

Simulated Autohydrolysis of Aspen Milled Wood Lignin in the Presence of Aromatic Additives: Structural Modifications

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Synopsis

In a previous article the authors have described changes in molecular weight which occur when aspen milled wood lignin is subjected to autocatalyzed hydrolysis (autohydrolysis) in the presence of three aromatic additives: 2-naphthol, resorcinol, and *p*-hydroxybenzoic acid. In the present work, the reactions of these additives have been studied from the viewpoint of their effect on the structure of the lignin. The use of milled wood lignin instead of aspen wood served to distinguish those reactions between the additives and the lignin, without involving the other wood components. The reaction products have been characterized by elemental analysis and UV and IR spectroscopy. It was concluded that keto groups, generated on the lignin side-chain during autohydrolysis, condense with the additives, which become incorporated into the lignin. This occurs most probably through an aromatic electrophilic substitution reaction. While 2-naphthol condensed primarily with the β -keto carbonyl groups, resorcinol attacked also the α -keto carbonyl groups. When *p*-hydroxybenzoic acid was the additive, its incorporation was accompanied by an increase in lignin carboxylic acid groups.

INTRODUCTION

Organic acids generated from labile ester groups by steaming catalyze the cleavage of hydrolyzable linkages in wood. The effects on lignin of this autocatalyzed hydrolysis (autohydrolysis) have been studied recently. It has been reported that initially the lignin becomes solvent soluble as a result of the formation of low-molecular-weight fragments. As autohydrolysis proceeds, these recombine to give, first, a high-molecular-weight soluble fraction, and from this, insoluble material.¹⁻⁵

The presence during autohydrolysis of various aromatic compounds affects the extractability of the lignin.⁶ For example, 2-naphthol is very effective in preventing lignin repolymerization and, thereby, the formation of unextractable material⁷; thus, when aspen chips autohydrolyzed in the presence of 2-naphthol were extracted with aqueous sodium hydroxide, low lignin pulps were produced, with properties similar to those of acid sulfite pulps.⁸ *p*-Hydroxybenzoic acid shows some effectiveness⁹ and may play a role as blocking agent generated from lignin itself during autohydrolysis.^{4,5} Resorcinol, if used in small amounts may act as a repolymerizing agent, increasing the amount of unextractable lignin. When used in excess, it prevents the formation of insoluble lignin.⁶

The structural modifications resulting from the simulated autohydrolysis of aspen milled wood lignin (MWL) in the presence of the three additives mentioned

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above, are discussed in this article. As in the previous work with aspen MWL, the material after autohydrolysis was separated into three fractions: (1) fraction insoluble in dioxane-water (9:1) (DI); (2) fraction soluble in dioxane-water (9:1) but insoluble in ether (DSEI); and (3) fraction soluble in ether (ES).

All of the characterization work was done on the DI and DSEI fractions. The ES material, which contained, besides the unreacted additive, a small amount of low-molecular-weight aromatic compounds originating from the lignin, was not studied further.

EXPERIMENTAL

Autocatalyzed hydrolysis (autohydrolysis) was carried out as described elsewhere.¹ Thus, 100 mg of aspen MWL, purified according to the procedure of Lundquist et al.¹⁰ ($C_9H_{9.36-8.74}O_{3.23-3.02}[OCH_3]_{1.36-1.37}$) was placed in a 25-ml stainless steel pressure vessel. The desired amount of additive and 0.6 ml water (pH 3.5, adjusted with acetic acid) were added, the vessel was deaerated, closed, and heated in a silicone oil bath at 170°C. At a predetermined time the vessel was cooled rapidly and opened. After the treatment the material was separated into DI, DSEI, and ES fractions. The first two were characterized by IR, UV, and elemental analyses, as described previously.⁵

RESULTS AND DISCUSSION

2-Naphthol

As indicated in Figure 1, when the amount of 2-naphthol present during autohydrolysis was increased, the DSEI samples showed an increasing absorption at 818 and 750 cm^{-1} . These bands indicate the presence of naphthalene rings substituted in positions 1 and 2.¹¹ Thus, position 1 of the 2-naphthol molecule was involved in the blocking of lignin repolymerization, as would be expected

