Lignin. 23. Macromolecular Characteristics of Alkali Lignin and Organosolv Lignin from Black Cottonwood[1a]

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ABSTRACT: Cottonwood platelets have been delignified in a flow-through reactor with an aqueous 1.0 N NaOH solution and also an acidic Organosolv solution. New procedures were developed to provide for nearly complete recovery of the lignins present in the effluent (sol phase) solutions. Results of measurements of number- and weight-average molecular weights of sol fractions from both alkaline and acidic experiments appear to support the concept that lignins exist in wood as polymers with effectively tetrafunctional branching points, as was deduced previously for western hemlock alkali lignin. Compared with hemlock lignin, cottonwood lignin manifests longer primary chains and a lower cross-linking density. These differences may contribute to the greater ease of delignification of cottonwood vs. hemlock and perhaps all angiosperms vs. gymnosperms.

Introduction

In recently published papers we have further developed the concept that lignin in wood may be modeled as a cross-linked polymer gel and that the delignification process may be viewed as one of degelation.[2-6] Hydrolysis of chemical bonds in the lignin polymer is thought to give rise to lignin fragments that thereupon dissolve in the ambient solvent. In our experiments, these lignin fragments have been continuously removed from the zone of reaction by use of a flow-through reactor (FTR).[3]

Prior studies have included the FTR delignification of western hemlock[3] with a 1.0 N NaOH aqueous solution. The weight- and number-average molecular weights and other related parameters associated with dissolved lignin fractions were evaluated. Application of degelation theory[2-6] suggested that gymnosperm lignin in woody tissue consists of "primary" linear chains cross-linked in a tetrafunctional manner.

Hemlock and other softwood lignins, in native or dissolved state, can be thought of as being constructed of "primary" linear chains in which the "C_6–C_3" structural units are linked in part by hydrolyzable ether bonds. Softwood structural units also provide additional seemingly less reactive sites, probably located in the C-5 position and/or in the three carbon side chains, and these sites seem to be responsible for branching. When branching occurs, the involved structural units assume trifunctionality, and two trifunctional units may pair up to form, in effect, a tetrafunctional branch point or cross-link.[5]

However, in hardwoods and other angiosperm lignins, the C-5 position in some structural units that are of the syringyl type is blocked by the presence of an additional methoxyl group. Thus the presence of these syringyl units in hardwood lignins may be expected to have some effect on the branching characteristics of the lignins. We now describe experiments and the results obtained in a study of the macromolecular properties of a hardwood, black cottonwood.

Experimental Section

Preparation of Wood Platelets. Small blocks of black cottonwood (*Populus trichocarpa*) were swollen under vacuum for 48 h with an ethanol–water mixture (1/1 (v/v)), and then cut into platelets (65 × 21 × 0.4 mm) with the aid of a microtome. Secondary components of wood were removed by two successive Soxhlet extractions for 72 h each, one with deionized water to remove tannins and then another with an ethanol–benzene mixture (1/2 (v/v)) to remove resins, fats, and waxes. Between extractions, the platelets were washed with ethanol to eliminate residual water.

Alkaline Aqueous Delignifications and Lignin Preparations. Our 150-mL FTR system and the procedure for its use have already been described.[3] In small-scale experiments, wood platelets (2 g) were positioned with the long side vertical in the FTR by use of cylindrical pieces of Teflon (3.2 mm in diameter and length) surrounding the woody tissue. Treatments were carried out at the desired temperatures and times (Table I) with 1.0 N NaOH flowing at the steady rate of about 17.5 mL min^{-1}. The resultant solutions were cooled immediately after exiting from the reactor. After termination of the reaction, the liquid in the reactor was filtered off. The cellulosic residue was broken into fibers by use of an electrically driven mixer (Braun Minipimer). The pulps were exhaustively washed on a filter with deionized water. The wash waters were collected and combined with the reaction liquid. The cellulosic residue was dried in air at ambient temperature for about 48 h. The undissolved fraction of the original lignin that remained in the cellulosic residue was determined by use of already described[3] Klason lignin or kappa number procedures (Table I).

To secure lignin fractions in amounts sufficient for use in characterization studies, two FTR delignification runs (R-8 and R-15) were conducted under substantially identical conditions using about 15 g of the extracted wood platelets, i.e., 1.0 N NaOH flowing at about 17.7 mL min^{-1} with heating at 160 °C for 4 h. The yield of both pulps was found to be about 44% and the kappa number about 9. During each run, the effluent liquids were collected as 10 successive samples.

The lignins were recovered and purified by two methods. In method 1, the lignins were precipitated by addition of hydrochloric acid to each effluent fraction to provide pH 2. The suspensions were then centrifuged for 15 min at 10000 rpm. The precipitates were washed several times with 0.01 N hydrochloric acid solution (about pH 2) and centrifuged for 15 min at 10000 rpm until the supernatant solution was colorless. The last washing was carried out with deionized water. Samples were transferred from the centrifuge bottle into weighed plastic beakers, freeze-dried, and again weighed. The lignin powders obtained were found to be soluble in several organic solvents, i.e., dioxane, tetrahydrofuran, 2-methoxyethanol, dimethylformamide, and dimethyl sulfoxide.

In method 2, the lignin fractions were first precipitated by addition of HCl to provide pH 2. To preserve the acid-soluble lignin, the two-phase system was then directly freeze-dried, whereby the volatile HCl was removed. The freeze-dried residue was extracted with dry dioxane to accomplish elimination of ash and other dioxane-insoluble substances, and the dioxane solution of lignin was again freeze-dried and weighed (Table II). The lignin powders obtained were still soluble in all of the organic solvents mentioned above.

