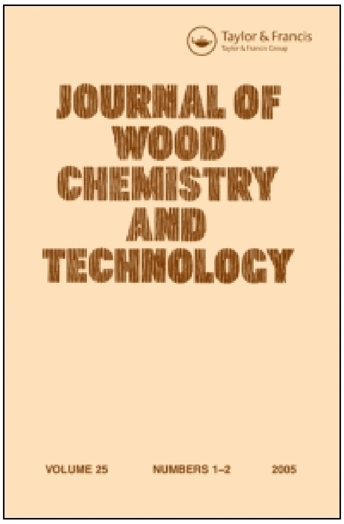

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CONDENSATION OF LIGNINS WITH CONIFERYL ALCOHOL IN ALKALINE AQUEOUS SOLUTIONS

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ABSTRACT

The condensation of coniferyl alcohol with dissolved lignins of low molecular weight (LMWL) has been investigated. In aqueous sodium hydroxide (soda), sodium hydroxide - sodium sulfide (kraft) or sodium hydroxide - anthraquinone (soda-AQ) solutions, lignin preparations were heated and molecular weight distributions of the resultant condensation products were estimated. When coniferyl alcohol dissolved in soda and kraft liquors was heated, self-condensation was observed, mainly to form oligomers with only a small proportion of the reaction products characterized by molecular weights greater than about 1000. When mixtures of LMWL and coniferyl alcohol were heated in sodium hydroxide solutions, condensation reactions occurred and progressed further with increased temperature and concentration of coniferyl alcohol. In contrast to results with sodium hydroxide solutions, heating in kraft liquors gave rise to a higher proportion of the oligomer fraction and a smaller proportion of higher molecular weight entities. These results seem to indicate that the presence of sulfide reduces the extent of condensation reactions in alkaline pulping. With soda-AQ solutions, condensation effects were found to be intermediate between those observed with soda and kraft liquors.

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INTRODUCTION

It has been shown by Gierer and Pettersson [1] that model compounds representing phenolic lignin structures of the β-aryl ether type react with simple phenols in alkaline solution to give condensation products. Formaldehyde, liberated from terminal hydroxymethyl groups in quinone methide intermediates, reacts with the added phenol to yield the corresponding diarylmethanes, as indicated by the results [2] of treatment of wood meal with soda liquors in the presence of 2, 4- or 2, 6- xylenol. Gierer and co-workers [2] proposed that conjugate additions and formaldehyde-phenol type condensations are the main reactions involved in the base-promoted conversion of lignin fragments into high-molecular residual lignins judging from experimentation with compounds of the p-hydroxy styrenes and β-hydroxypropiophenone series [3].

On the other hand, it has been suggested that coniferyl alcohol-like structures are intermediates formed in the course of the degradation of p-hydroxy-arylglycerol-β-aryl ether units as a result of heating lignins in sodium hydroxide-sodium sulfide solutions. This view was based on the observations that model compounds representing such units are in part converted, under these conditions, into coniferyl alcohol or related compounds [4-7].

When coniferyl alcohol is heated under soda or kraft pulping conditions, alkaline degradation of coniferyl alcohol and of coniferyl alcohol-like structures appears to occur but accounts for only a minor part of the conversion of these structures, whereas the major part reacts to form high molecular weight substances through conjugate addition reaction and contributes to the formation of residual lignins [3, 8-10].

After Mortimer [11] observed the presence of coniferyl alcohol as a reaction product formed in the course of alkaline delignification of gymnosperms, Kondo and Sarkanen [12] reported the results of a study of the formation and subsequent disappearance of coniferyl alcohol during kraft and soda-AQ pulping of western hemlock wood meal under isothermal conditions. The amount of coniferyl alcohol generated was found to increase to a sharp maximum and then to decline rapidly to a low value. The disappearance of coniferyl alcohol was attributed mainly to condensation with other components of dissolved lignins.

In the now-reported work, the condensation of coniferyl alcohol with lignins of low molecular weight (LMWL) dissolved in soda, kraft and soda-AQ liquors has been observed and monitored by estimation of the molecular weight distributions of the products formed under a number of reaction conditions.

