Simulated Autohydrolysis of Aspen Milled Wood Lignin in the Presence of Aromatic Additives. Changes in Molecular Weight Distribution

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Synopsis

The reactions between aspen milled wood lignin (MWL) and 2-naphthol, resorcinol, and p-hydroxybenzoic acid were studied under simulated autohydrolysis conditions. The material after the reaction was separated into a dioxane-insoluble fraction (DI), a dioxane-soluble but ether-insoluble fraction (DSEI), and an ether-soluble fraction (ES). In the absence of additive, the lignin first depolymerized and remained solvent soluble, then repolymerized to become insoluble. With 2-naphthol as additive, the amount of DI lignin decreased proportionally to the amount of additive present. When more than 0.1 mole of 2-naphthol/C-9 unit was present, no DI lignin was formed, that is, all the lignin was soluble. Gel permeation chromatography studies indicated that the additive was acting effectively as a blocking agent, preventing lignin repolymerization. Small amounts of resorcinol acted as a repolymerizing agent since two or more fragments of lignin could readily condense with a molecule of the very active additive. As a result of this bridging effect, the amount of DI lignin increased. As the amount of resorcinol was increased, it behaved more like a blocking agent and a reduction in the amount of DI lignin was observed. The presence of a large excess of resorcinol resulted in the formation of soluble lignin only. The molecular weight distributions supported the proposed dual role of resorcinol as a bridging or blocking agent. The use of an excess of p-hydroxybenzoic acid prevented the formation of DI material and resulted in low molecular weight soluble lignin.

INTRODUCTION

The cleavage of some hydrolyzable bonds in wood can be catalyzed by the organic acids generated from labile ester groups by steaming. As a result of this autocatalyzed hydrolysis (autohydrolysis), solvent-soluble lignin is formed initially. From this, unextractable lignin is obtained with more prolonged treatment.[1-4] The formation of soluble lignin is associated with the initial generation of low molecular weight fragments. These combine to form first a high molecular weight soluble fraction and, from this, the insoluble material.[4,5]

Besides those originally present in the aliphatic chains of the lignin molecule, additional hydroxyl and carbonyl groups are generated during autohydrolysis.[5,6] As a result of their protonation (Fig. 1), carbonium ions are obtained. These are known to be involved in acid condensation reactions of lignin.[7] Wayman and Lora[8] studied the effects of more than 20 aromatic compounds (mainly phenols) and found that they affected the formation of unextractable lignin during autohydrolysis. This was attributed to the reaction between the additive (nucleophile) and the lignin carbonium ions (electrophiles).

The reactions between lignin and phenols have been previously studied under
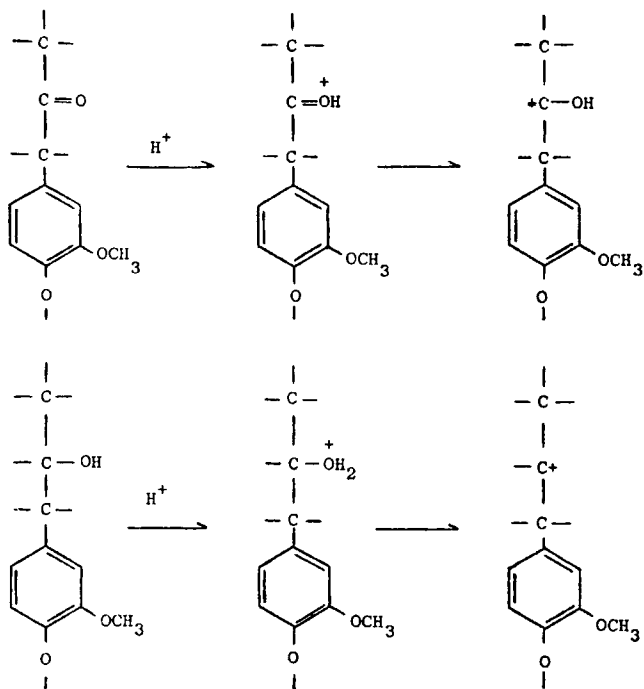
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Fig. 1. Formation of carbonium ions from aliphatic carbonyl (top) and hydroxyl (bottom) groups in lignin.