Acidic Organosolv Delignifications and Lignin Preparation. Platelets of the cottonwood were delignified in the 150-mL FTR generally following the procedures described above. Small-scale experiments were conducted with about 2 g of wood at temperatures of 150, 140, and at 130 °C. At 150 and 140 °C, the time of heating was varied. Conditions were chosen similar to those used in batch experimentation conducted by Tirtowidjojo[7] with K. V. Sarkanen and were as follows: solvent, methanol–water (70/30 (v/v)); catalyst, 0.01 M H_2SO_4; flow rate, 17 mL min^{-1}. The residual woody tissues were washed exhaustively on a filter

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Table I
Delignification of Cottonwood

time, min	yield,[a] %	K no.[b]	LFY,[c] %	lignin,[d] %	g[e]	s
0	100		76.7	23.3	1.00	
		Alkaline Aqueous Delignification[f]				
			170 °C			
31	50.1	26.8	47.9	2.2	0.094	0.906
45	49.7	19.7	48.1	1.6	0.069	0.931
60	43.2	8.53	42.6	0.6	0.026	0.974
80	42.7	6.25	42.3	0.44	0.019	0.981
94	38.2	6.20	37.8	0.40	0.017	0.983
150	38.6	3.64	38.4	0.20	0.009	0.991
			160 °C			
113	45.2	15.3	44.1	1.1	0.047	0.953
220	44.3	7.19	43.8	0.5	0.021	0.979
240	42.8	6.48	42.3	0.5	0.021	0.979
			150 °C			
90	53.7	47.5	49.5	4.2	0.180	0.820
		Acidic Organosolv Delignification[g]				
			150 °C			
30	58.1	61.0	52.2	5.8	0.249	0.753
45	55.0	17.2	53.4	1.6	0.063	0.937
60	50.0	13.6	48.9	1.1	0.047	0.953
90	49.3	9.9	48.5	0.8	0.034	0.966
120	47.7	6.3	47.2	0.5	0.021	0.979
240	45.1	3.1	44.9	0.2	0.009	0.991
			140 °C			
60	59.2	81.8	51.2	8.0	0.343	0.657
120	51.4	50.8	47.1	4.3	0.185	0.815
180	52.2	17.7	50.7	1.5	0.064	0.936
240	51.2	7.5	50.6	0.6	0.026	0.974
			130 °C			
180	59.3	84.2	51.1	8.2	0.352	0.648

[a] Oven-dry yield of carbohydrate residue is Y. [b] K no. = kappa number (0.165): K no. is the percentage of lignin remaining in the carbohydrate residue. [c] LFY = $[(1 - 0.165(\text{K no.}))/100]Y$ = lignin-free yield of carbohydrate residue. [d] Lignin remaining in residue as percentage of wood = LR = Y − LFY. [e] g is the fraction of the original lignin remaining in the carbohydrate residue = (LR)(23.3, where the Klason lignin content of the original wood was 23.3%. [f] FTR delignification of about 2 g of cottonwood conducted with 1.0 N NaOH aqueous solution with the flow at 17.5 mL min^{-1}. [g] FTR delignification of about 2 g of cottonwood conducted with an Organosolv solution (methanol–water 70/30 (v/v); 0.01 M H_2SO_4) with the flow at 17 mL min^{-1}.

Table II
Some Characteristics of Lignin Fractions

fraction	time, min	m_i, g	s	$\bar{M}_{n,i}$	$\bar{M}_{w,i}$[a]	A_2, mol cm^3 g^{-2}	δ	dn/dc, cm^3 g^{-1}	$\bar{M}_{w,i}/\bar{M}_{n,i}$
		Alkaline Aqueous Delignification (Run 15, Purification Method 2, Delignification at 160 °C)							
F-0	2.5	0.107	0.031						
F-1	7.7	0.235	0.100	2250[b]	4725[b]	0[b]	0.14[b]	0.187[b]	2.1[b]
F-2	13	0.324	0.195	3375	7760	0	0.12	0.192	2.3
F-3	21	0.274	0.275	3280	10280	$-1.2\ 10^{-3}$	0.10	0.184	3.1
F-4	30	0.301	0.363	3170	11430	$-2.1\ 10^{-3}$	0.11	0.188	3.6
F-5	40	0.394	0.478	3715	17575	$1.4\ 10^{-3}$	0.09	0.190	4.7
F-6	52	0.329	0.574	3540	24200	$1.3\ 10^{-3}$	0.10	0.192	6.8
F-7	70	0.234	0.642	5010	24050	$-0.6\ 10^{-3}$	0.11	0.195	4.8
F-8	95	0.479	0.782	4770	36200	$0.9\ 10^{-3}$	0.06	0.191	7.6
F-9	135	0.405	0.901	5900	43600	$1.7\ 10^{-3}$	0.04	0.189	7.4
F-10	240	0.213	0.963	6450	54900	$1.1\ 10^{-3}$	0.01	0.193	8.5
total		3.295							
		Acidic Organosolv Delignification (Run 29, Delignification at 150 °C)							
F-1**[c]	15	0.189	0.080	835	1500	$2.1\ 10^{-2}$	0.16	0.168	1.80
F-3	20	0.187	0.115	1420	2550	$1.5\ 10^{-2}$	0.15	0.159	1.80
F-4	25	0.209	0.180	2275	4005	$2.8\ 10^{-2}$	0.13	0.157	1.76
F-5	30	0.283	0.266	3065	6690	$0.97\ 10^{-2}$	0.13	0.156	2.18
F-6	35	0.279	0.352	5095	8880	$1.7\ 10^{-2}$	0.09	0.157	1.74
F-7	40	0.361	0.462	7660	13130	$2.9\ 10^{-2}$	0.10	0.158	1.71
F-8	50	0.452	0.601	4615	19330	$1.5\ 10^{-3}$	0.07	0.156	4.19
F-9	60	0.360	0.712	4180	29450	$1.1\ 10^{-3}$	0.04	0.157	7.05
F-10	70	0.192	0.771	9495	51470	$1.9\ 10^{-3}$	0.02	0.157	5.42
F-11	90	0.340	0.875	7985	59500	$1.8\ 10^{-3}$	0.02	0.159	7.45
F-12	120	0.088	0.905	8255	67790	$1.4\ 10^{-3}$	0.01	0.156	8.21
F-13	180	0.166	0.954	8350	69200	$2.3\ 10^{-3}$	0.01	0.157	8.29
F-14	252	0.059	0.972	7600	73680	$1.9\ 10^{-3}$	0.01	0.157	9.69
total		3.166							