EXPERIMENTAL

A. Isolation of Low Molecular Weight Kraft Lignins (LMWL)

Western Hemlock *Tsuga heterophylla* wood platelets (100 g o.d., average thickness = 0.7 mm, acetone-extracted) were treated in an autoclave with 1 L of a kraft liquor containing 21.2 gL^{-1} of NaOH and 8.60 gL^{-1} of Na_2S ("effective alkali" = 20% as Na_2O; "sulfidity" = 30%) for 1 hr at 100°C. After reaction, the solution was adjusted to pH 7 by addition of acetic acid and then extracted three times with chloroform. The extract was washed with water and dried over anhydrous Na_2SO_4. The $CHCl_3$ solution was concentrated on a rotary evaporator and poured into methanol. Precipitated inorganic sulfur was filtered off, and methanol was removed by distillation to yield a light brown oil which is hereafter identified as LMWL (1.0g, 3.4% yield based on Klason lignin in the wood).

B. Reaction Conditions

Coniferyl alcohol and LMWL, either alone or together, were dissolved in the appropriate solvent solution which was then de-areated with nitrogen gas. Three kinds of treating solutions were used, soda, kraft and soda-AQ, and in all cases the effective alkali concentration was fixed at 21.2 gL^{-1} as Na_2O. The kraft liquor contained 8.60 gL^{-1} of Na_2S. The soda-AQ liquor was prepared by adding AQ(0.1g L^{-1}) and glucose (2 g L^{-1}) to soda liquor. An aliquot (8 or 10 ml) of the prepared solution was transferred into a stainless steel autoclave. Air was replaced by nitrogen and the autoclave was then sealed and heated in an oil bath at constant temperature. Reaction conditions are shown in Table 1. After selected periods of time, the reaction was terminated by cooling.

C. Size Exclusion Chromatography ("SEC")

Estimation of the distribution of molecular size of the reaction products was carried out by means of the size exclusion chromatography procedures previously described [13]. The gel (Sephadex G-50, superfine, Pharmacia) was contained in a glass column (70 x 2.5 cm). Elution was conducted by use of aqueous sodium hydroxide solutions (0.1N) so prepared as to be carbonate-free and thereby providing constant alkalinity. An ISCO UA-5 monitor with a Type 6 double-beam optical unit operating at 280 nm served as a detector at the column outlet. Calibration of the size exclusion chromatography columns in terms of relative elution volume (V_r) and molecular weight was accomplished by use of fractions of paucidisperse kraft lignins for which molecular weights ($\bar{M}_w$) had been determined previously by use of ultracentrifuge sedimentation equilibrium measurements [13].

RESULTS AND DISCUSSION

A. Heating of Coniferyl Alcohol in Soda and Kraft Liquors

Coniferyl alcohol (10 mg) was dissolved in soda or kraft liquors (10 ml), and the solutions were heated at 170°C for 0.5, 1 and 2 hours. The molecular weight distribution ("MWD") profiles of

TABLE 1

Reaction Conditions[(a)] and MWD Ratios for Reaction Products

Cooking liquor	CA[(b)] mmol L^{-1}	Temp. °C	Time min	Relative area (MW)[(c)] I (<400)	II (400-600)	III (600-1000)	IV (>1000)
LMWL untreated			0	1.0	1.0	1.0	1.0
Soda	0	100	30	1.1	0.83	0.89	1.1
Soda	5.6	100	30	...	1.1	1.1	1.2
Soda	0	140	30	0.90	0.65	0.72	1.0
Soda	5.6	140	30	...	1.0	1.1	1.4
Soda	0	170	30	1.7	0.76	0.88	0.47
Soda	5.6	170	10	...	1.2	1.3	1.2
Soda	5.6	170	20	...	1.3	1.4	1.6
Soda	5.6	170	30	...	1.2	1.4	1.8
Soda	5.6	170	60	...	1.2	1.5	0.98
Soda	5.6	170	120	...	1.2	1.4	0.91
Soda	1.1	170	30	...	0.88	0.91	0.84
Soda	11.2	170	30	...	1.3	1.5	2.0
Kraft	0	140	30	1.9	1.3	1.3	0.62
Kraft	5.6	140	30	...	2.0	1.8	0.76
Kraft	0	170	30	1.8	1.1	1.3	0.46
Kraft	5.6	170	30	...	2.1	1.7	0.63
Soda-AQ	0	170	30	1.7	1.0	0.91	0.60
Soda-AQ	5.6	170	30	...	1.6	1.5	1.2

