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Lignin. 22. Macromolecular Characteristics of Alkali Lignin from Western Hemlock Wood[1a]

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ABSTRACT: Western hemlock wood platelets have been delignified with 1.0 N aqueous sodium hydroxide solution in a flow-through reactor. The extent of lignin removal was monitored by determination of the masses of residual lignin in the woody tissue (gel phase) and lignin fragments in the solution (sol phase). Increments of the reactor effluent were acidified to pH 2 to yield a series of acid-insoluble (AIL) and acid-soluble lignin (ASL) fractions. For the AIL, $\bar{M}_n$ and $\bar{M}_w$ values were obtained by vapor pressure osmometry and low-angle laser light scattering, respectively. For the ASL, the two molecular weight averages were estimated by size exclusion chromatography. Cumulative values of $\bar{M}_n$ and $\bar{M}_w$ for the sol-phase lignin were calculated and are interpreted in terms of previously proposed gel–sol transition concepts. The cross-links are found to be effectively tetrafunctional, and the cross-linking density appears to be about 0.07.

Introduction

The insolubility of native lignin gave rise to suggestions many years ago, for example, by Felicetta et al.[2] and by others,[3] that lignins exist in wood as branched-chain polymer gels which can be made soluble, and delignification can be accomplished, only by hydrolysis or chemical cleavage of certain linkages within the polymer.

On the basis of application of the theory of Flory[4] and Stockmayer[5] (F–S theory), quantitative treatment of the depolymerization process was first approached by Szabo and Goring,[6] who visualized a trifunctional polymerization proceeding in reverse to degrade a three-dimensional polymer gel. Gardner[7] and K. V. Sarkanen studied the dissolution of a model network polymer ("Sephadex", a cross-linked dextran, supplied by Pharmacia of Sweden) by chemical degradation and found experimentally, different from the behavior of lignin and in accord with F–S expectations, that the rate accelerated as total dissolution was approached. Bolker and Brenner[8] modified the Szabo–Goring model by introducing the concept of cross-linked "primary chains" of uniform length. Thereafter Yan and Johnson[9,10] assigned a "most probable" size distribution to the primary chains and applied an extended version of the Stockmayer distribution.[11,12] Glasser and Barnett,[13] Gierer and Wannstrom,[14] and others have called attention to the probable influence of lignin–hemicellulose and lignin–cellulose chemical bonds on the delignification process.

Pla[15] measured the molecular weight distribution (MWD) of dioxane lignin and discussed his results in relation to the results of Bolker and Brenner[8] and Bolker et al.[16]

As an alternative to these degelation concepts, another theory emphasizes physical effects.[17,18] It is proposed that there is a relationship between pore size and the molecular weight of degraded lignin whereby the pores exert a sieving effect with the result that smaller lignin molecules diffuse early through the smaller pores, and large molecules dissolve only after the pores have been appropriately increased in size. This mechanism may significantly influence delignification, but it is difficult to quantify, as has been discussed in some detail by Yan.[19]

At present we find it preferable to work with the degelation concept based on the F–S theory, which is a chemical model and considers only the existence or nonexistence of chemical bonds or linkages. In later studies it may become possible to add appropriate treatments to cope with some of the important chemical, geometric, and physical factors that must now be neglected, e.g., the possible linkages between lignins and some carbohydrates.

Several attempts have been made recently to characterize the polymeric structural changes of lignins during the course of delignification and degradation. These include the successive extraction of wood meal with dioxane–HCl[20] and the macromolecular characterization of the extracted lignin fractions,[21] the incremental delignification with NaOH and kraft liquors with examination of probable condensation phenomena during pulping,[22,23] and a theoretical interpretation based on the gel–sol transition with discussion of the effects of branching in lignin macromolecules.[24,25]

We now briefly summarize the structural concepts to be used in the present work. In softwoods, it appears that the predominant guaiacyl structural units are linked mostly in a head-to-tail fashion to form "primary" chains, i.e., with a glyceryl side chain as the "head" in a structural unit and a phenolic hydroxyl grouping as the "tail". Thus the β-O-4 bond, which is the most abundant linkage in lignins, is such a head-to-tail bonding. In addition, each unit appears to have certain functional groups by which branching and cross-linking are possible. For example, both the α and 5 positions of a structural unit may be reactive and form cross-links. Thus, lignins and/or lignin–carbohydrate assemblies seem to exist in wood as three-dimensional polymers or gels that are insoluble in

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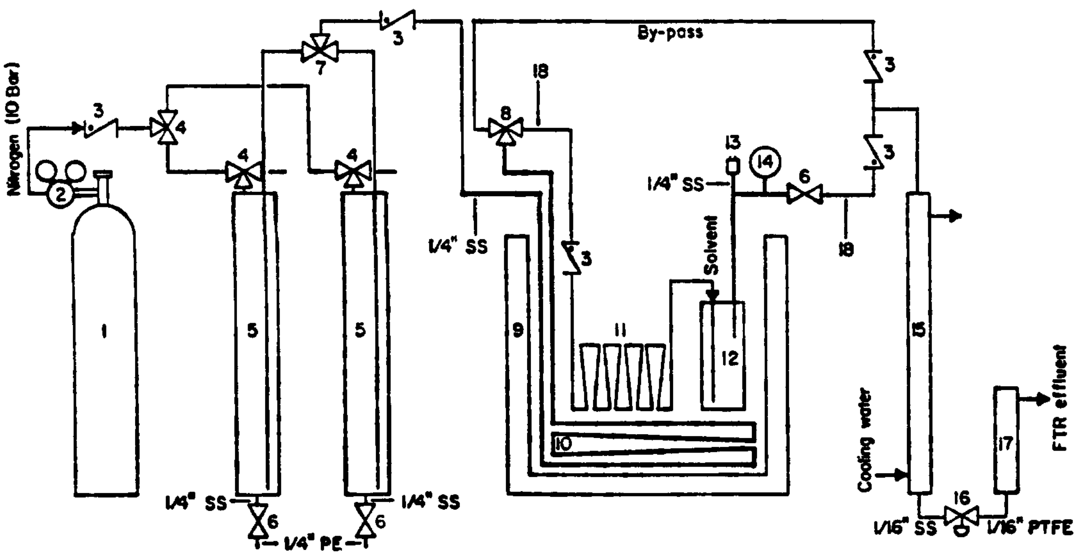