[a] Solvent refractive index = n_0 = 1.400 at λ 632.8 nm. [b] Determinations were made for the mixtures of F-0 + F-1. [c] F-1** = F-1 + F-2.

Table III
Masses of Organosolv Lignin Fractions[a] from Run 29

fraction	lignin,[b] g			g'[c]
	WI	WS	total	
F-1	0.023	0.047	0.070	0.978
F-2	0.045	0.071	0.119	0.942
F-3	0.084	0.103	0.187	0.885
F-4	0.071	0.138	0.209	0.820
F-5	0.071	0.212	0.283	0.734
F-6	0.126	0.153	0.279	0.648
F-7	0.172	0.189	0.361	0.537
F-8	0.232	0.220	0.452	0.398
F-9	0.251	0.108	0.360	0.288
F-10	0.139	0.054	0.192	0.229
F-11	0.226	0.114	0.340	0.125
F-12	0.067	0.021	0.088	0.095
F-13	0.094	0.072	0.166	0.046
F-14	0.002	0.056	0.059	0.028
totals	1.608	1.559	3.166	1.00

[a] Fractions from run 29 delignification of cottonwood at 150 °C. [b] WI indicates water insoluble; WS indicated water soluble. [c] $g' = 1 - s$.

Table IV
Mass Balance for Preparative Experiments[a]

balances	run 26 (180 min)		run 29 (252 min)	
	total, g	lignin, g	total, g	lignin, g
input				
wood[b]	11.19	2.61	14.0	3.26
output				
pulp[c]	5.27	0.073	6.43	0.067
lignin (WI)[d]	1.50	1.50	1.61	1.61
lignin (WS)[d]	1.10	1.10	1.56	1.56
other	3.31		4.43	
totals	11.18	2.673	14.03	3.237
(output/input) × 100 = %	99.9	102.4	100.2	99.3

[a] All results are on an oven-dry basis. [b] Klason lignin content of wood is 23.3%. [c] For runs 26 and 29, kappa numbers on carbohydrate residues were 8.35 and 6.34, respectively. [d] WI indicates water insoluble, WS indicates water soluble.

with the methanol–water solution (free of catalyst), with acetone, and finally with deionized water and then freeze-dried, weighed (Table I), and analyzed.

Preparative experiments, runs 26 and 29 using about 15 g of wood, were carried out at 150 °C for 180 and 252 min, respectively. In run 29, the effluent liquid was collected as 14 separate increments. The lignin contents of the original wood and the cellulosic residues were determined by use of above-described Klason lignin and micro kappa number procedures. The solids extracted into solution in runs 26 and 29 were almost completely soluble at ambient temperature in the solvent mixture utilized.

After separation of the run 29 cellulosic residues by filtration, the filtrate was vacuum evaporated at 40 °C. When most methanol had been removed, an abundant light brown precipitate of water-insoluble lignin, L-1, was formed. This precipitate was separated from the solution, by centrifugation for 15 min at 10000 rpm, and then washed several times with deionized water until the acidity of the washings reached nearly that of the water. Between each washing, the precipitate was settled and recovered by centrifugation for 15 min at 10000 rpm. The final aqueous suspension was then freeze-dried.

The acidic solutions, together with the washings, contained a nonnegligible fraction of water-soluble lignin, L-2, and also soluble carbohydrates. The recovery and purification of L-2 was accomplished as follows: neutralization to pH 4.5 by addition of a filtered aqueous solution of Ba $(OH)_2$, elimination of barium sulfate by filtration, vacuum evaporation in part at 40 °C, and freeze-drying. The solid material obtained was extracted with dry acetone to dissolve the lignins and to leave behind a residue of impure carbohydrates that was separated by filtration. To recover L-2, the acetone was evaporated at ambient temperature under a stream of nitrogen and the solids were dried under vacuum in a dessicator. The masses determined for the L-1, L-2, and total dissolved lignins are shown in Table III. The impure acetone-insoluble carbohydrate residue was freeze-dried, washed with acetone, filtered, and again freeze-dried to yield a white water-soluble solid.

In run 26 the total effluent was purified as described above and is being used for further analyses. The water-soluble and water-insoluble lignins were then combined and characterized with respect to $\bar{M}_n$ and $\bar{M}_w$. In run 29, each pair of the several fractions was combined. Mass balances for runs 26 and 29 are shown in Table IV.