conditions different from those prevailing during autohydrolysis, as, for instance, in connection with phenol pulping or with the production of plastics and other materials.[9] In order to gain further understanding of the interaction between lignin and aromatic additives under autohydrolysis conditions, it was decided to use aspen milled wood lignin (MWL) as a lignin model and to study the effects of 2-naphthol, resorcinol, and p-hydroxybenzoic acid. The 2-naphthol was selected since it prevents the formation of insoluble lignin and makes possible the use of the autohydrolysis–extraction process in the production of acceptable quality low-lignin pulps.[10] Resorcinol, on the other hand, may decrease the quantity of extractable lignin.[8] p-Hydroxybenzoic acid is generated from lignin itself during the autohydrolysis of aspen wood and, in a subsequent stage, probably assists in the prevention of the formation of unextractable lignin.[4,5]

EXPERIMENTAL

Aspen MWL, 100 mg, purified according to the procedure of Lundquist et al.[11] $[(C_9H_{8.36-8.74}O_{3.23-3.02}[OCH_3]_{1.36-1.37})]$, was placed in a small glass beaker specially designed to fit 25-ml stainless steel pressure vessels.

Following the procedure described in more detail elsewhere,[5] 0.6 ml water (pH 3.5, adjusted with acetic acid) plus the desired amount of additive were added, and the vessel was deaerated, closed, and heated in a silicone oil bath at 170°C. After 30 min, the vessel was cooled rapidly and opened. After the treatment the material was separated into three fractions: (1) materials insoluble in dioxane–water (9:1) (DI); (2) material soluble in dioxane–water (9:1) but insoluble in ether (DSEI); and (3) material soluble in ether (ES).

The ES fraction (which, besides unreacted additive, contained a small amount of low molecular weight aromatic compounds originating from the lignin) was not studied further. Yields were determined for the DI and DSEI fractions. Gel permeation chromatograms of the latter were obtained on a Sephadex G100 column (35 cm long × 2.5 cm ID) according to procedures published previously.[4,12] Most chromatograms took the shape of a bimodal curve. The first peak was eluted within the exclusion volume (54 ml) determined by running blue dextran ($M_w \simeq 2 \times 10^6$) through the column. As indicated by Bolker et al.,[13] this peak represents the accumulation of all the molecules with hydrodynamic volume greater than that acceptable to the chromatographic medium. In this work, the chromatograms were used to estimate the proportion of high and low molecular weight materials. To this effect they were divided into two fractions: (1) a high molecular weight lignin (HML) including material eluted up to fraction number 30 (elution volume less than 77 ml), and (2) a low molecular weight lignin (LML) including material eluted after fraction number 30 (elution volume more than 77 ml).

Having in mind considerations discussed elsewhere,[5] weight fractions for HML and LML were calculated as area fractions and used to estimate yields based on the starting material.

RESULTS AND DISCUSSION

2-Naphthol

When 2-naphthol was added during simulated autohydrolysis of aspen MWL at 170°C for 30 min, the amount of DI lignin decreased proportionally to the quantity of additive present in the reaction medium (Fig. 2). When more than about 0.1 mole 2-naphthol/C-9 unit was present, the formation of DI material was prevented completely.