Figure 1. (1) Nitrogen tank; (2) pressure regulator; (3) check valve (Nupro SS-2C-10); (4) 3-way ball valve (Whitey SS-41XS2); (5) solvent tank (94 cm long SS cylinder, o.d. 6 cm); (6) bellows valve (Nupro SS-4H); (7) selector valve (5-way ball valve, Whitey SS-43ZF2); (8) 3-way trunnion ball valve (Whitey SS-83XTF2); (9) constant temperature bath, bath oil, glycerol, controller, Braun 1480 E; (10) primary heating coil for solvent; (11) secondary heating coil for solvent; (12) flow-through reactor (the 150-mL FTR); (13) thermocouple; (14) pressure gauge; (15) heat exchanger (o.d. of jacketing tube, $^1/_2$ in., length, 60 cm); (16) metering valve (Nupro SS-2SG); (17) variable area flow meter (Cole-Parmer Cat. No. GR-3219-19); (18) disconnection point; tubing Type 316 SS, unless indicated otherwise, o.d. $^1/_8$ in; PE = polyethylene; SS = stainless steel; PTFE = poly(tetrafluoroethylene).

any solvent, although the gels, as a result of cleavage of chemical bonds, may be degraded to yield soluble entities or a sol phase. Mathematical derivations for the lignin gel–sol transition and associated kinetics have been discussed for both batch[19,26] and continuous flow-through procedures.[24]

This work was conducted to provide additional information concerning the nature of the polymeric structure of lignins. To try to eliminate complications possibly caused by lignin condensation and other side reactions, delignifications were carried out in a flow-through reactor (FTR), which has been preliminarily described elsewhere.[27] Western hemlock (*Tsuga heterophylla*) wood has been delignified by use of an aqueous sodium hydroxide solution, and the resultant dissolved lignins have been characterized. In a subsequent paper, similar investigations of the delignification of a hardwood (black cottonwood, *Populus trichocarpa*) with both aqueous sodium hydroxide and acidic Organsolv solutions will be reported.

Experimental Methods

Preparation of Wood Platelets. A 7-cm-thick disk of air-dried western hemlock wood was cut tangentially into 1–2-cm-thick blocks. As preparation for further cutting, the blocks (sapwood) were soaked in an ethanol–water (1/1, v/v) solution under vacuum for 2 days. This soaking softened the wood, and thereafter, by use of a microtome, the blocks were easily cut into thin platelets of uniform thickness (0.4 mm). These cuts were perpendicular relative to the planes of the prior tangential cuts. Before the platelets were used in the delignification experiments, they were extracted exhaustively with a mixture of ethanol and benzene (1/2, v/v) in order to remove nonlignin extractives.

Flow-Through Reactor (FTR) and Delignification Procedure. The overall FTR system is shown in Figure 1. Reactor A (Figure 2) is a commercially manufactured 150-mL PTFE-lined laboratory autoclave (Berghof/America, Inc., Catalog no. 7150). Inlet and outlet ports were added to permit its use as a flow-through unit.

Prior to delignification, a glycerine bath was heated to the desired temperature, the solvent tanks were filled, and the reactor vessel and liner were preheated in a hot-air oven to about 150 °C. Before the reactor was connected to the system, a flow of solvent was started through the bypass line and cooling water was flowed through the condenser–cooler.

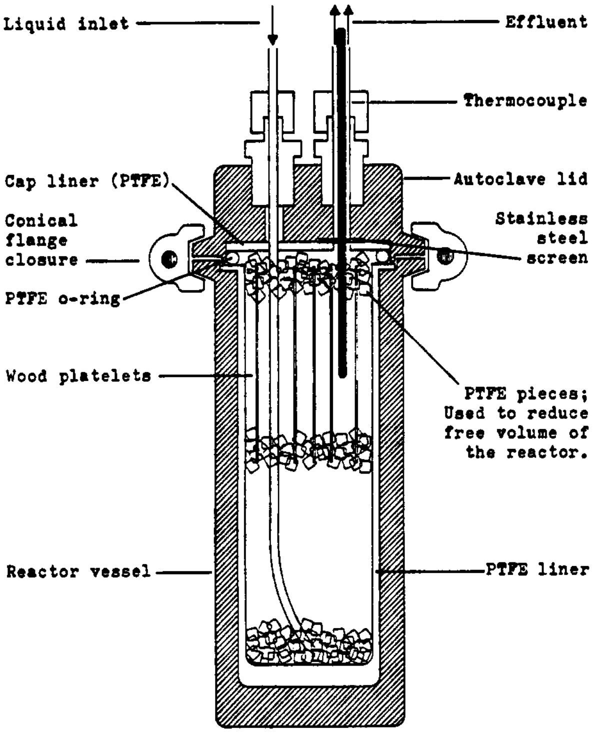

Figure 2. Flow-through reactor A.