Fractions L-1 and L-2 were soluble in dioxane, 2-methoxyethanol, dimethylformamide, and dimethyl sulfoxide. L-2 was also soluble in acetone.

Analyses and Calculations. The carbon, hydrogen, and methoxyl contents of three alkali lignin fractions from run 15 (purification method 2) and of three Organosolv lignin fractions from run 29 were determined by quantitatively microanalysis in Galbraith Laboratories (Knoxville, TN), and oxygen was calculated by difference (Table V). The values of $\bar{M}_n$ and $\bar{M}_w$ were determined by use of previously described procedures[3] using a vapor pressure osmometer (VPO) and a low-angle laser light scattering (LALLS) apparatus, respectively. The calculation procedures used were the same as those previously described.[3]

Results and Discussion

Alkaline Aqueous Delignifications. Small-scale delignification experiments were conducted, and the temperature and time of reaction were varied. The extent of reaction was monitored by determining the yield of the cellulosic residue and its lignin content. From these results, along with the determined content of Klason lignin in the original wood (23.3%, oven-dry basis), values were calculated for lignin-free yields ("LFY") of carbohydrate materials and for the undissolved fractions of lignin, g. It is found (Table I, symbols have defined in an earlier paper[3]) that delignification at 170 °C is nearly complete in 90 min. The values of LFY as a function of residual lignin (Figure 1) indicate that the degree of selectivity of removal of lignin vs. carbohydrate components tends to decrease markedly as g falls below about 0.1.

Two larger scale delignification experiments, runs 8 and 15, were conducted under nearly the same experimental conditions and provided samples that were purified by use

Table V
Analytical Characteristics of Certain Cottonwood Lignin Fractions

fraction	% C	% H	% O[a]	% $-OCH_3$	unit wt[b]	calcd C_6–C_3 unit
			Alkali Lignin[c]			
F-1	56.79	6.02	37.19	13.91	210.1	$C_9H_{9.82}O_{3.94}(OCH_3)_{0.94}$
F-5	59.44	6.22	34.34	15.43	202.1	$C_9H_{9.55}O_{3.33}(OCH_3)_{1.01}$
F-10	58.85	6.17	34.98	13.14	200.8	$C_9H_{9.87}O_{3.54}(OCH_3)_{0.85}$
			Organosolv Lignin[d]			
F-1	61.37	6.15	32.48	21.24	203.09	$C_9H_{8.32}O_{2.73}(OCH_3)_{1.39}$
F-6	60.56	5.93	33.51	21.71	206.96	$C_9H_{7.93}O_{2.88}(OCH_3)_{1.45}$
F-10	59.98	5.99	34.00	23.05	211.53	$C_9H_{8.02}O_{2.92}(OCH_3)_{1.57}$

[a] Calculated by difference. [b] For alkali lignin $\bar{M}_0 = 205$; for Organosolv lignin $\bar{M}_0 = 207$. [c] Fractions from run 15 alkaline aqueous delignification using purification method 2. [d] Fractions from run 29 acidic organosolv delignification of cottonwood at 150 °C.

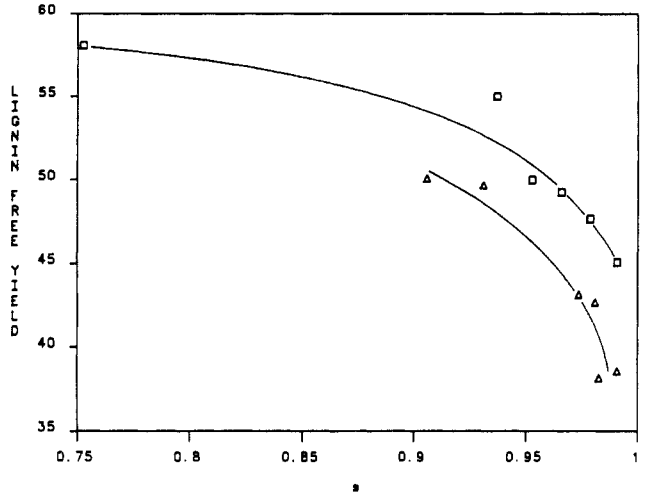

Figure 1. Lignin-free yield (LFY) vs. mass fraction of sol-phase lignin (s): (△) alkaline aqueous solution at 170 °C; (□) acidic Organosolv solution at 150 °C.

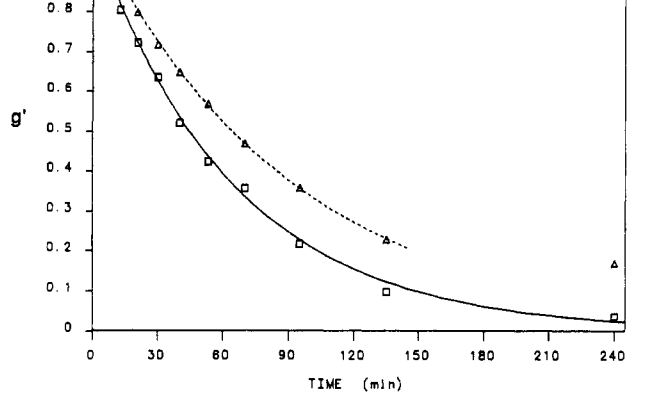

Figure 2. Mass fraction of lignin calculated as remaining in wood vs. time of delignification in alkaline aqueous solutions; purification methods: (△) 1; (□) 2.

of methods 1 and 2, respectively. From the cumulative measured weights of the lignins dissolved in the various periods of time and the weights of lignin present in the original woody tissue (Table II and Figure 2), the weight fractions of dissolved lignins, s, have been calculated (Table II).