(a) the concentration of LMWL was 2 g L^{-1} in all experiments.

(b) CA = coniferyl alcohol.

(c) MW = molecular weight.

reaction products which were formed by the heating in the soda liquor are shown in Figure 1A as a function of treatment time. It can be seen that coniferyl alcohol in part is converted into oligomers and higher molecular weight substances. The absorbance of Peak B, reflecting the presence of dimers and similar products (molecular weight = 300-400), increased as a function of time whereas the absorbance of Peak A, indicating the presence of monomer or monomers, decreased.

The MWD profiles of reaction products obtained by heating coniferyl alcohol in kraft liquor are shown in Figure 1B. As a result of treatment for thirty minutes, a large amount of Peak D substances (molecular weight 350 - 500) was formed. After 1 and 2 hours of heating, the absorbance of Peak C, consisting mainly of dimers, increased while the absorbance of the Peaks A and D substances decreased.

It has been demonstrated by Gierer and Lindeberg [10] that heating of coniferyl alcohol in kraft liquor yields, in addition to degradation and condensation products, a variety of hydrosulfides and sulfides, and that heating of diconiferyl sulfide in kraft liquor gives rise to monomeric and oligomeric entities, and polymeric entities to the extent of about one third and two thirds respectively. It is probable, that the Peak D substances reflect the presence of hydrosulfides and sulfide derivatives.

It is notable that higher (>1000) molecular weight substances were formed to an almost negligible degree of a result of heating coniferyl alcohol in either soda or kraft liquors.

B. Effect of Treatment Conditions on Condensation of Coniferyl Alcohol and LMWL

The MWD profile of the isolated LMWL is shown in Figure 2A. In order to investigate semi-quantitatively the change in the MWD of LMWL brought about by heating with coniferyl alcohol under a variety of conditions, the MWD profiles were divided into the four