In a delignification experiment that was conducted to provide acid-insoluble lignin samples sufficiently large for molecular weight studies, the hot reactor was taken from the oven and filled quickly with extracted air-dried wood platelets (14.490 g, oven-dry basis, lignin content = 28.53% of 4.136 g). The reactor was closed and pressurized (10 bar) with compressed nitrogen. When a steady pressure indicated no leaks, the thermocouple was connected to a temperature recorder and the reactor was placed in the bath and connected to the flow system. The delignification run was started by opening valve 6 at the reactor's outlet and switching valve 8 so that the solvent was directed into the reactor. Flow rate (F) averaged 30 mL min^{-1}. The run was terminated by closing the reactor outlet valve 6, switching the solvent to bypass, quickly disconnecting the reactor, lifting it from the bath, and immersing it in running cold water until the gauge pressure dropped to

Table I
Characteristics of Western Hemlock Lignin Sol Fractions[a]

	fraction									
parameter	1	2	3	4	5	6	7	8	9	10
time, min	10	20	39	59	85	100	115	149	175	420
m_i(AIL), g	0.408	0.318	0.539	0.488	0.491	0.229	0.187	0.278	0.117	0.236
m_i(ASL), g[b,c]	0.083	0.048	0.056	0.036	0.037	0.020	0.008	(0.019)	(0.007)	(0.018)
$\bar{M}_{n,i}$(AIL)	1150	1810	3160	2745	5050	4195	4950	5240	5630	7150
$\bar{M}_{w,i}$(AIL)	2660	5215	7860	12440	28475	32160	38500	41400	51350	66200
$\bar{M}_{w,i}/\bar{M}_{n,i}$	2.3	2.9	2.5	4.5	5.6	7.7	7.8	7.9	9.1	9.3
$A_2 \times 10^3$[d]	−3.0	−2.2	0	−4.1	0	0	−0.05	0	−0.2	−0.02
δ	0.18	0.16	0.090	0.060	0.040	0.040	0.020	0.012	0.010	0.010
dn/dc, cm^3 g^{-1}	0.26	0.26	0.24	0.19	0.21	0.23	0.20	0.21	0.19	0.24
$\bar{M}_{n,it}$	874	1236	1913	1956	2777	2360	3360	2929	3206	3220
$\bar{M}_{w,it}$	2316	4611	7177	11628	26515	29576	36924	38741	48602	61463

[a] Cellulosic residue: Kappa number = 8.12, lignin content = 1.17%, and residual lignin = 0.0685 g. [b] For all fractions $\bar{M}_n$ (ASL) = 400, $\bar{M}_w$ (ASL) = 630. [c] Values for fractions 8, 9, and 10 were estimated. [d] Units of A_2 are mol cm^3 g^{-2}. [e] $\bar{M}_{n,it}$ and $\bar{M}_{w,it}$ signify the mean molecular weight of each total fraction, i.e., AIL + ASL.

substantially zero (a few minutes). Free volume (V) of reactor A was about 105 mL, so that the mean residence time ($\bar{t}$) of the fluid was about

$$\bar{t} = V/F = 105/30 = 3.5 \text{ min} \tag{1}$$

Symbols are defined in Appendixes I and II.

Some delignification experiments were carried out by using small FTR-B, which provided a total volume of 5 mL. Reactor B was charged with 1.1 g of wood platelets, leaving a free volume of approximately 1.5 mL. Mean residence time of fluid in this reactor, at a flow rate of 19 mL min^{-1}, was about 5 s.

Determination of Lignin in Wood Residues and Pulps. In each experiment the residual cellulosic material recovered from the FTR was first suspended in water in a beaker and then disintegrated into small sticks or pulp, depending on the extent of delignification, by an electrically driven mixer (Braun Minipimer). The disintegrated material was transferred into a filter funnel (Millipore 47-mm filter holder; Whatman filter GF/C) in which it was washed with 0.01 N sodium hydroxide, warm tap water, and deionized water and thereafter was dried and weighed. The washing waters were added to the filtrates.

The lignin content of all delignified wood samples that did not disintegrate into pulp, as well as that of the hemlock wood, was determined by TAPPI Standard Method T222, including the acid-soluble lignin, which was evaluated by using TAPPI Useful Method 250. The lignin content of all pulp samples was determined by using TAPPI Useful Method 246 (Micro Kappa number) and our experimentally determined correlation between the Kappa number and lignin content for western hemlock: lignin percentage = 0.144 × (Kappa number).

The final cellulosic residue weighed 5.866 g (40.5% yield) and showed Kappa number = 8.12, which is reflective of the presence of 1.17% or 0.069 g of lignin. This corresponds to the fraction of delignification accomplished:

$$s = 1 - \left(\frac{\text{residual lignin}}{\text{original lignin}}\right) = 1 - \left(\frac{0.069}{4.136}\right) = 0.98 \tag{2}$$

Preparation of Acid-Insoluble (AIL) and Acid-Soluble (ASL) Lignin. The effluent from the FTR was collected as several successive fractions, and the AIL was precipitated by adding concentrated hydrochloric acid to establish pH 2. Each lignin suspension was centrifuged, and the precipitates were resuspended in 0.01 N hydrochloric acid and centrifuged again. This washing was repeated five times. Finally, each AIL sample was suspended in deionized water, transferred from a centrifuge bottle into a weighed plastic beaker, freeze-dried, and weighed (Table I).