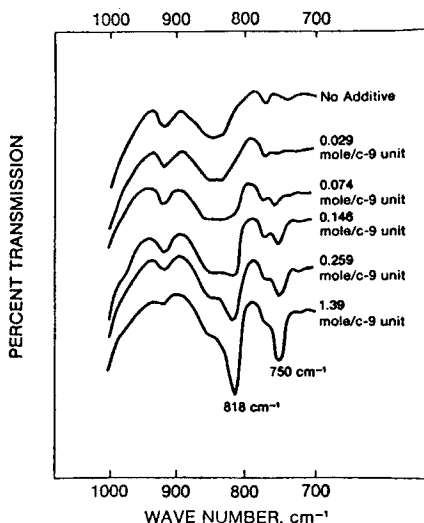


Fig. 1. 700–1000 cm^{-1} spectrum of DSEI samples obtained after simulated autohydrolysis of aspen MWL in the presence of various amounts of 2-naphthol.

for an electrophilic substitution reaction taking place between the additive and carbonium ions generated in the lignin molecule as a consequence of the acidity of the medium.¹² The participation of position 1 in the blocking reaction has been further confirmed by the fact that when 2-naphthols that have position 1 blocked (e.g., 1-nitro-2-naphthol, 2-hydroxy-1-naphthaldehyde) were present during the steaming of aspen wood, the effectiveness of the additive decreased compared to 2-naphthol.⁹ Consistent with this view, when the additive was a 2-naphthol substituted in position 3 (e.g., 2-hydroxy-3-naphthoic acid) no decrease in the extractability of the lignin was observed. It should be noted that in the condensation of 2-naphthol with lignin model compounds in the presence of mineral acids, position 1 is also the reactive site.^{13,14}

DSEI samples obtained in the absence of any additives showed considerable absorption at 1700–1720 cm^{-1} .⁵ This was attributed to the presence of β -carbonyl groups (resulting from the hydrolysis of β -ether linkages) and carboxylic acid groups (resulting from the reincorporation of low-molecular-weight aromatic acids generated by the hydrolysis of the corresponding esters). The presence of 2-naphthol during simulated autohydrolysis caused a decrease in the absorption of 1700–1720 cm^{-1} for the DSEI samples (Fig. 2). This indicates that, with the presence of the additive in the reaction medium, the aromatic acids generated during autohydrolysis had fewer opportunities to act as blocking agents and be incorporated into the DSEI material. On the other hand, the presence of 2-naphthol diminished the number of β -keto groups by condensing with either their precursor hydroxyl groups or the already formed β -carbonyl groups.

When less than 0.1 mole of 2-naphthol was present during autohydrolysis, formation of insoluble lignin was not completely prevented.¹ DI samples obtained under these circumstances showed IR features similar to those of DI obtained on autohydrolysis in the absence of additives.⁵ Thus, the bands at 872 and 890 cm^{-1} , characteristic of lignins condensed in position 6, were present. The absorption at 1700–1720 cm^{-1} was very small, indicating that those β -keto groups that were not involved in blocking participated in the condensation reactions, resulting in the formation of insoluble lignin.

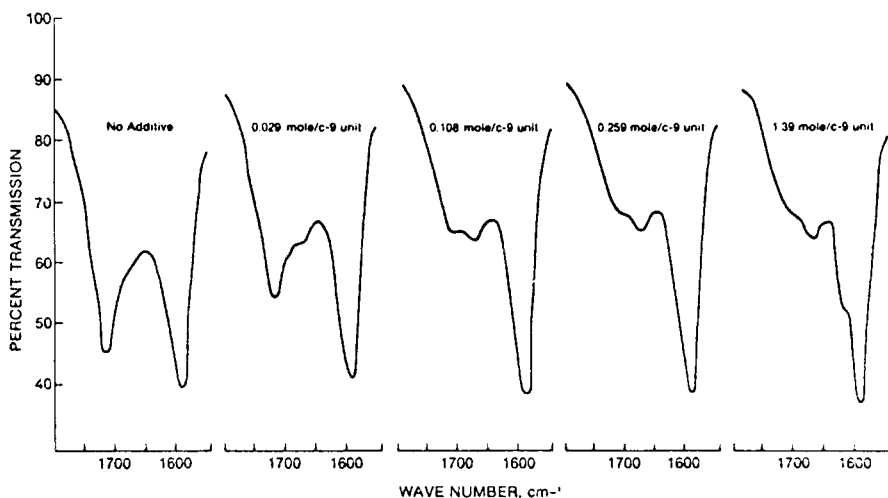


Fig. 2. 1550–1800 cm^{-1} spectrum of DSEI lignins obtained after simulated autohydrolysis of aspen MWL in the presence of various amounts of 2-naphthol.