From this data the apparent weight fractions of undissolved lignins, g', were calculated by use of the relationship, $g' = 1 - s$. Values of g' are plotted in Figure 2 vs. time. The trend of these curves agrees with results reported by numerous authors.[8-13] From these values it is evident that major amounts of dissolved lignins were not recovered by use of methods 1, whereas the dissolved lignins obtained by method 2 (Table II) represented nearly all of the lignin mass removed from the wood.

From early delignification results for samples from purification method 2, a pseudo-first-order process rate constant was calculated, $k_{R15} = 0.0155\ \text{min}^{-1}$, and this value suggests cleavage of β-O-4 ether bonds.[2,14]

Acidic Organosolv Delignifications. Small-scale delignifications provided data (Table I) that permitted the calculation of the lignin-free yield of carbohydrate residues, "LFY", and of the fraction of original lignin remaining in the solid or gel phase, g, after various conditions of reaction. Figure 1 shows, as already found for alkaline delignification, that when g is decreased below about 0.1, the

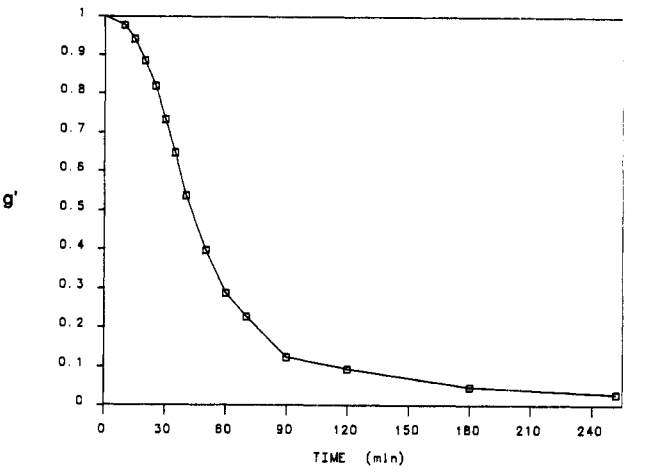

Figure 3. Mass fraction of lignin calculated as remaining in wood vs. time of delignification in acidic Organosolv solution at 150 °C.

selectivity of the solvent for removal of lignins vs. carbohydrates falls substantially, as is indicated by the rapid decrease in the LFY.

For the preparative experiments (runs 26 and 29), good mass balances were obtained (Table IV) and the delignifications were nearly complete. Of the dissolved lignins, the water-soluble proportions totaled about 42 and 49% for the experiments conducted for 180 and 252 min, respectively.

As delignification run 29 proceeded, the effluent from the FTR was collected incrementally to provide 14 samples (Table II) that were purified as described above. From the mass observed for each fraction, the total mass of lignin in solution after various reaction times was calculated. From these data, along with the mass of lignin originally present in the wood, the fractions of the original lignin remaining undissolved at different times, identified as g', were evaluated and are plotted vs. time in Figure 3.

One there observes at first a moderate rate of delignification, next an increased rate, and finally a somewhat slower rate again. This complex behavior is rather different from our earlier observations concerning the behavior of hemlock and cottonwood during delignification with an aqueous 1.0 N NaOH solution.

The shape of the curve in Figure 3 in the range $g' = 1.0$–0.5 follows the pattern called for by the Flory–Stockman (F–S) degelation vs. extent of cross-link cleavage.[15] This shape was also observed experimentally by Gardner[17] and K. V. Sarkanen in the dissolution vs. time of a cross-linked dextran gel ("Sephadex", Pharmacia, Uppsala), which was studied because they thought this gel to be possibly similar in macromolecular structure to lignin as it exists in woody tissue. However, in the lower range of g or g', Gardner and Sarkanen found that the remaining model gel quite rapidly went completely into solution, whereas in present experimentation the rate of decrease in g' becomes progressively less as time is increased and appears to approach asymptotically toward $g' = 0$. This difference perhaps comes about because all bonds between structural units in Sephadex are of the same type and hydrolyzable, whereas, in lignins, different types of hydrolyzable bonds seem to exist and the slow hydrolysis of some of these gives rise to the effects that we observe in the low range of g'.

These lignin results possibly manifest an experimental realization of a theoretical situation described in Figure 3 of a paper by Yan.[16] A description was there given of a kinetic scheme based on the concept that delignification proceeds as a result of two different but simultaneous

Table VI
$\bar{M}_n$[a] for Lignin Fractions at Several Temperatures

temp, °C	F-5	F-7	F-9	F-10	F-12
Alkaline Aqueous Delignification[b]					
25	3700	4980	5900	6420	
37	3745	5000	5930	6410	
45	3695	5030	5860	6400	
60	3715	5010	5900	6450	
Acidic Organosolv Delignification[c]					
25	3030	7650			8200
37	3045	7700			8150
45					8200
60	3065	7660			8255

[a] $\bar{M}_n$ values were determined by vapor pressure osmometry in 2-methoxyethanol. [b] Fractions from run 15 using purification method 2. [c] Fractions from run 29.

first-order processes, i.e., the breaking of cross-links and the cleavage of primary chains. More recently, this concept was extended[2] by considering that the primary chains are cleaved as a result of the breaking of three different types of chemical bonds, each with its characteristic reaction velocity constant. The cleavage of cross-links may proceed also as its own characteristic rate. Since these ideas have already been discussed at some length,[16] it seems sufficient now to point out that the shape of the present experimental curve (Figure 3) is qualitatively similar to that of the theoretical curve described in the referenced Yan paper and thus seems to give some support for the kinetic scheme. However, several other phenomena, which cannot at present be evaluated, may exert important influences on the kinetics of delignification, e.g., differences in cross-linking density of lignins in middle lamella vs. secondary wall, equality of access of reactants to bonds to be cleaved, proportion and location of noncleavable linkages, and transport phenomena.