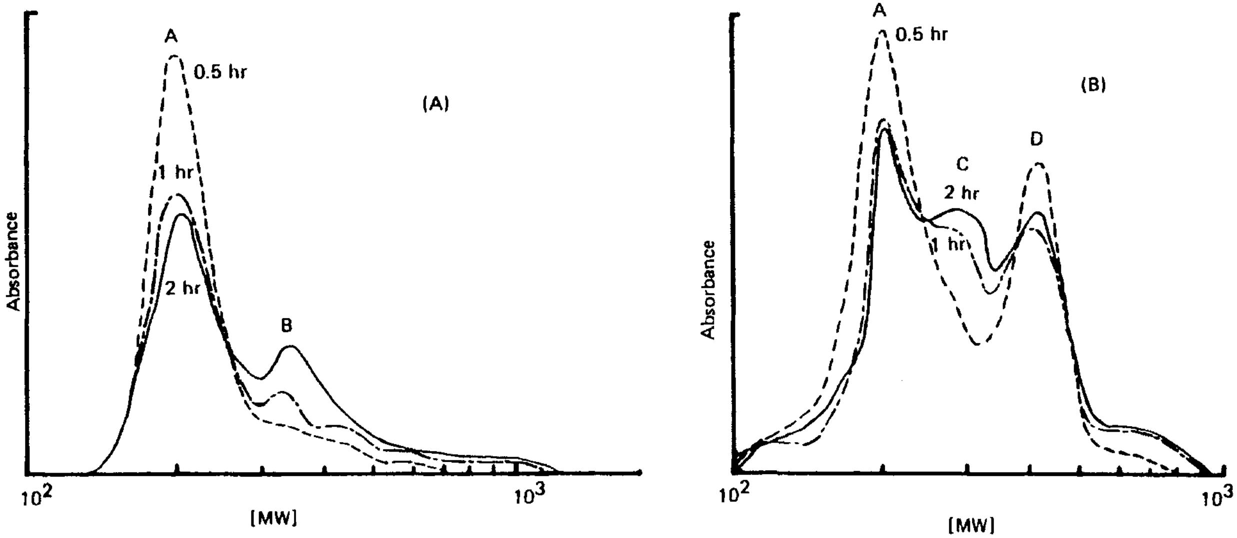

Figure 1. MWD profiles of coniferyl alcohol (CA) reaction products after heating: (1A) in soda liquor; or (1B) in kraft liquor.

regions, as shown in Figure 2A. The ranges of molecular weights associated with the substances observed in each region are approximately as follows: I (<400), II (400 - 600), III (600 - 1000) and IV (>1000). To indicate the degree which condensation reactions had proceeded, the area of each MWD region after reaction was compared with the area before the reaction, and the resultant ratios are shown in Table 1. The addition of coniferyl alcohol, and also the shifts in absorptivity of lignins which occur as a result of heating under alkaline conditions, bring about some changes in absorbance of radiation at 280 nm. These effects act to make the now reported results only qualitative in nature, but in future work it is hoped to clarify this issue by determination of the absorptivities of appropriate fractions.

The effects of temperature on the MWD profiles are shown in Figures 2B (100°C), 2C (140°C), and 2D (170°C). In Figure 3A, where changes in the relative area of each region are shown as functions of temperature, it can be seen the condensation of LMWL with coniferyl alcohol increases substantially when the treatment temperature is advanced from 100°C to 170°C, as evidenced by the important growth which occurs in the relative area of Region IV.

The effects of reaction time on the MWD profiles are shown in Figures 4A (0 - 30 min.) and 4B (30 - 120 min.). In Figure 3B it is seen that the relative area of the oligomer fractions (Regions II and III) increased slightly early in the treatment and then remained about constant up to 120 minutes. However, a major increase in the higher molecular weight polymers (Region IV) was observed after about 30 minutes reaction time, and thereafter this proportion decreased.

These results seem to indicate the progress initially of condensation reactions to yield higher molecular weight entities and, simultaneously or in any case thereafter, hydrolysis reactions to yield smaller molecules as we have previously suggested[14]. Also, it is of interest that the MWD profiles observed for the 60 and 120 minute experiments are nearly