To isolate ASL, the several acidic solutions from which the AIL fractions had been separated, including the solutions arising from two successive washings, were extracted with chloroform and the chloroform solutions were dried with anhydrous sodium sulfate. Chloroform was removed in a rotary vacuum evaporator, and the residual ASL was weighed (Table I). The last three out of the ten fractions recovered were not extracted because of difficulties associated with handling the large volumes of solutions which were very dilute with respect to ASL.

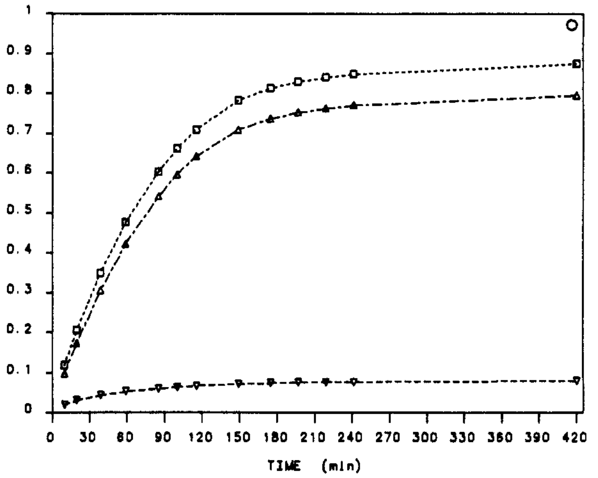

Figure 3. Mass fraction of lignin sol vs. delignification time: based upon ○ = lignin in final wood residue, S; for lignin recovered from solution, s, □ = AIL + ASL, △ = AIL, ▽ = ASL.

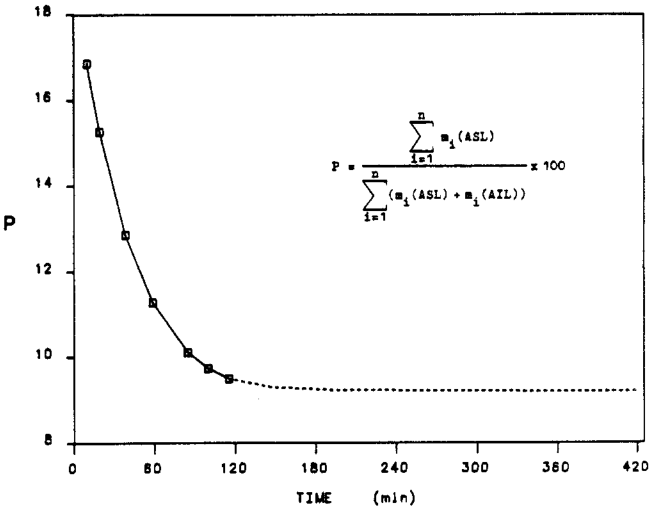

Figure 4. Mass percent of ASL, P, relative to total mass of lignin in individual effluent fractions vs. delignification time.

For each fraction, the total mass of the recovered lignins, AIL + ASL, was calculated. These values were summed progressively for the several collected fractions. Each sum was divided by the total lignin originally present in the wood, 4.136 g, to yield the cumulative mass fraction of dissolved lignin, s (Table II and Figure 3). The small amounts of ASL present in fractions 8–10 were estimated by extrapolating the cumulative percentages of ASL vs. AIL + ASL, found with earlier fractions, up to the delignification corresponding to fractions 8–10, as shown in Figure 4.

Table II
Characteristics of Alkali Lignin from Western Hemlock Wood

	time, min									
	10	20	39	59	85	100	115	149	175	420[a]
s^b	0.119	0.207	0.351	0.478	0.604	0.662	0.710	0.783	0.814	0.876
$\bar{M}_{n,j}'$	874	99	1243	1376	1553	1613	1663	1729	1751	1804
$\bar{M}_{w,j}'$	2318	3299	4890	6676	10893	12615	14209	16454	17616	20685
$\bar{x}_n'$	4.80	5.49	6.83	7.56	8.53	8.87	9.14	9.50	9.62	9.91
$\bar{x}_w'$	12.7	18.1	26.9	36.7	59.9	69.3	78.1	90.4	96.8	113.7
r'	2.65	3.30	3.93	4.85	7.02	7.82	8.54	9.52	10.06	11.47
p'	0.76	0.78	0.82	0.83	0.85	0.85	0.86	0.86	0.86	0.87
ρ'	0.060	0.072	0.065	0.068	0.070	0.070	0.069	0.068	0.068	0.068
α_f	0.161	0.205	0.230	0.253	0.281	0.287	0.292	0.296	0.299	0.303
$\bar{y}_w'$	7.4	8.2	10.2	11.0	12.1	12.5	12.9	13.4	13.5	13.8
$1/\bar{x}_w'$	0.079	0.055	0.037	0.027	0.017	0.014	0.013	0.011	0.010	0.009

[a] After 420-min reaction time, 0.983 weight fraction of the original lignin had been removed from the wood. [b] Cumulative weight fractions of recovered dissolved lignins, AIL + ASL, based on mass of lignin present in the original wood.

Table III
Composition of Two AIL Fractions

fraction	% C	% H	% O[a]	% OCH$_3$, %	unit[b] wt	calcd[c] C$_6$–C$_3$ units
6	64.76	5.86	29.38	13.15	183.2	$C_9H_{8.30}O_{2.56}(OCH_3)_{0.77}$
8	64.16	5.88	29.96	13.43	181.1	$C_9H_{8.39}O_{2.64}(OCH_3)_{0.79}$

[a] Calculated by difference. [b] Mean unit weight = $\bar{M}_0$ = 182. [c] Mean C$_6$–C$_3$ units = $C_9H_{8.35}O_{2.6}(OCH_3)_{0.78}$.