The incorporation of 2-naphthol by lignin during simulated autohydrolysis was also supported by UV spectroscopy. Thus, the alkali-acid difference spectrum (Fig. 3) of the corresponding DSEI samples showed three bands at 290, 300 and 360 nm. Upon NaBH_4 reduction, the absorption at 360 nm was shifted to 355 nm; only a small decrease in intensity was observed, indicating that conjugated carbonyl groups were not the only chromophores responsible for the absorption in that region of the spectrum. This fact, and the appearance in the 290–300 nm region of two peaks (instead of one in the case of the DSEI samples obtained after autohydrolysis in the absence of additives,⁵ indicate the existence of a new chromophore in the structure of the ionized sample. This new chromophore can be associated with the incorporation of 2-naphthol, whose difference spectrum shows absorption at 283, 295, and 350 nm.⁹

Earlier work by Dischendorfer and Ofenheimer¹⁴ has shown the formation of cumarone structures by condensation of 2-naphthol with benzoin under strong acid conditions. Upon autohydrolysis of lignin in the presence of 2-naphthol, the peaks exhibited by the difference spectrum of the reduced lignin were very close to the peaks shown by the difference spectrum of 2-naphthol itself. This suggests that the hydroxyl group remained free and did not undergo etherification as required for the formation of cumarone structures.

Elemental analysis (Table I) also confirmed the incorporation of the additive by the lignin, as indicated by the increase in carbon content and the decrease in methoxyl content. In order to take into account the incorporation of 2-naphthol C_9 formulas have been calculated as $\text{C}_9\text{H}_w\text{O}_x(\text{OCH}_3)_y(\text{C}_{10}\text{H}_7\text{O})_z$. Since the variations of OCH_3 content and $\text{OCH}_3/\text{C-9}$ unit are relatively small during simulated autohydrolysis of aspen MWL in the absence of additives,⁵ the value of y was assumed to be 1.37 (the y value for aspen MWL and for DSEI obtained without additives). The other subindices were calculated with the results shown in Table I. It has been reported previously¹ that the presence of about 0.1 mole of additive/C-9 unit is required in order to completely prevent the formation of DI lignin. As indicated in Table I this resulted in the actual incorporation of about 0.07 mole/C-9 unit in the DSEI lignin. When the quantity

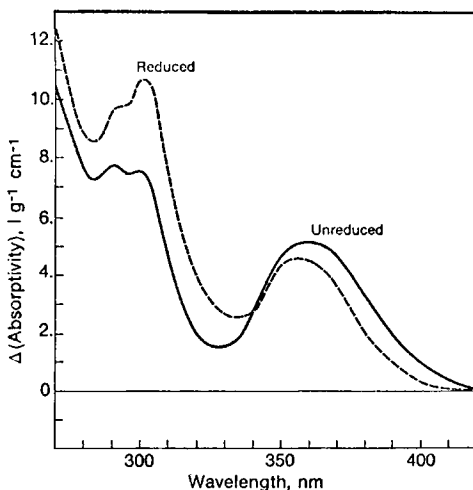


Fig. 3. Alkali-acid difference spectrum of a DSEI sample obtained after simulated autohydrolysis of aspen MWL (30 min at 170°C) in the presence of 1.38 mole of 2-naphthol/C-9 unit.

TABLE I
Chemical Analysis and C₉ Formulas of DSEI Lignins After Stimulated Autohydrolysis of Aspen MWL in the Presence of 2-Naphthol

2-Naphthol added (mole/C-9 unit)	C (%)	H (%)	O (%)	OCH ₃	C ₉ formulas	Molecular weight
0	58.62	5.51	35.87	20.05	C ₉ H _{7.58} O _{3.38} (OCH ₃) _{1.37}	212.13
0.108	61.22	5.86	32.92	19.49	C ₉ H _{8.14} O _{3.04} (OCH ₃) _{1.37} (C ₁₀ H ₇ O) _{0.07}	217.91
0.146	61.80	5.96	32.24	19.08	C ₉ H _{8.39} O _{3.01} (OCH ₃) _{1.37} (C ₁₀ H ₇ O) _{0.11}	222.59
0.259	62.61	6.11	31.28	18.67	C ₉ H _{8.74} O _{2.93} (OCH ₃) _{1.37} (C ₁₀ H ₇ O) _{0.15}	227.48
0.437	62.69	5.87	31.44	17.98	C ₉ H _{8.38} O _{3.07} (OCH ₃) _{1.37} (C ₁₀ H ₇ O) _{0.20}	236.21
1.393	63.21	5.85	30.94	16.91	C ₉ H _{8.58} O _{3.20} (OCH ₃) _{1.37} (C ₁₀ H ₇ O) _{0.29}	251.15
MWL	59.15	5.92	34.93	20.08	C ₉ H _{8.36} O _{3.23} (OCH ₃) _{1.36}	210.20
	59.96	6.19	33.85	20.42	C ₉ H _{8.74} O _{3.02} (OCH ₃) _{1.37}	207.53

