous fraction increases compared with that of starting wood after the first few minutes of acylation of mechanochemically activated aspen wood. This and the higher availability of amorphous parts of the wood to the reagents accelerate the acylation. The acylated wood obtained after 120 min of reaction is a crystalline substance with two types of crystal structures.

The acylation rate constant and reaction order remain practically constant if the mole ratio WOH:AA:BA is increased to 1:10:10 at 100ºC. Thus, the rate constant is $8.81\cdot10^{-3}$ min^{-1} at mole ratio 1:1:1; the reaction order, 1.48. At a mole ratio 1:10:10, the values are $8.95\cdot10^{-3}$ min^{-1} and 1.53, respectively. Therefore, the mechanism remains unchanged.

These trends enable us to conclude that lignin and xylan found in the wood lignocarbohydrate matrix are esterified fastest. The principal wood components can be placed in the following sequence of decreasing reactivity (according to acylation rate k) for esterification: lignin > xylan > cellulose.

EXPERIMENTAL

Air-dried resin-containing aspen wood chips (0.5-0.75 mm) were used in the study. Acylation of wood preliminarily ground in a rotating ball mill (15 min, 2000 rpm) with $Mg(ClO_4)_2$ (catalyst) by acetic anhydride and butyric acid and the isolation and purification of products were performed as before [2]. The content of acyls in the resulting products was determined after saponification by alcoholic base using GLC according to the literature [9].

The kinetics of wood O-acylation were studied by varying the duration in a series of syntheses. Transformations of the principal wood components during its acylation were studied by isolating acylated lignin, cellulose, and xylan from the resulting products. Literature methods [3, 5] were used to determine the total content of acyls and estimate the degree of transformation of hydroxyls. The kinetics of transformation of principal wood components were studied in the range 80-120°C using the optimal process parameters that were previously determined [2].

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