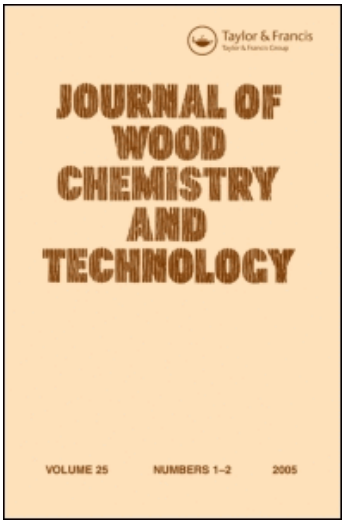

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CONDENSATION OF LIGNIN IN DIOXANE-WATER-HCl

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ABSTRACT

Black spruce sawdust, when treated batchwise, in accordance with the principles of the gel degradation theory, with dioxane: H_2O:HCl (90:8:1.8 by volume) at various extents of lignin solubilization, gave a series of lignin fractions. The undialyzed lignin preparations, characterized by Klason lignin, methoxy contents, microanalysis, and U.V. absorptivity, were found to be reasonably uniform in composition. Gel permeation chromatography with a combination of refractive index (RI) and Low Angle Laser Light Scattering (LALLS) detection gave fractions that qualitatively resembled those obtained by the degradation of synthetic model polymer gels. In efforts to quantitatively correlate molecular weights ($\bar{M}_w$) of these lignins with the existing gel degradation models, however, the problems of lignin fluorescence, association and recondensation were encountered. During the batchwise dioxane:H_2O:HCl extraction of wood, irreversible recondensation of the lignin fragments took place, limiting analysis of the results in the context of the gel degradation theory, revealing however, a salient feature of delignification.

INTRODUCTION

Earlier investigations on the mechanism of chemically liberating fibres from wood, have provided the motivation for funda-

mental studies of gelation and gel degradation[1]. Theoretical expressions essentially based on the Flory-Stockmayer statistics of gelation were experimentally examined for their applicability beyond the gel point. By studying crosslinking reactions in model polyester polymerizations beyond the gel point, the validity of the expressions was quantitatively confirmed, and their limitations were delineated. On stepwise degradation of such model networks, increasing soluble fractions were obtained at each step, and their weight-average molecular weights increased as the degelation point was approached. The molecular weights and distributions of these fractions were in close quantitative agreement with theory, i.e., they represented a near-mirror image of the molecular weights of sol fractions obtained on crosslinking beyond the gel point. Similar results were obtained by degrading a model network prepared by the random crosslinking of monodisperse primary chains of polystyrene, a network thought to be a closer analogy to lignin.

Experimental support has thus been obtained for treating random network degradation by reversing the statistics of the Flory-Stockmayer theory of gelation.

Among the most important features of any delignification experiment is probably the observation that the molecular weights of the solubilized products become progressively higher as delignification proceeds[2-7]. The pioneering work of Szabo and Goring[8] which was followed by Bolker and Brenner[9], and Bolker *et al.*[7], considers delignification as the reverse of network formation in the region beyond the gel point. The random degelation of a crosslinked network is thought to follow a path which is the reverse of its formation. In broad terms, the Szabo and Goring treatment envisages delignification as the reverse of polymerizing trifunctional monomers, while the Bolker and Brenner approach

is the reverse of forming a network by the random crosslinking of monodisperse pre-formed chains. The difference between the two treatments is that: (a) Szabo and Goring assume that all ether bonds in lignin are of comparable reactivity; while (b) Bolker and Brenner proposed that the primary sites of crosslinking were the benzyl ether groups, which are known to be the most reactive under acid conditions of all the ether linkages found in lignin.

Evidence for the network structure of protolignin comes from the viscosity, polydispersity, and molecular weight data of soluble lignins[2,10]. The random degradation of a crosslinked network is expected (according to the gel degradation theory) to yield polymeric fragments of spherical configuration whose molecular weights, yields, and polydispersity ratios will increase as bond fragmentation increases within the network. The network theory of protolignin finds progressively wider acceptability among researchers in the field as the experimental evidence pointing towards its validity grows. Although there is still a lack of agreement on the precise architecture of protolignin, major efforts towards solving this controversial issue are emerging from the application of the gel degradation theory and its modifications[11-15].