Gel permeation chromatography of the DSEI fractions (Figs. 3 and 4) demonstrates clearly that 2-naphthol acted as a preventive of lignin repolymerization, which, as has been shown previously,[4,5] is responsible for the formation of unextractable materials. When the amount of additive was increased and the
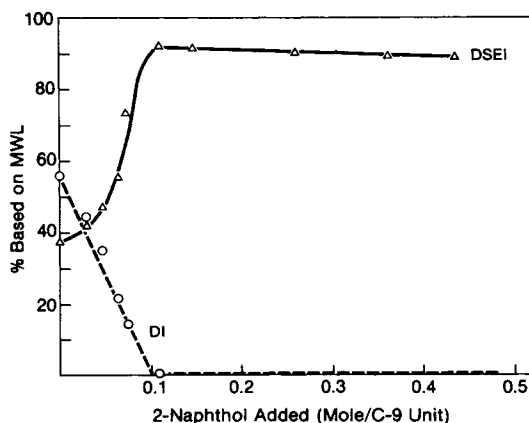

Fig. 2. Yield of DI (O) and DSEI (△) fractions after simulated autohydrolysis of apsen MWL in the presence of various amounts of 2-naphthol.
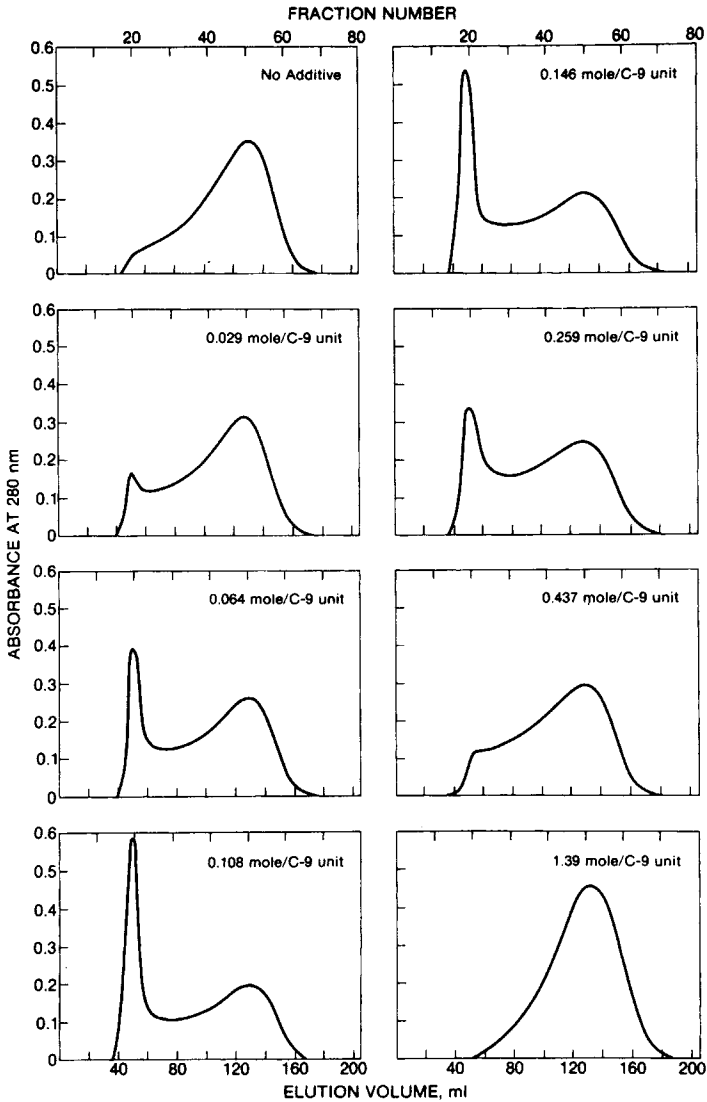
FRACTION NUMBER

Fig. 3. Gel permeation chromatograms of DSEI lignins after MWL in the presence of various amounts of 2-naphthol.