Characterization of AIL. The carbon, hydrogen, and methoxy contents of two arbitrarily selected AIL fractions (Table III) were determined by Galbraith Laboratories (Knoxville, TN). The number-average molecular weights, $\bar{M}_n$, were evaluated (Table I) by use of a vapor pressure osmometer (Knauer) and a previously described procedure.[15] The solvent was 2-methoxyethanol (methylcellosolve), and all measurements were made at 60 °C. Calibration of the measuring cells was carried out by using benzil (M = 210). The weight-average molecular weights, $\bar{M}_w$, and related parameters for the several AIL fractions were measured (Table I) by a light scattering procedure using a Chromatix Model KMX-6 instrument, as described in Appendix II.

The refractive index of the solvent was determined at λ = 632.8 nm and 20 ± 0.01 °C by using an Abbe refractometer. The refractive index gradient with concentration of solute in the 2-methoxyethanol solvent, dn/dc, was evaluated at 20 ± 0.01 °C and λ = 632.8 nm by using a Brice Phoenix BP 200 differential refractometer (Table I).

Characterization of Acid-Soluble Lignins. Eight small-scale delignification experiments were carried out by using FTR-B and for times varying from 5 to 360 min. In each experiment the total reactor effluent was collected as one sample. The alkaline solutions were acidified to pH 2, the precipitated AIL was filtered off, and the ASL was recovered by chloroform extraction, as described above. Each ASL sample was examined by size exclusion chromatography (SEC) using a Sephadex G-50 (superfine) gel (Pharmacia Fine Chemicals) with a 0.5 N sodium hydroxide solvent. The column (diameter 2.65 cm, length 59.9 cm) was calibrated with known phenolic compounds and with previously described[28] kraft lignin standards to yield the equation log (M) = 4.47 - 2.25 K.

In another experiment, an ASL preparation was chromatographed and the eluted liquids were collected as six fractions. Values of molecular weight for the modes of each of these fractions were estimated by SEC (Figure 5).

Results and Discussion

To secure the lignins to be studied with respect to macromolecular characteristics, thin platelets of hemlock wood were delignified at 170 °C in a flow-through reactor (FTR) by use of an aqueous 1.0 N sodium hydroxide solution, and in a separate paper[29] we shall compare the results obtained with a FTR vs. a conventional batch reactor. The effluent was collected incrementally as a series of fractions. By acidifying each of these to pH 2, acid-insoluble lignins (AIL) were precipitated, separated, and prepared for study. By chloroform extraction of the acidified filtrate, acid-soluble lignins (ASL) were recovered.

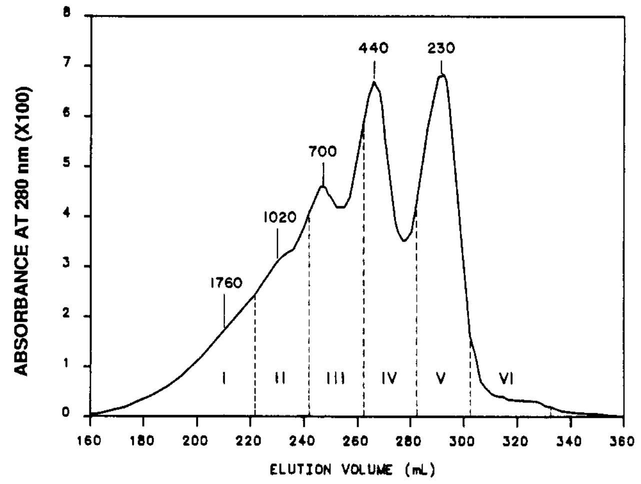

Figure 5. Typical size exclusion chromatogram for acid-soluble lignin (ASL). Fractions collected in preparative SEC runs are numbered I–VI. Mode molecular weights were estimated from the calibration curve; $\log_{10} M$ = 4.47–2.25 K.

Masses of the several ASL and AIL fractions are shown in Table I.

Cumulative mass fractions of the isolated AIL and ASL samples, s_i, were calculated relative to the Klason lignin contained in the original wood (Table II and Figure 3). The data indicate that ASL continues to come into solution throughout the entire delignification period. Although experimental difficulties prevented high-precision measurements, the estimated percentage of ASL recovered, relative to the total dissolved lignin, at first decreases and then comes to a nearly constant value of about 9% (Figure 4).

Table II and Figure 3 show that the final sum of the mass fractions of the AIL and the ASL recovered from the solution, s = 0.88, is significantly less than the final value of mass fraction of lignin removed from the wood, s = 0.98, as judged by determination of the lignin contents of the original wood and of the final delignified cellulosic residue. This departure is believed to be random and to arise as a result of losses of AIL in the washing procedures and of ASL by incomplete extractions.

Molecular Weights of Acid-Insoluble and Acid-Soluble Lignins. The number-average molecular weights,

$\bar{M}_{n,i}$, of the AIL fractions, as determined by vapor pressure osmometry, are relatively small (Table I) but show a steady increase as the delignification process advances. With $\bar{M}_{w,i}$, from low-angle laser light scattering measurements, a more striking increase occurs, and this gives rise to a significant increase in polydispersity of the lignin sol as delignification proceeds, as noted earlier.[20,21,24]

The second virial coefficients, A_2, differ for the several fractions studied, and some are negative or equal to zero (Table I). They are similar in magnitude to those reported by Plastre.[30]

Optical anisotropy, as represented by the parameter δ, tends to increase as the molecular weight decreases. The numerical values of δ show that $\bar{M}_{w,i}$ calculations, which do not take anisotropy into account, may give rise to large errors in estimates of molecular weight; i.e., uncorrected values in the present work are 20%-50% too high.