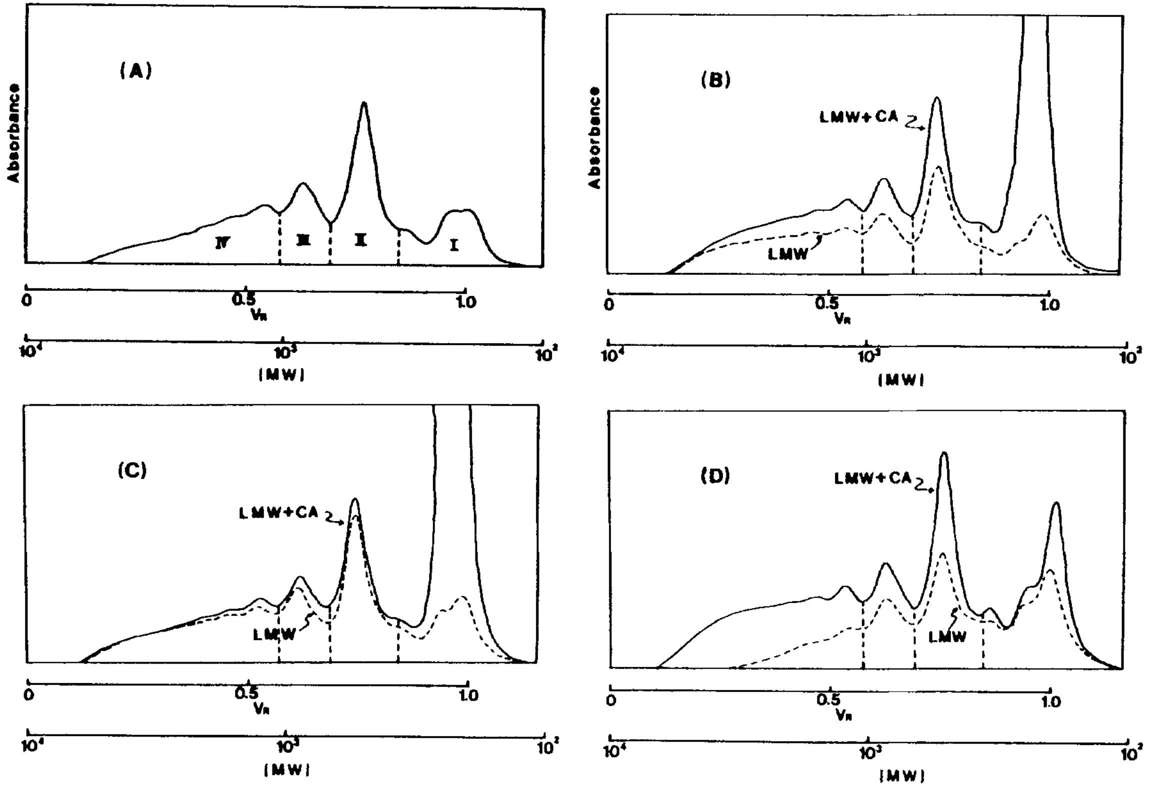

Figure 2. SEC and MWD profiles: (2A) of low molecular weight kraft lignin (LMWL); (2B) of LMWL +CA, after heating in soda liquor at 100°C for 30 min; (2C) of LMWL +CA, after heating in soda liquor at 140°C for 30 min; and (2D) of LMWL +CA, after heating in soda liquor at 170°C for 30 minutes.