Our recent work which has experimentally examined the reversibility of gelation on synthetic model networks, has provided qualitative data and quantitative equations for the process[1]. This paper represents an attempt to correlate the knowledge gained from these model experiments with results obtained by the degradation of lignin. Dioxane-HCl delignification experiments, designed in accordance with the requirements of the gel degradation theory, were performed. The soluble lignins were characterized by microanalysis, methoxy content, U.V. absorptivity, and Klason lignin content. Their molecular weights and distributions

were evaluated by Gel Permeation Chromatography/Low Angle Laser Light Scattering, GPC/ LALLS. The process of delignification by acidolysis is thus qualitatively visualized.

RESULTS AND DISCUSSION

Analyses and Molecular Weight Measurements

Extraction with dioxane:H_2O:HCl by the method of Pepper was used for the delignification experiments[16,17]. Dioxane ensured sufficient swelling, thus satisfying the primary requirements of the gel degradation theory, i.e. uniform reagent accessibility and random bond cleavage. Another requirement of a gel degradation experiment is that it be done in a batchwise mode. Accordingly, the swollen black spruce wood sawdust was refluxed in the delignification medium, and the detached lignin was allowed to remain in solution for the duration of the experiment. The detached lignin fragments were thus given the opportunity for further cleavage after their original detachment. The experiment was then repeated with fresh wood and reagents for another (more extended) period of time. The procedure for purifying the lignin sols did not include any dialysis separation techniques such as those applied by [Rezanowich *et al.*[2]]. Dialysis was avoided because the purpose of this work was to examine the average molecular weights of these sols in the context of the gel degradation theory. Any exclusion of material from the measurements, therefore, would defeat the overall objectives.

Table 1 shows the analyses which chemically characterize the five samples of dioxane lignin which were isolated. The elemental analysis of these lignins closely agrees with that reported by Bolker *et al.*[7] for pure cuoxam lignin. The methoxy contents shown in Table 1 range around 15% for up to four hours delignifi-

Table 1

Analyses of Black Spruce Dioxane Lignins

Delignification time (h)	% C	% H	% O[a]	% CH_3O	U.V. absorption[b] coeff. (cm^{-1} L g^{-1})	Total lignin[c] content, %
0.5	61.61	5.80	31.6	15.05	19.6	-
2.0	62.90	5.90	31.2	15.04	21.0	93.6
3.0	63.51	5.63	30.8	15.06	22.0	95.1
4.0	63.36	5.62	31.0	14.94	23.2	93.7
6.0	63.78	5.74	30.4	14.31	23.6	93.6

(a) By difference
(b) At 280 nm
(c) The sum of Klason and acid soluble lignin
All results given are the averages of duplicate runs

cation time. This is in close agreement with the results that Pepper et al.[16] and Rezanowich et al.[2] obtained in isolating black spruce dioxane lignins. It is also quite comparable to the value obtained by Ekman and Lindberg[18] (14.98%) for pine dioxane lignin.

The ultraviolet absorption coefficients at 280 nm, measured in tetrahydrofuran, are in fair agreement with those for dioxane lignins purified by dialysis[2], and also agree in exhibiting an increasing trend with increasing degree of solubilization. If accepted as criteria for purity of the samples, the results in Table 1 may characterize them as reasonably pure.