of 2-naphthol present in the reaction medium was increased, a larger amount of it was incorporated into the DSEI lignin. However, it must be noted that all of the 2-naphthol added did not go into the DSEI fraction. When a large excess of 2-naphthol was present, the amount incorporated in the DSEI fraction seemed to level off at around 0.3 mole/C₉ unit.

From Table I it is seen that the lignin part of the C₉ formulas (that is, excluding [C₁₀H₇O]_z) resembled aspen milled wood lignin, rather than the DSEI sample obtained on autohydrolysis in the absence of additives. This has been tentatively explained by assuming that the additive (especially if present in excess) reacted with the lignin as soon as hydrolysis took place, without allowing time for the occurrence of rearrangements in the side chain.⁹

Resorcinol

As in the case of 2-naphthol, the addition of resorcinol caused a modification in the IR spectrum in the 700–1000 cm⁻¹ region, characteristic of the substitution pattern of the aromatic ring. Thus, the DSEI samples showed an increase of the absorption at 850 and 979 cm⁻¹ (Fig. 4). These bands correspond to the aromatic C—H out-of-plane in-phase and out-of-phase deformations, respectively, and their position is consistent with the 1,2,4-trisubstitution pattern^{15,16} to be expected if resorcinol was being substituted in a carbon atom ortho to one hydroxyl group and para to the other, as would be the case for an electrophilic substitution reaction.

The DI samples showed absorptions at 872 and 890 cm⁻¹, characteristic of the 1,2,4,6- and 1,3,4,5,6-substitution patterns that have been reported for other DI lignins.⁵ These samples also exhibited signs of the incorporation of resorcinol, as demonstrated by the shoulder appearing at 979 cm⁻¹ and in agreement with the bridging action of this additive.

Also in the present case the increasing addition of resorcinol caused a gradual decrease in intensity at 1700–1720 cm⁻¹ in DSEI lignins (Fig. 5). This can be explained as a result of the condensation of resorcinol with β-carbonyl groups or their precursors. For DI samples the absorption at this frequency range was small, indicating that here also the β-keto groups participated in the formation of insoluble lignin.

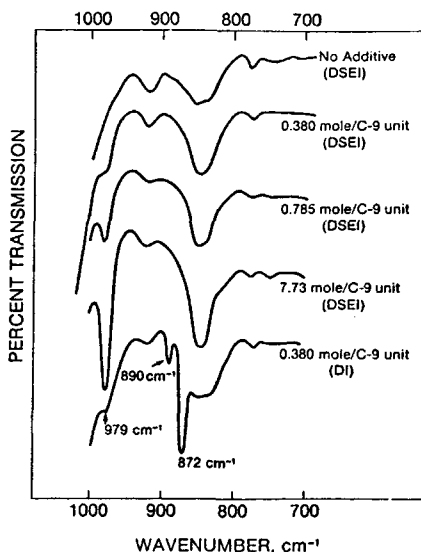


Fig. 4. 700–1000 cm^{-1} spectrum of DSEI and DI samples obtained after simulated autohydrolysis in the presence of various amounts of resorcinol.

With the addition of resorcinol, the absorption at 1670 cm^{-1} gradually decreased and eventually disappeared in DSEI as well as DI lignins. This indicates that the conjugated carbonyl groups, which were partially unaffected by 2-naphthol (see Fig. 2), were attacked by resorcinol. This was probably due to the fact that the higher reactivity of resorcinol caused more extensive condensation with the more resistant α carbonyl groups and their precursors.

