

Delignification of wood by oxygen in low-molecular-weight alcoholic media

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ABSTRACT: *This paper examines the process of selective wood delignification by oxygen in low-molecular-weight alcohols (methanol, ethanol, propanol) in the absence of acidic or basic reagents. A mechanism of lignin transformation during oxidation is proposed.*

KEYWORDS: *Alcohols, delignification, lignins, media, molecular weight, oxygen, wood*

Delignification of wood in organic solvents, alcohols in particular, is a promising method of pulp production that has undergone intensive development in recent years. However, the use of alcohols as reaction media requires high temperature—more than 190°C for softwood—even in the presence of active inorganic reagents (acids, bases) (1–5).

We have developed a lower-temperature method of wood delignification using oxygen in low-molecular-weight alcohols (6–8). This process selectively delignifies wood in the absence of acidic or basic catalysts.

We are in the midst of an extensive study of oxidation of wood complexes in aprotic solvents, and results of our earlier work are summarized in the literature (9). Preliminary work was carried out using a variety of organic solvents, including acetone. This report presents results obtained using ethanol, methanol, and propanol. Based on such criteria as pulp yield and mechanical properties, low-molecular-weight alcohols show much greater promise as a pulping medium than acetone.

Results and discussion

Oxidation of spruce sawdust

Oxidation in anhydrous alcoholic media. Oxidation of lignin in several simple aliphatic alcohols (methanol, ethanol, 1-propanol) occurred at similar rates, as seen in Table I. This demonstrates a moderate influence of nonspecific solvation on the process.

The rate of lignin oxidation is much higher in anhydrous alcoholic media than in aprotic solvents. For example, at 160°C, almost 50% of lignin can be dissolved in 1-propanol in 1 h, while less than 10% lignin is dissolved in acetone (9). Because the dielectric permeabilities of 1-propanol (20.1) and acetone (20.7) are nearly the same, it is apparent that specific solvation has far more influence on the process of lignin oxidation than electrostatic interaction.

Kinetic studies show that dissolution of major wood components during oxidation can be described by a first-order equation, as seen in Fig. 1. The rate of oxidation of lignin at 150°C ($k = 5.77 \times 10^{-5} \text{ s}^{-1}$) is five times higher than the rate of destruction of carbo-

hydrates ($k = 1.34 \times 10^{-5} \text{ s}^{-1}$). Figure 2 shows that the formation of carbon dioxide is proportional to the amount of dissolved lignin. This demonstrates that the rate of decarboxylation of acids is greater than that of the reactions resulting in their formation.

Both homolytic and heterolytic stages take place during delignification. Addition of a catalytic amount of sulfuric acid (0.19M) to alcohol increases the rate of lignin and carbohydrate dissolution by a factor of 1.5. However, the low reactivity of carbohydrates in the absence of an acid catalyst (Table I) is evidence that heterolytic reactions do not play an important role in anhydrous solvents because of their low acidity.

The results in Table II show that oxidation is accelerated in the presence of oxidation promoters (dicumyl peroxide and CuCl_2). Given the comparatively low activation energy of lignin oxidation (109 kJ/mole), these results suggest that the process proceeds as a radical chain reaction.

Oxidation in aqueous alcoholic media. The chemical reactivity of the major wood components increases when water is added to a solvent. However, the solubilities of lignin and polysaccharides do not have the same dependence on the mixture's water content. Figure 3 shows that carbohydrate dissolution during oxidation of wood increases with increasing water content. Dissolution is mostly the result of acid hydrolysis of polysaccharides. Lignin dissolution, on the other hand, reaches a maximum and then falls off with increasing water content in the reaction mixture. Since water tends to suppress radical reactions, its stimulating effect on the oxidation of lignin can be explained by the greater role of heterolytic