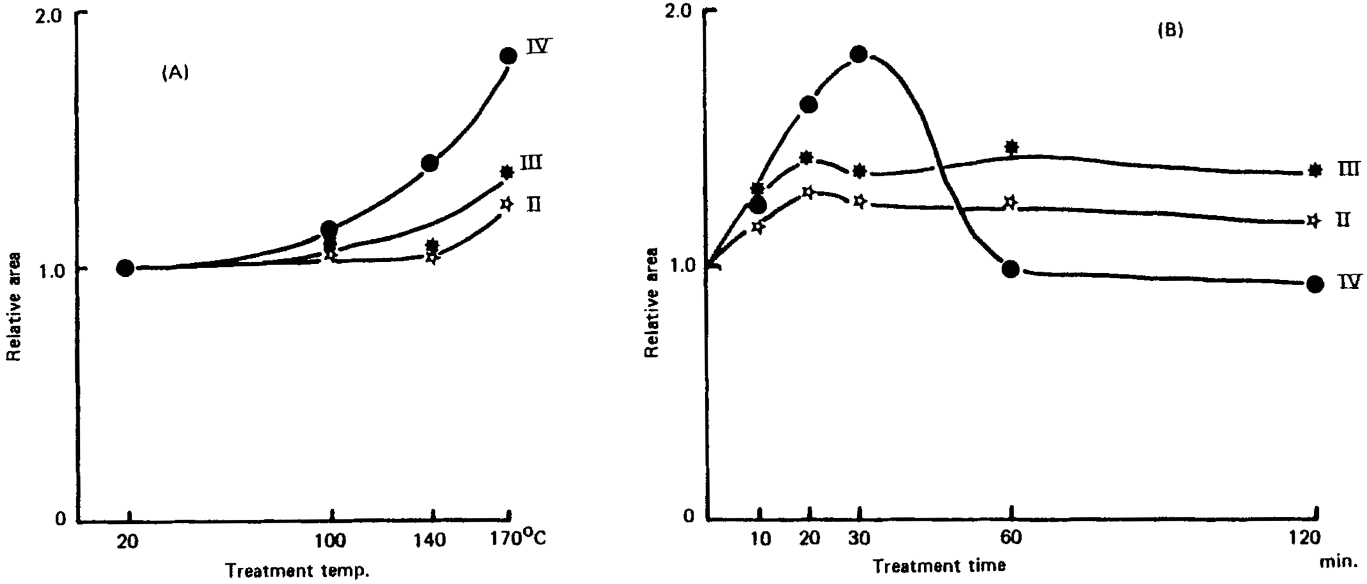

Figure 3. The effect on the condensation reactions of LMWL and CA in soda liquor: (3A) of heating temperature; and (3B) of heating time. Roman numerals refer to the data in Table 1.

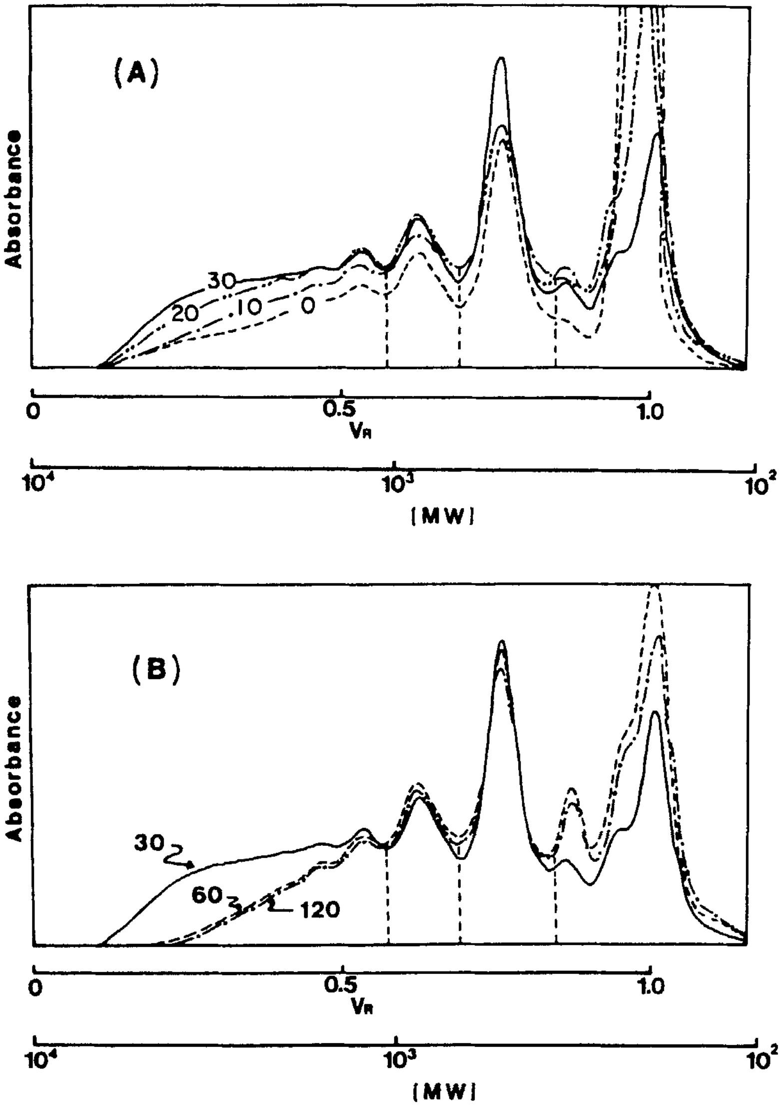

Figure 4. SEC and MWD profiles of LMWL + CA: (4A) after treatment with soda liquor at 170°C for 0, 10, 20 and 30 minutes; and (4B) after treatment for 30, 60 and 120 minutes.