The dn/dc values found for the different fractions vary with $\bar{M}_w$. This variation is not regular and perhaps reflects some degree of heterogeneity in the fractions. The reported measurements have been repeated and are reproducible.

To permit conversion of molecular weight to degree of polymerization, the chemical composition of two AIL samples was determined (Table III). Results can be represented approximately by the formula $C_9H_{8.34}O_{2.6}(OCH_3)_{0.78}$, which corresponds to a mean weight of $\bar{M}_0 = 182$ for a C_9 structural unit. It is presumed that these characteristics apply to all of the ASL.

Size exclusion chromatography (SEC) of ASL provided a characteristic pattern (Figure 5) showing a number of peaks. The molecular weight values assigned to the modes of these peaks (230, 440, 700, and 1020) suggest the presence of compounds corresponding approximately to monomeric, dimeric, trimeric, and some larger fragments of lignin. Eight ASL samples, which were generated during the early, middle, and latter phases of delignification, were examined, and each was found to yield a SEC pattern almost identical with the one shown in Figure 5, a finding indicating that similar low molecular weight cleavage products continue to be formed throughout the process of delignification.

Preliminary experimentation indicated that the absorptivities at 280 nm of ASL fractions I-V were similar to each other and to those found for AIL. For the present purposes, it was assumed that the absorbance shown in Figure 5 is linearly related to mass.

On this basis and by using the pattern of Figure 5 with column calibration data, calculations were made to yield $\bar{M}_n \cong 400$ and $\bar{M}_w \cong 630$ for the total ASL material, and these values were assumed to be applicable for all times during the delignification period.

Characteristics of the Sol Lignin. To characterize the total mass in the individual fractions, the masses and molecular weight averages of both the AIL and ASL were used to calculate the mean molecular weights, $\bar{M}_{n,it}$ and $\bar{M}_{w,it}$, for each combined fraction (Table I).

For the sol fraction of the total lignin, which is constituted progressively by grouping individual sol samples, we have calculated the cumulative average molecular weights, $\bar{M}_{m,j}'$ and $\bar{M}_{w,j}'$ at the different stages of the delignification by use of the expressions

$$\bar{M}_{n,j}' = \sum_{i=1}^{j} w_i / \sum_{i=1}^{j} (w_i/\bar{M}_{n,it}) \tag{3}$$

and

$$\bar{M}_{w,j}' = \sum_{i=1}^{j} (w_i)(\bar{M}_{w,it}) / \sum_{i=1}^{j} w_i \tag{4}$$

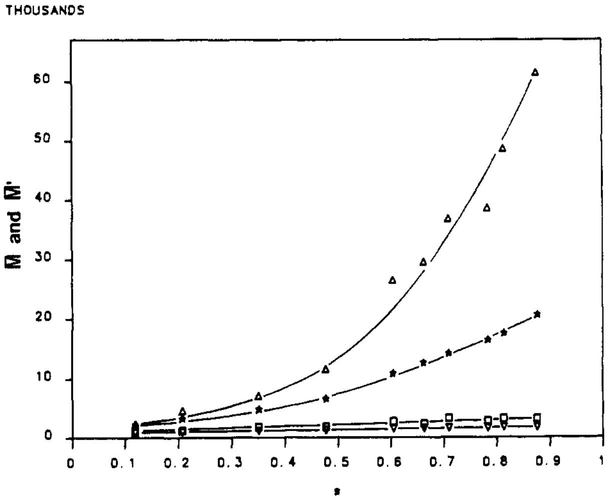

Figure 6. Molecular weight vs. mass fraction of lignin sol, s, for individual fractions, $\Delta = \bar{M}_w$, □ = $\bar{M}_n$, and cumulated fractions, $* = \bar{M}_w'$, $\nabla = \bar{M}_n'$.

and results are shown in Table II and Figure 6. Following Flory,[4] we have used a prime sign to emphasize the symbols signifying quantities for the sol phase.

From these data certain structural parameters were calculated (Table II) by use of the following relationships and of procedures described in prior papers:[22,23]

$$\bar{x}_w' = \bar{M}_{w,j}'/M_0 \tag{5}$$

$$\bar{x}_n' = \bar{M}_{n,j}'/M_0 \tag{6}$$

$$r' = \bar{x}_w'/\bar{x}_n' \tag{7}$$

Assuming the existence of Flory's "most probable distribution"[4] for the y-meric "primary" chains, the weight fractions are

$$w_y = y(1-p')^2(p')^{y-1} \tag{8}$$

and the weight- and number-average degrees of polymerization for the primary chains may be represented as

$$\bar{y}_n' = 1/(1-p') \tag{9}$$

$$\bar{y}_w' = (1+p')/(1-p') \tag{10}$$

Assuming also a most probable distribution for the cross-linked molecules,[5] we have