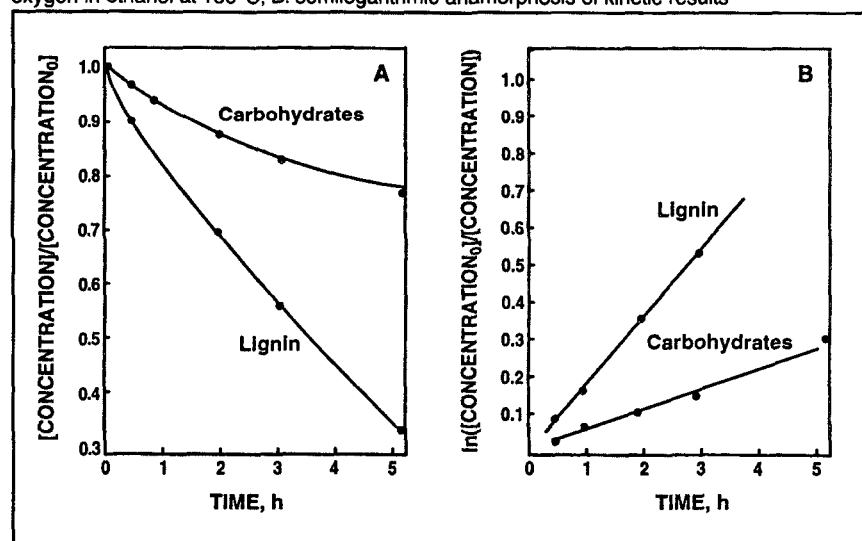
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I. Oxidation of spruce sawdust by oxygen in four different solvents*

	Dielectric permeability (ε)	Pulp yield, %	Lignin content, %	Dissolved material, % on moisture-free wood	
				Lignin, %	Carbohydrates, %
Methanol	32.6	85.5	24.5	26.8	8.8
Ethanol	24.3	86.4	24.4	26.3	7.8
1-Propanol	20.1	86.4	24.9	26.0	8.2
Water	84.2	59.0	28.5	41.2	40.0

*Pulping conditions: 153°C, 2 h.

1. A: rate of dissolution for lignin and carbohydrates during oxidation of spruce sawdust by oxygen in ethanol at 150°C; B: semilogarithmic anamorphosis of kinetic results



II. Oxidation of spruce sawdust in ethanol in the presence of oxidation promoters*

Additive	Dosage, % on moisture-free wood	Pulp yield, %	Lignin content, %	Dissolved material, % on moisture-free wood	
				Lignin	Carbohydrates
Control	...	82.7	22.6	31.3	9.5
Dicumyl peroxide	4.0	59.5	18.3	62.9	31.2
CuCl ₂ ·2H ₂ O	3.7	71.2	15.9	60.4	15.3

*Pulping conditions: 150°C, 2 h.

stages in the whole process. These stages produce intermediates that are more active in the oxidation reaction than native lignin.

The chemical reactivity of lignin in water-alcohol media is about the same as in water-acetone. However, the effect of water addition on the acidity of protic and aprotic solvents is markedly different (9, 10). Therefore, we conclude that the rate-determining stage is not ionization but, rather, is deprotonization of a cation intermediate. Deprotonization leads to formation of an unsaturable group and significantly increases chemical reactivity of the macromolecule in oxidation reactions. Phenolic compounds with conjugate double bonds in a side chain can be oxidized much more easily than phenols with substituents. The greater rate of lignin oxidation in mixed solvents (alcohol-water), compared with oxidation in water, can be explained by a reduced significance of condensation reaction with an increase in the ratio of organic solvent to water.