These five dioxane lignins, when examined on a Gel Permeation Chromatograph equipped in series with a Refractive Index (RI) and a Low Angle Laser Light Scattering (LALLS) detector, gave the chromatograms of Figure 1. The dotted lines represent the LALLS responses while the solid lines represent the RI

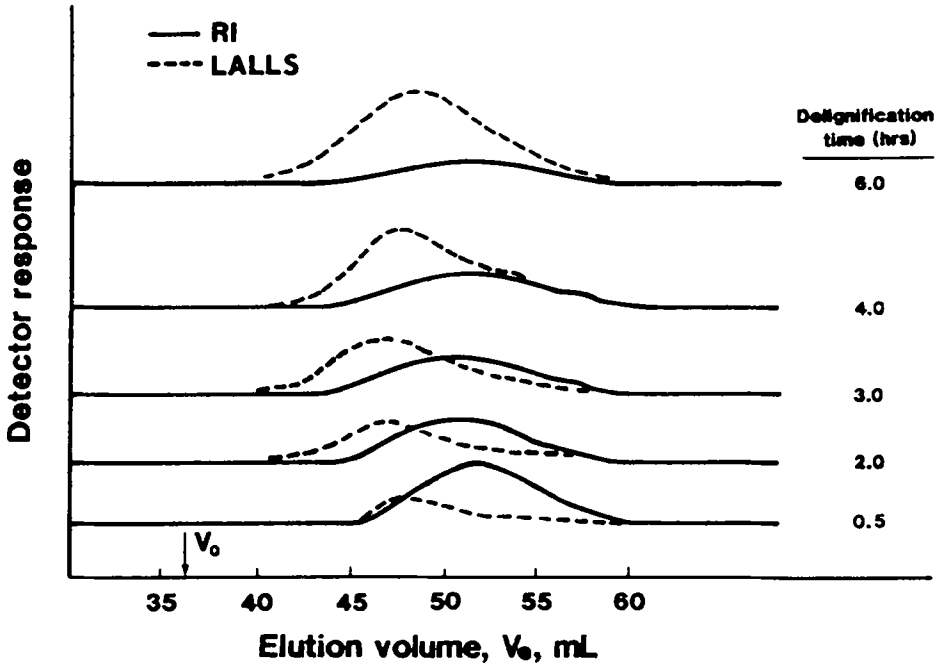

FIGURE 1. The GPC/LALLS outputs of the batchwise dioxane lignin preparations of Tables 1 and 2.

responses. Since the RI detector responds linearly to refractive index differences, its response is a function of concentration. The LALLS detector responds linearly to the scattering intensity, which is a function of concentration and molecular weight. The points of interest in this figure are:

(a) All RI responses are broad, becoming progressively broader as delignification time increases. Maximum broadness is shown in the sample isolated after six hours of delignification.

(b) The LALLS maximum response lies above the high molecular weight end of these distributions and becomes progressively more pronounced with increasing delignification time.

Further interpretation of the results in Figure 1 first requires a discussion of the recently discovered phenomenon of lignin fluorescence. On analyzing kraft lignin solutions by the same technique, Kolpak et al.[19] observed a bimodal response in the LALLS detector and a unimodal response in the RI detector. The second LALLS peak, representing the lower molecular weight material, was unexpected. Although the extinction coefficient of their sample was as low as 0.12 mL/mg.cm at the wavelength of the He/Ne laser used, they observed the disappearance of this second low molecular weight peak of the LALLS detector when an interference filter, which removed the effects of fluorescence, was placed between the scattering cell and the photomultiplier tube. A small shift of the maximum LALLS response (towards the high molecular weight) was also observed in the presence of the filter. The explanation Kolpak et al.[19] gave for the phenomenon was that the power of the laser radiation was great enough to cause fluorescence in lignin while the power of the xenon lamp, used in their fluorescence spectrometer, was not. Similar findings have also been reported by Hanson and Cietek [20], and by Kim and Fricke[21]. Hanson and Cietek, who used an identical instrument to ours and to that of Kolpak et al.[19], observed no bimodality of the LALLS response in the absence of an interference filter. What they observed was the shifting of the maximum of the LALLS peak to higher molecular weights when the filter was placed in the instrument. The results in Figure 1 were recorded without any corrections allowing for the reported fluorescence, because the extinction coefficient of these samples at 633 nm was found to be very near zero.