$$\bar{x}_n' = \frac{\bar{y}_n'}{1-\bar{y}_n'\rho'/2} \tag{11}$$

$$\bar{x}_w' = \frac{\bar{y}_w'(1+\rho')}{1-(\bar{y}_w'-1)\rho'} \tag{12}$$

$$\rho' = 2(1-p'-1/\bar{x}_n') \tag{13}$$

$$p' = \frac{\bar{x}_w'-\rho'-1}{\bar{x}_w'+1+(1+2\bar{x}_w')\rho'} \tag{14}$$

The expressions for $\bar{y}_n'$ and $\bar{y}_w'$ in eq 9 and 10 were substituted for $\bar{y}_n'$ and $\bar{y}_w'$ in eq 11 and 12, respectively, to yield eq 13 and 14 relating $\bar{x}_w'$ and $\bar{x}_n'$ to p' and ρ'. Experimentally found values of $\bar{x}_w'$ and $\bar{x}_n'$ for each fraction were then utilized with eq 13 and 14 to calculate p' and ρ' for each fraction (Table II). From each pair of these parameters, the branching coefficient was evaluated[5]

$$\alpha_f = \frac{p'\rho'}{1-p'(1-\rho')} \tag{15}$$

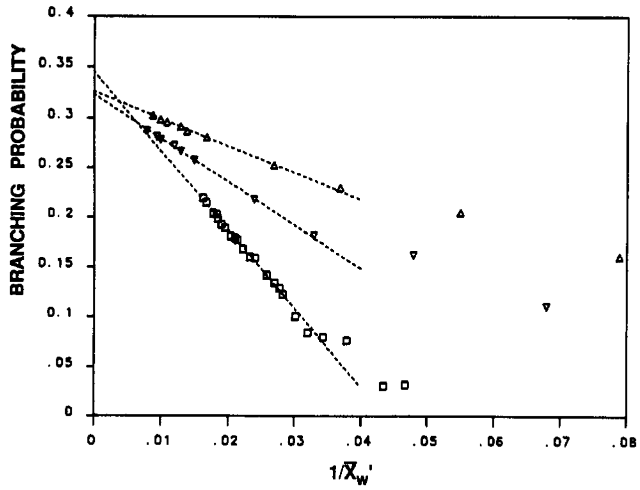

Figure 7. Chain branching probability, α, vs. reciprocal weight-average DP of primary chains: △ = AIL + ASL; ▽ = ASL; □ = acidic Organosolv spruce, (ref 25).

which is the probability that a chain issuing from a branching structural unit will end in another branching unit.

According to Flory,[4] α_f reaches a critical value, α_c, at the gel point

$$\alpha_c = (f - 1)^{-1} \tag{16}$$

and α_c can be reached from both the pregel and postgel directions. Thus the gel point is approached as the weight-average DP in the *pregel* stage in polymerization or else as the weight-average DP of the sol molecules in the *postgel* stage in depolymerization (assuming that depolymerization is the reverse of polymerization) approaches infinity, or as $1/\bar{x}_w' \rightarrow 0$.

Figure 7 shows that the relationship between α_f and $1/\bar{x}_w'$ is nearly linear and extrapolates to $\alpha_f = \alpha_c = 0.33$ at $1/\bar{x}_w = 0$. This value indicates that the functionality of the presumed pairs of cross-linked units in the lignin polymer is 4. The result is in accord with the findings of Pla and Yan[25] for the sol lignins arising from the acidic dioxane–water delignification of spruce wood. However, in that experiment only about 56% of the lignin in the original woody tissue was converted to the sol phase, and now we show that the same relationship applies when nearly all of the lignin has entered the sol phase.

Other calculated parameters are shown in Figure 8 as a function of sol phase fractions. Also included are values of the parameters calculated for the AIL fractions only and for the acidic Organosolv spruce lignin fractions described by Pla and Yan.[23] Notable is the major importance of the ASL contribution to the total AIL and ASL results. The spruce lignin parameters are significantly different from those found for hemlock, perhaps because only about 56% of the spruce lignin, vs. nearly all of the hemlock lignin, was investigated.

In general the results of this work seem to be in at least qualitative harmony with the sol molecular weight–degelation expectations of the F–S theory and to indicate that lignins in wood may be modeled as assemblies of linear "primary" polymer molecules which are tetrafunctionally cross-linked. This concept is useful in that its application permits the calculation of a number of parameters that may prove to be fundamental macromolecular characteristics of lignins. No other approach is known to us that offers similar opportunities. However, certain problems still remain, especially with delignification kinetics compared with the results of Gardner[7] and Sarkanen, and these will be discussed in a forthcoming paper along with the presentation of additional experimental results.

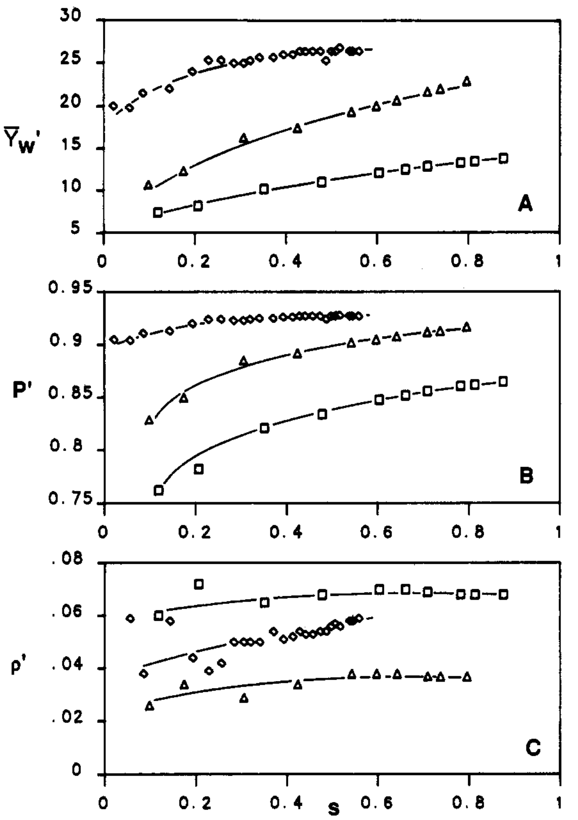

Figure 8. Macromolecular structural parameters for lignins vs. mass fraction in sol phase, s: (A) Yw' = weight-average MW of primary chains; (B) p' = extent of reaction of primary chains, C: ρ' = cross-linking density, where □ = AIL + ASL, △ = ASL for alkaline hemlock lignin, and ◇ = acidic Organosolv spruce lignin, (ref 15, 25).