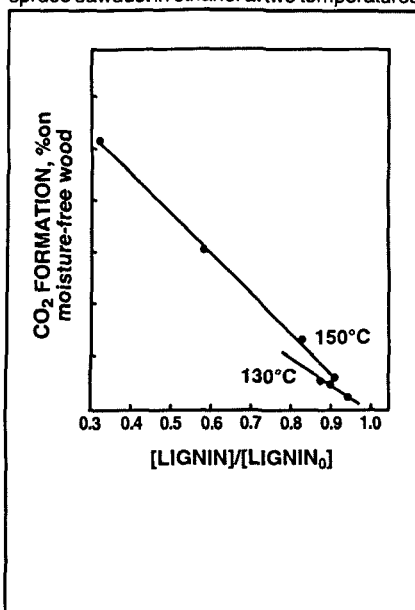
In aqueous ethanol solutions, the effective activation energies of lignin oxidation in 60% and 80% ethanol are 149 kJ/mole and 134 kJ/mole, respectively. These values are higher than those in anhydrous alcohol (103 kJ/mole), suggesting that the rate-determining stage of the process is heterolytic in the presence of water. As in the case of absolute alcohols, the process of delignification in aqueous alcohols can be described with a first-order equation, as seen in Fig. 4.

Oxidation of wood chips

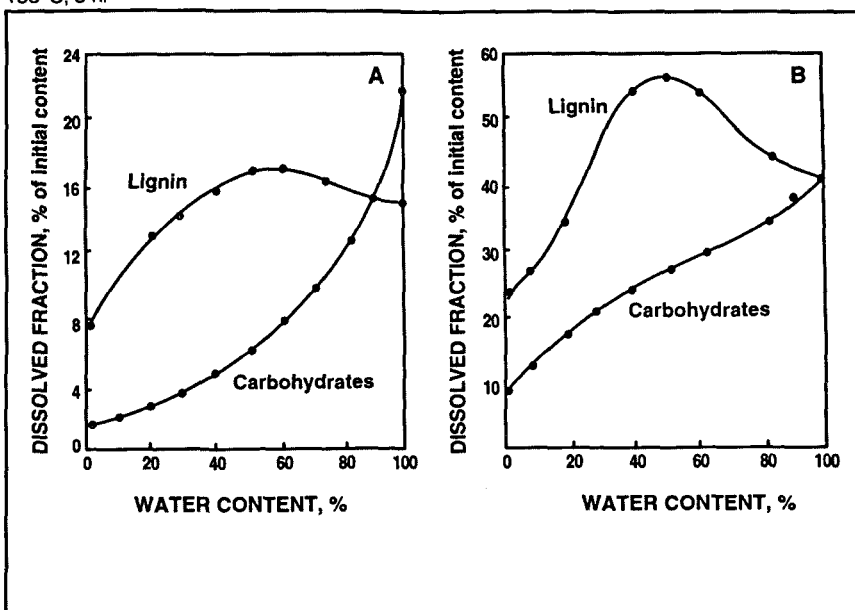
Results for delignification of spruce chips with oxygen in 60% ethanol are presented in Table III. These results mirror the results observed for oxidation of spruce sawdust.

The delignification products accumulated in the solution are of lignin and polysaccharide origin. The loss of the mass of carbohydrate components of wood lies within 29-35%, depending on the degree of delignification. (The amount of carbohydrates transferred into the solution differs, depending on the degree of destruction.) Oxidate separation diagrams used in these studies were obtained in earlier research and are provided in the literature (9, 10). Some of the delignification products were separated as a water-soluble fraction containing

2. Formation of carbon dioxide as a function of lignin concentration during oxidation of spruce sawdust in ethanol at two temperatures



3. Dissolution of lignin and carbohydrates during oxidation of spruce sawdust as a function of water content in reaction medium. A: aqueous ethanol, 130°C, 3 h; B: aqueous 1-propanol, 153°C, 3 h.



both neutral (sugar) and acidic (non-volatile acids) compounds. Yields of water-soluble products are listed in Table IV.