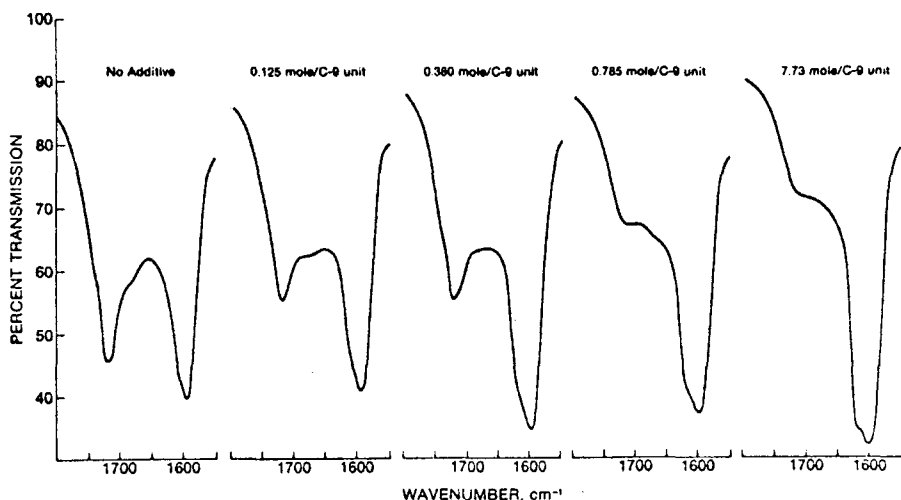


Fig. 5. 1550–1800 cm^{-1} spectrum of DSEI samples obtained after simulated autohydrolysis of aspen MWL in the presence of various amounts of resorcinol.

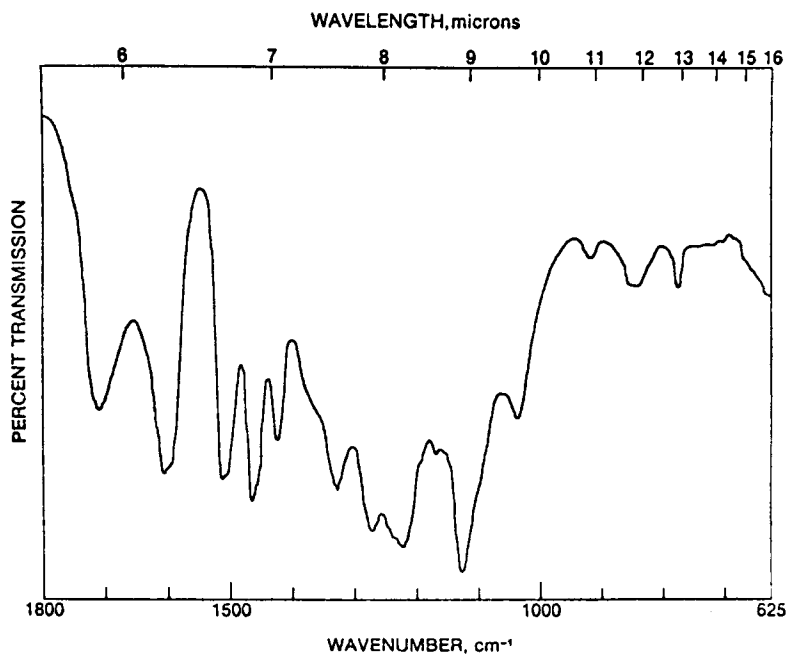


Fig. 6. IR spectrum of a DSEI sample obtained after simulated autohydrolysis of aspen MWL in the presence of *p*-hydroxybenzoic acid (6.0 mole/C-9 unit).

p-Hydroxybenzoic Acid

It has been indicated above that when 2-naphthol or resorcinol were used as additives, the prevention of lignin self-condensation resulted in a reduction of the absorption at 1700–1720 cm^{-1} , since the blocking agent condensed with the β -carbonyl groups (or their precursors) and prevented the incorporation of *in situ* generated aromatic acids. In the case of the addition of *p*-hydroxybenzoic acid (6.00 mole/C-9 unit), the absorption in this region was quite prominent for the DSEI fraction (Fig. 6) and is attributed exclusively to the carboxylic acid groups introduced by the incorporation of the additive.

The IR spectrum also showed an increase in the absorption at 775 cm^{-1} , which is within the range expected for 3,4-substituted benzoic acids, as expected if the blocking reaction corresponds to the electrophilic substitution of the added compound.

CONCLUSIONS

Aromatic compounds added during autohydrolysis of aspen milled wood lignin are incorporated into the lignin. This occurs most probably through an aromatic electrophilic substitution reaction of the additive with keto or hydroxyl groups in the lignin side chain. While 2-naphthol condensed primarily with the β -keto carbonyl groups, resorcinol attacked also the α -carbonyl groups. When *p*-hydroxybenzoic acid was the additive, its incorporation was accompanied by an increase in lignin carboxylic acid groups.

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