formation of DI lignin was prevented, there was an increase in HML soluble material. This suggests that the additive had reacted with the HML soluble precursors of the DI lignin, stabilizing them and preventing the formation of the unextractable structures. When the amount of additive was just enough to completely prevent the formation of DI lignin, the yield of HML soluble material was maximum. When more 2-naphthol was added, it reacted with the LML material preventing formation of HML–DSEI lignin. As the excess of 2-naphthol became larger, no HML was formed and only low molecular weight materials (LML and ES) were obtained.
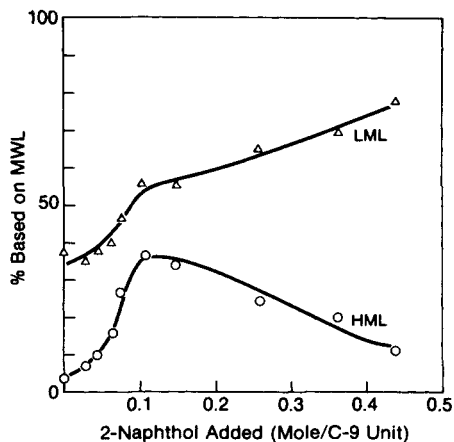
Fig. 4. Effect of 2-naphthol on the yield of HML (O) and LML (△) after simulated autohydrolysis .of aspen MWL.

Resorcinol

When less than 0.125 mole resorcinol/C-9 unit was present during simulated autohydrolysis, the DI lignin increased and the DSEI lignin decreased as the amount of resorcinol added was increased (Fig. 5). With further additions of resorcinol, the yield of DI lignin decreased and eventually became nil, while the yield of DSEI material increased, eventually reached a maximum, and started to decline. (A run not included in Fig. 5 was done using 7.73 mole resorcinol/C-9 unit of MWL. After autohydrolysis at 170°C for 30 min, the material was completely soluble in 90:10 dioxane–water and the yield of DSEI lignin was 90.7%.)

The observed behavior agrees with the participation of resorcinol in two electrophilic substitution reactions during autohydrolysis. When small amounts of the additive were present, not all of the recondensable lignin fragments L^+ were scavenged by the additive via blocking (top, Fig. 6). Some were available for bridging (bottom, Fig. 6), and thereby an increase in the amount of DI lignin was observed. The participation of resorcinol in this bridging reaction is sup-
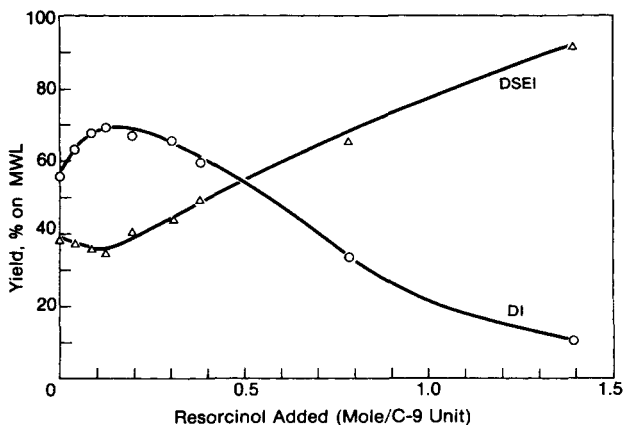

Fig. 5. Effect of resorcinol on the yield of DI (O) and DSEI (△) lignins after simulated autohydrolysis of aspen MWL.
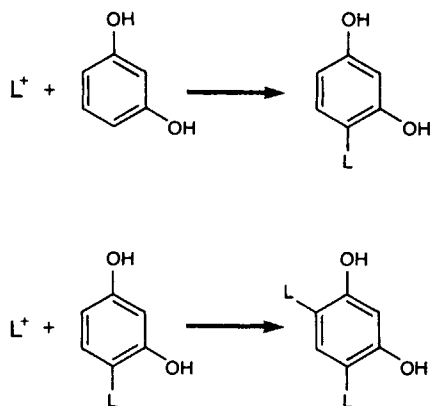
Fig. 6. Resorcinol as blocking (top) and bridging (bottom) agent during autohydrolysis.

ported by previous reports on the acid-catalyzed condensation of 1 mole resorcinol with more than 1 mole of the lignin model compounds vanillyl and veratryl alcohols.[14,15] When higher amounts of resorcinol were used, the blocking reaction prevailed and a decreasing number of L^+ participated in repolymerization through the additive. When a large excess of resorcinol was present, virtually all L^+ were scavenged by the additive in one step, thereby neither bridging nor lignin intermolecular self-recondensation could take place, and as a result, completely soluble material was obtained.