At the beginning of the delignification about 65% of the dissolved lignin turns out to be water-soluble (Table III and Figure 4). As delignification progresses, the dissolving materials consist to an increasing degree of water-insoluble lignins, as is shown on a cumulative basis in Figure 4.

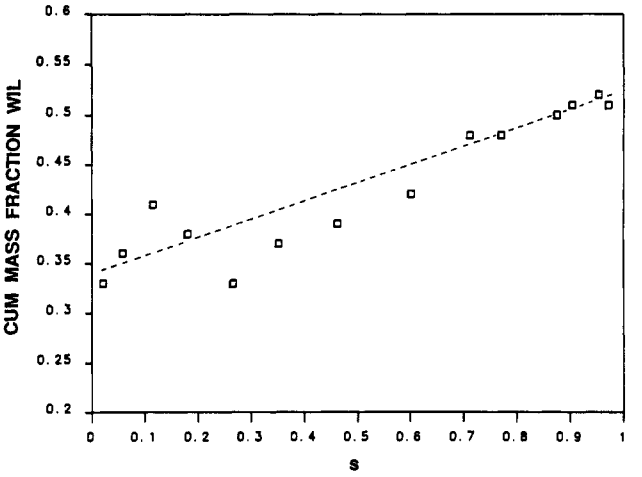

Figure 4. Cumulative mass fraction of water-insoluble Organosolv lignin (WIL) vs. mass fraction in sol phase.

Molecular Weights. The analytical characteristics of three samples each from alkaline run 15 (F-1, F-5, and F-10) and acidic run 29 (F-1, F-6, and F-10) were determined, and the results showed (Table V) that moderately good consistency prevails in the respectively compositions. The average molecular weights of the C_6–C_3 structural units of the alkaline and acidic preparations are estimated to be $\bar{M}_0$ = 205 and 207, respectively.

$\bar{M}_n$ values were determined for selected lignin fractions of each type at 25, 37, 45, and 60 °C (Table VI) and were found to be substantially independent of temperature. Thus association effects apparently were not significant under the experimental conditions used.

For the several samples of the two types of lignin, the molecular weights, $\bar{M}_n$ and $\bar{M}_w$, and related parameters were determined and are shown in Table II. The molecular weight values found for the individual and also the cumulated samples, which are plotted in Figure 5, show that, as s becomes greater, $\bar{M}_n$ increases slightly and $\bar{M}_w$ increases markedly. Thus an important increase in polydispersity occurs in the lignin sol as delignification pro-

Table VII
Sol Properties of Lignin Fractions

fraction	$\bar{M}'_{w,j}$	$\bar{M}'_{n,j}$	$\bar{M}'_{n,j}/\bar{M}'_{w,j}$	$\bar{x}_w'$	$1/\bar{x}_w'$	$\bar{x}_n'$	p'	ρ'	α_f	$\bar{y}_w'$
Alkaline Aqueous Delignification (Run 15)										
F-1*[a]	2250	4725	2.1	23.1	0.0433	11.0	0.906	0.006	0.055	20.3
F-2	2685	6200	2.3	30.3	0.0330	13.1	0.919	0.008	0.085	23.7
F-3	2835	7390	2.6	36.1	0.0277	13.9	0.921	0.014	0.137	24.3
F-4	2910	8370	2.9	40.9	0.0244	14.2	0.920	0.018	0.174	24.0
F-5	3070	10580	3.5	51.7	0.0193	15.0	0.921	0.024	0.220	24.3
F-6	3140	12860	4.1	62.9	0.0158	15.4	0.922	0.026	0.233	24.6
F-7	3270	14050	4.3	68.7	0.0146	16.0	0.925	0.025	0.237	25.7
F-8	3465	18020	5.2	88.1	0.0114	16.9	0.927	0.027	0.255	26.4
F-9	3665	21380	5.8	105	0.0095	17.9	0.931	0.025	0.257	28.0
F-10	3770	23540	6.2	115	0.0087	18.4	0.933	0.026	0.265	28.8
Acidic Organosolv Delignification (Run 29)										
F-1**[b]	835	1500	1.80	7.25	0.138	4.03	0.749	0.0059	0.0173	6.97
F-3	1050	2020	1.92	9.76	0.103	5.07	0.798	0.0102	0.0386	8.90
F-4	1300	2730	2.10	13.19	0.0758	6.28	0.833	0.0155	0.0716	10.98
F-5	1600	4020	2.51	19.42	0.0515	7.73	0.858	0.0254	0.1329	13.08
F-6	1920	5200	2.71	25.12	0.0398	9.28	0.880	0.0250	0.1546	15.67
F-7	2340	7100	3.03	34.30	0.0292	11.30	0.899	0.0240	0.1770	18.80
F-8	2640	9920	3.76	47.92	0.0209	12.75	0.907	0.0286	0.2187	20.50
F-9	2800	12950	4.62	62.56	0.0160	13.53	0.910	0.0319	0.2444	21.22
F-10	2960	15900	5.37	76.81	0.0130	14.30	0.913	0.0332	0.2598	21.99
F-11	3200	21100	6.59	101.93	0.0098	15.46	0.918	0.0337	0.2754	23.39
F-12	3260	22500	6.90	108.70	0.0092	15.75	0.920	0.0337	0.2785	24.00
F-13	3370	25000	7.42	120.77	0.0083	16.28	0.922	0.0335	0.2832	24.64
F-14	3405	25900	7.61	125.12	0.0080	16.45	0.9225	0.0335	0.2849	24.81

[a] F-1* = F-3 + F-1. [b] F-1** = F-1 + F-2.