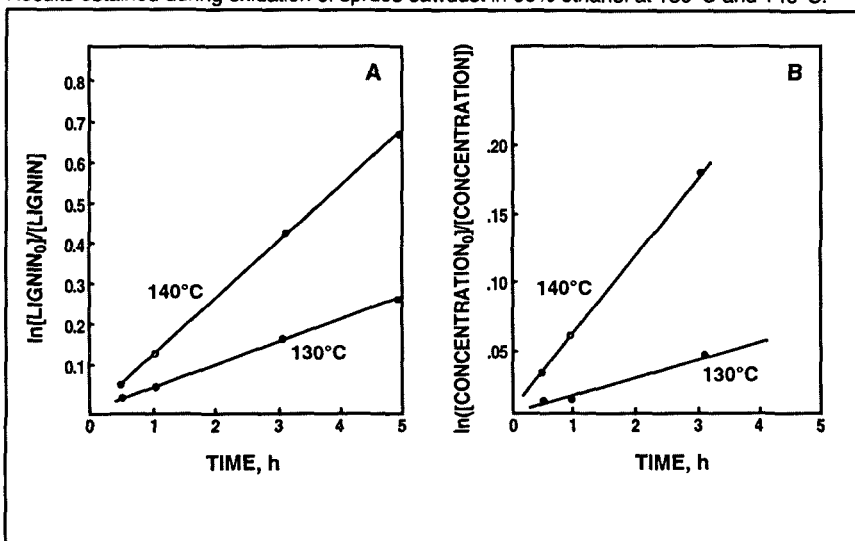
About 80% of the lignin in the solution is of polymeric origin. Hence, only some of the phenylpropane groups are attacked by oxygen, most probably those containing free phenolic hydroxyl. Some of the lignin (about 20%) was transformed into low-molecular-weight compounds, one third of these being of aromatic origin. This quantity is represented in Table IV as ether-soluble substances, namely the phenols and aromatic acids.

The major low-molecular-weight products were vanillin and vanillic acid. This finding supports the suggestion that phenol groups participate in the process of oxidation. The phenol and aromatic acid fractions were analyzed by gas-liquid chromatography (10).

Conclusion

Oxidation of the main components of wood can be accomplished using molecular oxygen in alcoholic and aqueous alcoholic media. The results presented in this report show that the rate of lignin destruction during oxidation far exceeds the rate of dissolution for carbohydrates. This suggests that wood can be delignified

4. Semilogarithmic anamorphoses of (A) lignin dissolution and (B) carbohydrate dissolution. Results obtained during oxidation of spruce sawdust in 60% ethanol at 130°C and 140°C.



III. Delignification of spruce chips with molecular oxygen in 60% ethanol solution

Pulping time, h	O ₂ concentration, % on moisture-free wood	CO ₂ formation, % on moisture-free wood	Pulp yield, %	Lignin content, %	Solution pH
4.5	11.7	4.1	55.8	10.3	2.9
5.0	13.1	5.2	51.1	6.9	2.8
5.5	13.9	5.6	51.1	5.8	2.7
6.0	18.1	...	48.8	4.4	2.7

IV. Yields of soluble products from oxygen pulping of spruce chips in 60% ethanol at 150°C, % on moisture-free wood

	Pulping time, h			
	4.5	5.0	5.5	6.0
Volatile acids (evaluated in CH ₃ COOH), %	3.6	4.9	4.8	5.3
Sugar, %	14.0	15.9	16.2	16.5
Nonvolatile acids, %	3.5	3.6	3.8	3.9
Lignin, %	17.6	19.6	17.9	18.6
Ether-soluble substances, %	1.82	2.03	2.26	2.92
Phenols	0.38	0.54	0.61	1.06
Aromatic acids	1.21	1.27	1.32	1.49
Neutral	0.23	0.22	0.33	0.37

V. Results for pulps obtained from oxygen delignification in aqueous alcoholic media

Solvent	Wood	Pulping conditions*		Yield, %	Lignin content, %	Mechanical properties		
		Temp., °C	Time, min			Breaking length, km	Tear resistance, mN	Crush resistance, kPa
Propanol	Spruce	155	210	48.6	5.5	6.4	410	265
	Aspen	140	360	61.8	5.0	7.05	340	270
Ethanol	Spruce	155	150	50.6	6.5	7.05	460	290

* Pulping conditions: 60% alcohol, liquor/wood = 10 L/kg.

in the absence of acidic or basic reagents by oxidation with molecular oxygen in aqueous alcoholic media (ethanol, methanol, propanol). The results in **Table V** indicate that oxygen-alcoholic pulping provides a high-yield pulp from both softwood and hardwood chips.