The dual role of resorcinol as blocking–bridging agent is also illustrated by gel permeation chromatography studies (Fig. 7 and Table I). When small amounts of resorcinol were present, little HML was found in the DSEI material since it was being used for the production of additional amounts of DI lignin. When the amount of resorcinol was increased between 0.125 and 1.35 mole/C-9 unit, the formation of DI lignin was partially prevented, and as was observed with 2-naphthol, the amount of HML and LML increased. When 7.73 mole resorcinol/C-9 unit was used, the formation of DI material was prevented completely, and the absence of HML in the DSEI fraction became apparent, since the repolymerization of LML could be blocked.

The conclusion drawn previously[8] that resorcinol was a detrimental additive must be qualified. If the amount of additive is large enough, resorcinol will behave like a blocking agent. However, it should be kept in mind that while in the case of 2-napthol around 0.1 mole/C-9 unit was enough to obtain autohydrolyzed material completely soluble in dioxane–water (9:1), the minimum amount of resorcinol required to get the same effect was more than 1.39 mole/C-9 unit. This is a consequence of the fact that while resorcinol easily undergoes more than one substitution, 2-naphthol is almost exclusively substituted only in position 1, thus decreasing substantially the possibility of bridging.[8]

p-Hydroxybenzoic Acid

When 6.00 mole p-hydroxybenzoic acid/C-9 unit was used during simulated autohydrolysis, the material obtained was completely soluble in dioxane–water (9:1) and gave 78.2% yield of DSEI lignin. The molecular weight distribution of the DSEI sample showed only low molecular weight material. These obser-
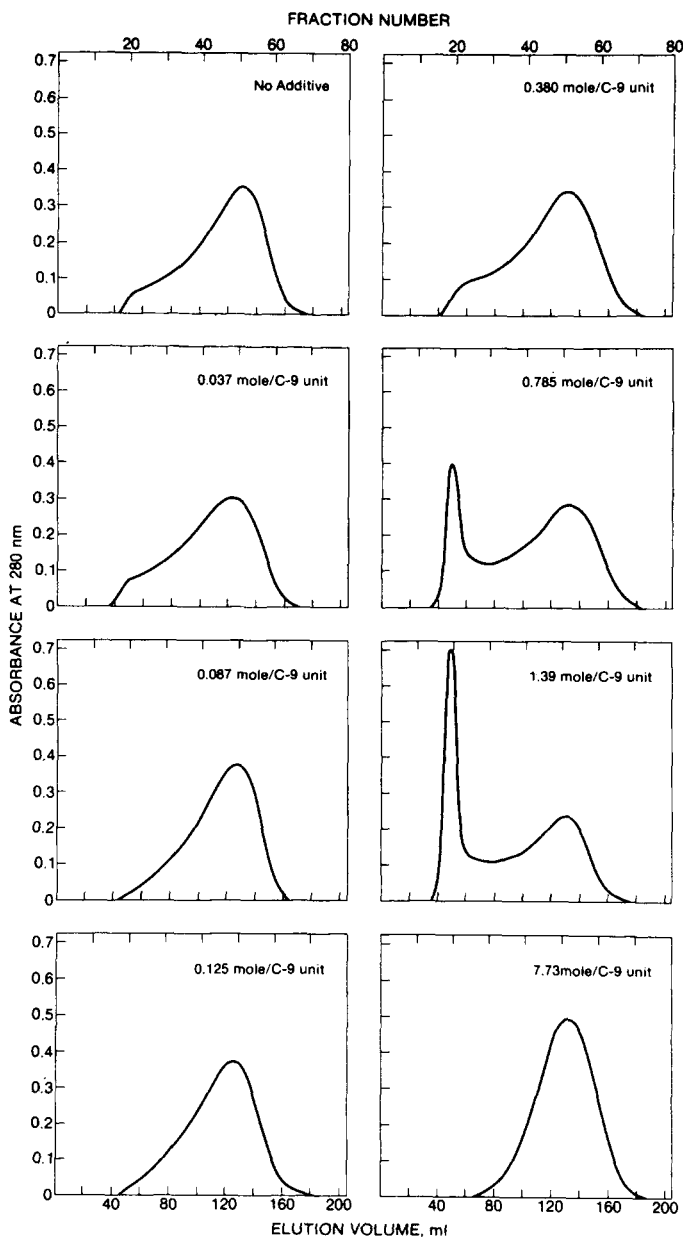
Fig. 7. Gel permeation chromatograms of DSEI lignins after simulated autohydrolysis of aspen MWL in the presence of various quantities of resorcinol.