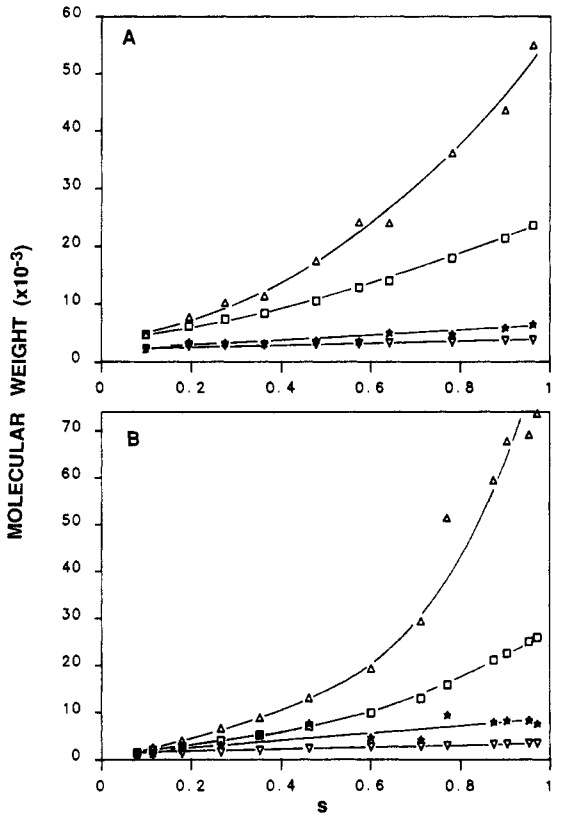

Figure 5. Average molecular weights of fractions vs. mass fraction in sol phase: (A) alkaline aqueous delignification; (B) acidic Organosolv delignification. Individual: (△) $\bar{M}_w$, (★) $\bar{M}_n$. Cumulated: (□) $\bar{M}_w'$, (▽) $\bar{M}_n'$.

ceeds, and this is the behavior expected for degradation of a cross-linked polymer gel.[15,18]

Values were obtained for the second virial coefficient, A_2, of the several fractions studied (Table II). These are quite different depending upon the fractions considered, and some are negative or zero. However, they are of the same order of magnitude as those found by Plastre.[18]

The optical anisotropy (Table II), as measured by the parameter δ tends to decrease as the molecular weight of the fractions increases. The numerical values of δ show that, if anisotropy is not accounted for, there results a significant error in the determination of molecular weights; i.e., values for molecular weights would be from 20% to 50% too high for the samples investigated. Within experimental error, the values of dn/dc found for the different fractions are in each case identical and amount to about 0.19 for alkali lignins and 0.16 for Organosolv lignin.

The results now obtained for cottonwood are similar to those previously observed for hemlock wood.

Structural Parameters of Lignins. The sol fraction of the lignin, s, is constituted progressively as the whole of the dissolved lignin. From the results shown in Table II and with the aid of the equations described previously,[2,3] we have calculated, for the sol lignins, the *cumulative* molecular weight averages, $\bar{M}'_{w,j}$ and $\bar{M}'_{n,j}$, the polydispersity indices, $\bar{M}_w'/\bar{M}_n'$, the weight- and number-average degrees of polymerization, $\bar{x}_w'$ and $\bar{x}_n'$, the extent of reaction of the primary chains, p', the cross-linking density, ρ', the chain branching probability, α_f, and the weight-average degree of polymerization of the presumed primary chains, $\bar{y}_w'$. Results are shown in Table VII.

According to Flory,[15] α_f reaches a critical value, α_c at the gel point, where $\alpha_c = (f-1)^{-1}$, where f is a functionality.

Thus the gel point and α_c are approached as $\bar{x}_w'$ approaches infinity or as $1/\bar{x}_w'$ approaches zero. In Figure 6, the calculated values for α_f are plotted against $1/\bar{x}_w'$. The curves are assumed to be linear at small values of $1/\bar{x}_w'$ and have been extrapolated to $1/\bar{x}_w' = 0$. The limiting values found are all about 0.33, similar to our previously reported value of 0.32 for hemlock wood lignin. These experimental results are in approximate agreement with the theoretical value of 0.33 expected[15] for a tetrafunctional branch-point system but substantially distant from the value of 0.50, which should be associated with a trifunctional branch-point assembly (Table VIII).

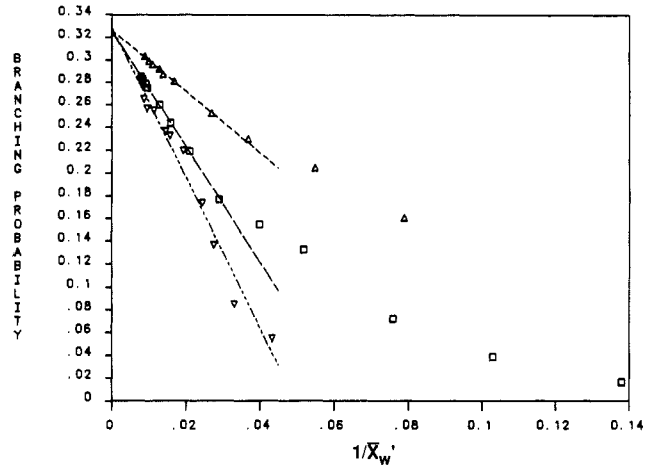

Figure 6. Branching probability vs. reciprocal of cumulative weight-average degree of polymerization of sol-phase lignins: (□) cottonwood–Organosolv; (▽) cottonwood–NaOH; (△) hemlock–NaOH.