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Appendix I: Symbols (See Also Appendix II)

Roman Letters

A_2	second virial coefficient
AIL	acid-insoluble lignin
ASL	acid-soluble lignin
c	concentration in g L^{-1}
dn/dc	refractive index increment
F	flow rate in mL/min
f	functionality of a branch point
FTR	flow-through reactor
g	gel fraction
$\bar{M}_{n,i}$	number-average molecular weight of the ith fraction
$\bar{M}_{n,j}'$	number-average molecular weight of the ith fraction and previous fractions
$\bar{M}_{w,i}$	weight-average molecular weight of the ith fraction
$\bar{M}_{w,j}'$	weight-average molecular weight of the ith and previous fractions
p'	extent of reaction of linear chains in the sol
r	polydispersity

s	sol fraction
t	time
$\bar{t}$	mean residence time in FTR
V	free volume in reactor
$w(y)$	weight distribution of linear y-mers = weight fraction of the y-mer
$\bar{x}_n'$	number-average DP of cross-linked molecules in the sol
$\bar{x}_w'$	weight-average DP of cross-linked molecules in the sol
y	DP of primary chains
$\bar{y}_n'$	number-average DP of primary chains in the sol
$\bar{y}_w'$	weight-average DP of primary chains in the sol

Greek Letters

α_c	critical value of α_f at gel point
α_f	branching probability defined by eq 15
ρ'	cross-linking density in the sol
δ	optical anisotropy

Appendix II: Light Scattering Procedures

The light source was a 2-mW, vertically polarized helium–neon laser beam at 632.8-nm wavelength. The instrument was equipped with a polarizer which was used to measure both horizontal and vertical components of the scattered light and thus to evaluate the optical anisotropy of the solute. At $\lambda = 632.8$ nm, the samples studied presented a nonnegligible degree of fluorescence. This emitted radiation was eliminated by use of an interference filter, centered on 632.8 nm with a passing band of 4 nm and located between the measuring cell and the detector. Taking into account the index of refraction of the solvent used and also the geometry of the system, the real angle at which the measurements were taken was about 4°.

The volume of the measuring cell was 150 μL, and the sample volume in the cell participating effectively in the scattering amounted to about 0.1 μL. The solvent used was 2-methoxyethanol, and the temperature was ambient. Solvent and solutions were dedusted by filtration through a Teflon Millipore membrane (pore size = 0.2 μm).

The magnitude of the incident intensity, necessary for the calculation of the Rayleigh ratio, was deduced directly from measurement of the transmitted intensity obtained after passing the beam through the measuring cell. The Rayleigh ratio was calculated from the expression

$$R(\theta) = (G(\theta)/G(0))D(\sigma l)^{-1} \qquad \text{(A-1)}$$

where $R(\theta)$ is the Rayleigh ratio, which depends on the angle θ, $G(\theta)$ is the scattered intensity, $G(0)$ is the transmitted intensity, D is the attenuation factor used for the measure of $G(0)$, σ is the solid angle corresponding to the point of measurement of the scattered light, and l is the length of path of the incident beam through the scattering fluid.

The lignin molecules presented optical anisotropy and caused depolarization of the incident beam. We measured, in each experiment and for different concentrations, the two components of the scattered light, vertical (V) and horizontal (H). The corresponding Rayleigh ratios are expressed for the case of small angles[30,31]

$$\Delta R_V(\theta) = KC\bar{M}_w(1 - 2A_2\bar{M}_wC + 4\delta) \qquad \text{(A-2)}$$

$$\Delta R_H(\theta) = KC\bar{M}_w(3\delta) \qquad \text{(A-3)}$$

where θ is the angle between the incident beam and the direction of observation and K is a constant term equal, for incident polarized light, to

$$K = \frac{4\pi^2 n_0^2}{\lambda_0^4 N_{Av}}\left(\frac{dn}{dc}\right)^2 \quad \text{as } \theta \to 0 \qquad \text{(A-4)}$$

and where n_0 is the index of refraction of the solvent, λ_0 is the wavelength of light in vacuum, N_{Av} is Avogadro's number, and dn/dc is the gradient of the index of refraction of the lignin in solution with respect to concentration in the solvent used.

The effect of the optical anisotropy on $\Delta R_V(\theta)$ was eliminated by considering the expression

$$\Delta R(\theta) = \Delta R_V(\theta) - (4/3)\Delta R_H(\theta) \qquad \text{(A-5)}$$

or

$$\Delta R(\theta) = KC\bar{M}_w(1 - 2A_2\bar{M}_wC) \qquad \text{(A-6)}$$

which can be represented[32] as

$$\frac{KC}{\Delta R(\theta)} = \frac{1}{\bar{M}_w} + (2A_2)(C) \qquad \text{(A-7)}$$

Registry No. Alkali lignin, 8068-05-1.

References and Notes

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