vations indicate that the additive prevented the formation of DI material by blocking the repolymerization of the DSEI fractions.

CONCLUSIONS

The formation of insoluble material may be prevented if 2-naphthol, resorcinol, or p-hydroxybenzoic acid are present during the simulated autohydrolysis of aspen MWL. The action of the additive is associated with the blocking of lignin

TABLE I
Yield of HML and LML After Simulated Autohydrolysis of Aspen MWL in the Presence of
Resorcinol

Resorcinol added, mole/C-9 unit	HML % on MWL	LML % on MWL
0.037	4.6	32.4
0.087	1.9	33.6
0.125	1.8	32.8
0.198	5.0	35.0
0.302	3.7	40.1
0.380	6.5	43.0
0.785	17.4	47.1
1.39	35.8	55.7
7.73	0.5	90.2

repolymerization and depends on the type and amount of additive used. Even small quantities of additives that easily undergo just a single electrophilic substitution reaction are effective in preventing lignin repolymerization. The addition of small amounts of compounds that readily undergo more than one electrophilic substitution promotes lignin recondensation. However, if an excess of this type of compounds is used, repolymerization may be prevented.

References

1. J. H. Lora, M.A.Sc. Thesis, University of Toronto, Toronto, Ontario, 1976.

2. J. H. Lora and M. Wayman, *Tappi,* 61(6), 47 (1978).

3. J. H. Lora and M. Wayman, Report 27 in *Poplar Research, Management and Utilization in Canada,* D. C. F. Fayle, L. Zsuffa, and H. W. Anderson, Eds., Ontario Ministry of Natural Resources, 1979.

4. M. G. S. Chua and M. Wayman, *Can. J. Chem.,* 57, 1141 (1979).

5. J. H. Lora, Ph.D. Thesis, University of Toronto, Toronto, Ontario, 1979.

6. M. G. S. Chua and M. Wayman, *Can. J. Chem.,* 57, 2603 (1979).

7. K. V. Sarkanen and C. H. Ludwig, *Lignins,* Wiley–Interscience, New York, 1971, pp. 182–184.

8. M. Wayman and J. H. Lora, *Tappi,* 61(6), 55 (1978).

9. F. E. Brauns and D. A. Brauns, in *The Chemistry of Lignin,* Supplement Volume, Academic, New York, 1960, Chap. XVII.

10. J. H. Lora and M. Wayman, *Tappi,* 61(12), 88 (1978).

11. K. Lundquist, B. Ohlsson, and R. Simonson, *Svensk. Papperstidn.,* 80(5), 143 (1977).

12. T. I. Obiaga and M. Wayman, *J. Appl. Polym. Sci.,* 18, 1943 (1974).

13. H. I. Bolker, H. E. W. Rhodes, and K. S. Lee, *J. Agric. Food Chem.,* 25(4), 708 (1977).

14. B. Leopold, *Acta. Chem. Scand.,* 5, 1393 (1951).

15. B. O. Lindgren, *Acta. Chem. Scand.,* 3, 1011 (1949).