Table VIII
Cross-Linking Density and Functionality in Different Lignins

species	solvent	s[a]	ρ'[b]	α_c[c] $f=3$[d]	α_c[c] $f=4$[d]	α_c[c] expt
hemlock[e]	H_2O–NaOH	0.92	0.07	0.5	0.33	0.32
spruce[f]	dioxane–HCl	0.56	0.05	0.5	0.33	0.35
cotton-wood	H_2O–NaOH	0.96	0.02	0.5	0.33	0.34
cotton-wood	MeOH–H_2O–H_2SO_4	0.97	0.03	0.5	0.33	0.33

[a] s is the degree of delignification. [b] ρ' is the cross-linking density in the sol. [c] α_c is the branching coefficient at gel point. [d] Theoretical values from $\alpha_c = (f-1)^{-1}$. [e] Reference 2. [f] Reference 4.

The values of certain other calculated parameters for the sol phase (Table VII are found to become greater with increasing time of reaction or extent of delignification, i.e., the weight-average degree of polymerization of the primary chains, $\bar{y}_w'$, (Figure 7A), the extent of reaction of primary chains, p' (Figure 7B), and the cross-linking density, ρ' (Figure 7C).

The increase in these several parameters with the increase in degree of delignification may arise as a result of differences in the characteristics of the lignins being dissolved. For example, Berry and Bolker[19] have presented evidence that the cross-linking density is about twice as high in middle lamella as in secondary-wall lignin. Since secondary-wall lignin is solubilized preferentially in the early stages of delignification, it is to be anticipated that, as experimentally observed, the cross-linking density of the dissolving lignins increases as delignification progresses.

Parameters are also shown in Figure 7 for our previously reported experiments[3] concerning the delignification of western hemlock wood with aqueous 1.0 N NaOH solutions. At a given sol fraction (or degree of delignification),

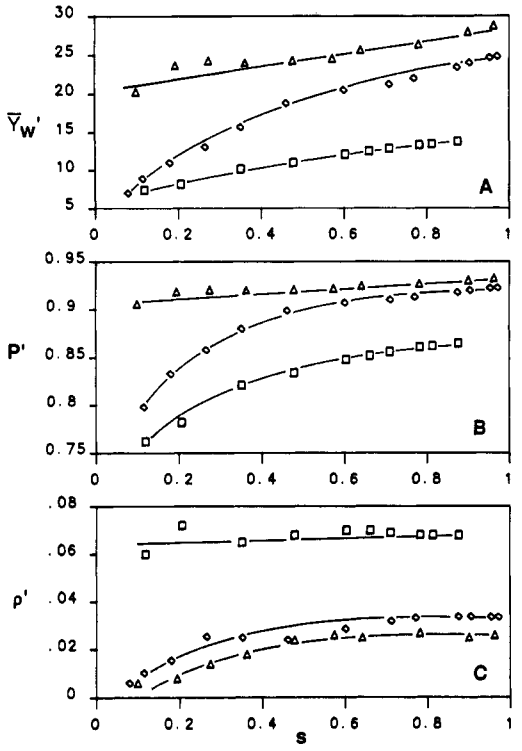

Figure 7. Macromolecular structure parameters for lignins vs. mass fraction in sol phase: (A) Y_w' = weight average of primary chain; (B) p' = extent of reaction; (C) ρ' = cross-linking density, where (△) cottonwood–NaOH; (◇) cottonwood–Organosolv; (□) hemlock–NaOH.

the cottonwood lignin seems to manifest longer primary chains and a lower cross-linking density than the lignins from hemlock[3] and spruce[2] woods.

The lower cross-linking density in cottonwood is compatible with the concept that the additional methoxyl groups in hardwood lignin units tend to reduce the chance of chain branching or cross-linking and to increase the chance of preserving the length of the primary chains during delignification. These differences may contribute significantly to the greater ease of lignification of cottonwood vs. hemlock and perhaps all angiosperms vs. gymnosperms.

The above-stated treatment of our experimental results by use of Flory–Stockmayer concepts must be viewed with caution because the primary assumption on which this elegant statistical theory is built is very probably not applicable to lignins. Thus Flory[15] assumes that "...all functional groups are chemically equivalent and hence equally reactive..." and "...independent of the size or structure of the molecule (or network) to which they are attached...", whereas delignification appears to proceed as a result of hydrolysis of perhaps three different types of bonds[2] out of the many described, for example, by Glasser.[20]

In spite of this difficulty, we conclude that lignins can be modeled in terms of cross-linked polymer gels which manifest tetrafunctional branch points. The model readily yields parameters that seem to provide plausible quantitative descriptions, perhaps characteristic of the differences among lignins derived from the several species of woods. No other model known to the writers provides this capability, which should prove useful pending the completion of additional experimentation and the development of improved formulations.

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Registry No. Alkali lignin, 8068-05-1; Organosolv lignin, 8068-03-9.

References and Notes

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