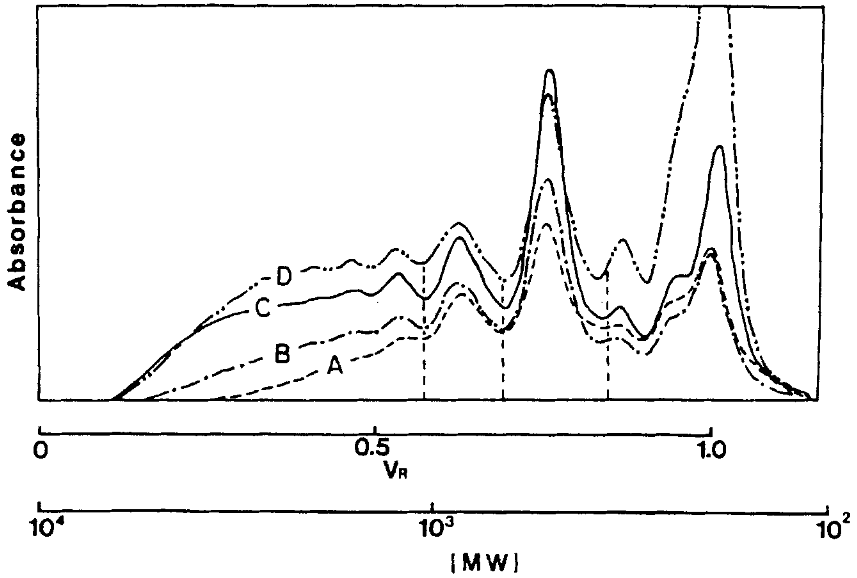

Figure 5. SEC and MWD profiles of LMWL + CA after heating in soda liquor at 170°C as a function of CA concentration. Curve A = 0; B = 1.1; C = 5.6; D = 11.2 mmol L^{-1}.

identical, apparently indicating that "omega"[14] lignins had come into existence, i.e., lignins in which no linkages remained which were hydrolyzable under the reaction conditions used.

The effects of coniferyl alcohol concentration on the MWD profiles are shown in Figure 5 and on the relative areas in Figure 6. While Regions II and III increased slightly with higher coniferyl alcohol concentration, Region IV grew dramatically when the coniferyl alcohol concentration was elevated progressively up to 11 mmol L^{-1}. Thus, an increase in coniferyl alcohol concentration seems to advance the condensation of LMWL and to increase the proportion of higher molecular weight reaction products.

C. The Effect of Solvent Systems

Mixtures of LMWL and coniferyl alcohol were heated at 170°C with soda, kraft and soda-AQ liquors, and the MWD profiles of the