The results of kinetic studies and analysis of the products of lignin destruction lead us to suggest that delignification during the proposed oxygen-alcohol process follows two main routes, as depicted in **Fig. 5**. According to these paths, lignin transformation is likely to take place both in anhydrous and aqueous media. Path A mainly occurs in anhydrous media, while dissolution of lignin in the presence of water is more specific to Path B.

Experimental

Materials

Oxidation was carried out in methanol, ethanol, 1-propanol, and 2-propanol. Spruce sawdust (0.25–0.50 mm) and standard-size chips of spruce and aspen were used as test materials. The content of alcohol in aqueous alcoholic solutions is given in volume percentage.

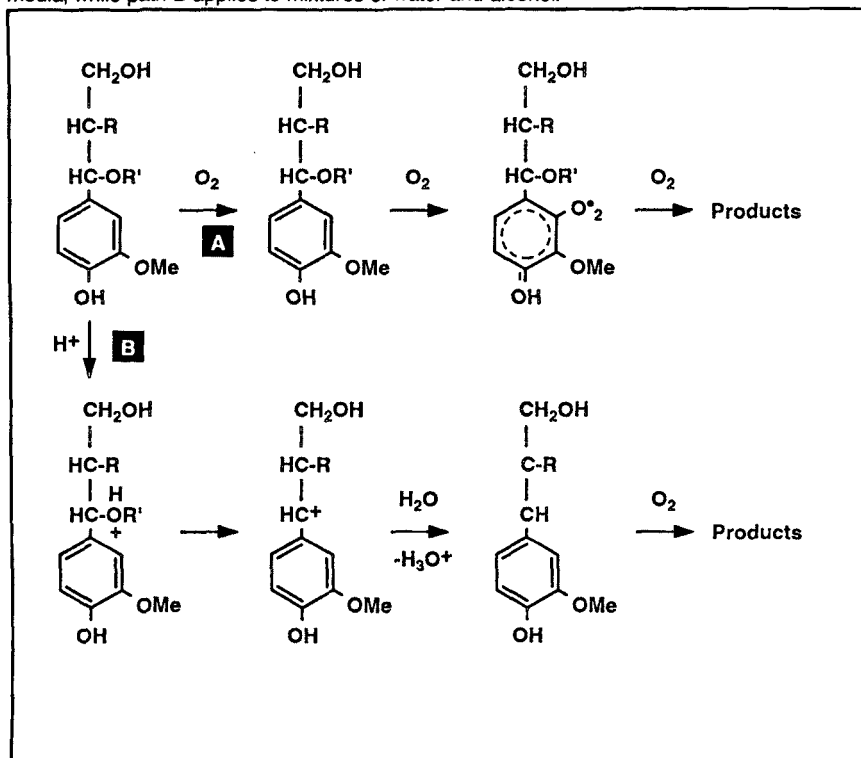
Pulping

Oxidation of wood chips and sawdust was carried out in aqueous alcoholic media. Chips were treated in a 2-L rocking digester (50 cycles/min); sawdust was treated in a rocking 1-L digester (50 cycles/min). Both digesters were made of stainless steel and equipped with an electric heating jacket. During the study of oxidation kinetics using spruce sawdust (1-L digester), the time of pulping was measured from the moment of oxygen injection after reaching isothermality (0.5 h). The overall pulping times reported for the wood chips (2-L digester) include the time needed to achieve isothermality (1 h).

The conditions of oxidation for the wood chips were as follows:

- Liquor-to-wood ratio: 10 L/kg
- Oxygen pressure: 2 MPa
- Temperature: 150°C
- Ethanol-to-water ratio: 60/40 v/v. **II**

5. Proposed cleavage reactions for lignin transformation. Path A applies to 100% alcoholic media, while path B applies to mixtures of water and alcohol.



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