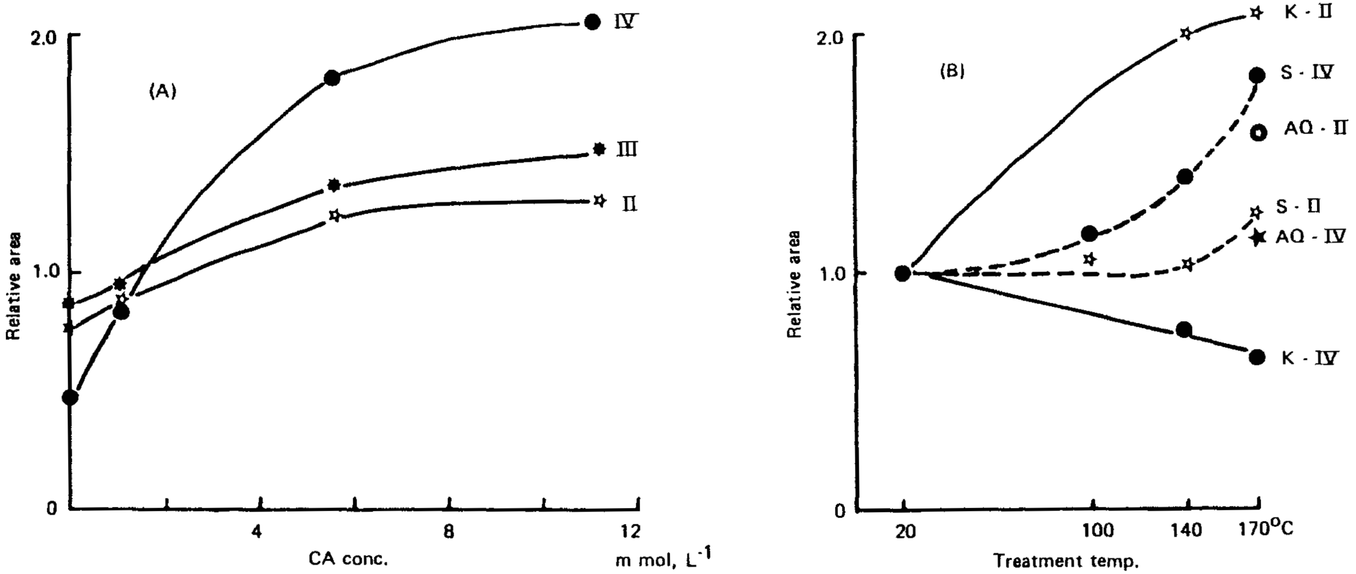

Figure 6. The effect: (6A) of CA concentration on the condensation of LMWL + CA in soda liquor; and (6B) of reaction environment on the condensation of LMWL and CA. S = soda, K = kraft, AQ = soda-AQ. Roman numeral refer to the data in Table 1.

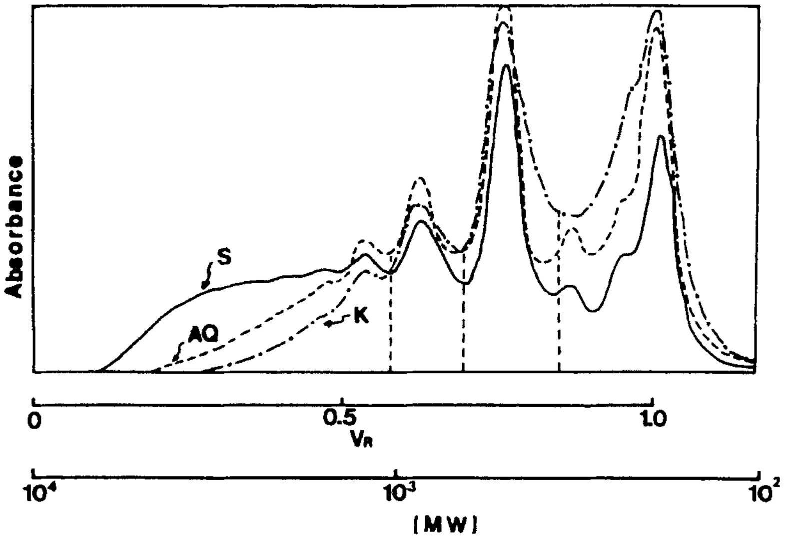

Figure 7. SEC and MWD profiles of LMWL + CA after heating in soda, kraft and soda-AQ liquors at 170°C for 30 min. S = soda; K = kraft; AQ = soda-AQ.

resultant reaction products are shown in Figures 7. In Figure 6B the relative areas are compared.

With the kraft solution, the determined MWD profiles were quite different from those obtained with the soda solution in that the former yielded a higher proportion of oligomers (Regions II and III) and a smaller proportion of the higher molecular weight fraction (Region IV) as indicated in Figure 7. The higher molecular weight fraction (Region IV) decreased as the temperature was increased, again suggesting the simultaneous progress of condensation and hydrolysis reactions.

The role of sulfide in hastening delignification is significant and it has been postulated that its functions are two. On one hand, sulfide may promote and accelerate the cleavage of ether linkages in phenolic units, and thereby advance the fragmentation of the lignin macromolecule into soluble entities. On the other hand, it may also reduce the extent of undesirable condensation reactions. The results shown in Figure 7 seem to provide evidence that the presence of the sulfide ion decreases the extent of condensation reactions in kraft pulping. With the soda-AQ liquor, the condensation of LMWL with coniferyl alcohol proceeded to a degree which was intermediate between the results obtained with the soda and the kraft treatments.

Further research is in progress with the objective of establishing quantitative relationships in relation to the condensation reaction of lignins.

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