In the light of the preceding discussion of fluorescence, one would expect that all the LALLS maximum responses of Figure 1 would be moved to the left (i.e., lower elution volumes) if an interference filter were placed in the instrument. Such hetero-

Table 2

Yields, Molecular Weights, and Refractive Index Increments, of the Dioxane/HCl Lignins at Various Stages of Delignification

Sample No., Delignification Time (h)	% of Lignin Isolated from Wood	W_S (a)	dn/dc (mL g^{-1})	$\bar{M}_w \cdot 10^{-4}$ ($g\ mol^{-1}$) (b)	$\bar{M}_n \cdot 10^{-4}$ ($g\ mol^{-1}$) (b)	$\bar{M}_w/\bar{M}_n$
DL 0.5	3.0	0.111	0.1817	1.14	0.66	1.71
DL 2.0	8.7	0.321	0.1882	1.87	1.02	1.83
DL 3.0	10.2	0.376	0.1826	2.47	1.45	1.70
DL 4.0	13.0	0.480	0.1833	3.92	2.78	1.41
DL 6.0	20.3	0.749	0.1913	4.81	2.89	1.66

(a) Calculated from the Klason lignin content of wood, W_S = % lignin isolated/ Klason lignin content

(b) Average of two GPC/LALLS runs

Second virial coefficient used: 5×10^{-5} mol mL g^{-2} [19,35].

geneity is what in fact one expects to observe if delignification proceeds via the random degradation of a polymer network[22-24] and that was repeatedly observed during our model gel degradation experiments[1].

The molecular weight averages of the five lignin samples, determined by GPC/LALLS, are reported in Table 2. The weights of the sol fractions (W_S) are also shown, as calculated from lignin yields and Klason lignin content in the original wood sample. The refractive index increments, determined individually on each sample, are also shown. These last physicochemical results are actually considerably higher than the average of 0.122 mL g^{-1} reported by Rezanowich et al.[2].

In agreement with all previous reports[2-7,10], the molecular weights of the solubilized lignins increased progressively with increasing solubilization. The polydispersity ratios ($\bar{M}_w/\bar{M}_n$) of

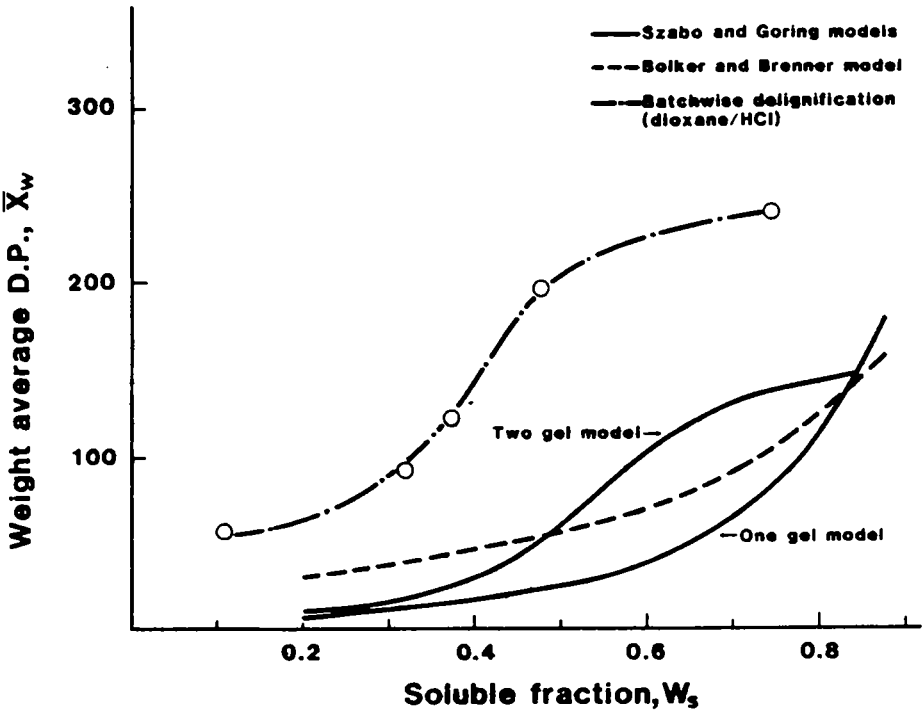

FIGURE 2. The plot of X_w versus W_S for the batchwise delignification of wood with dioxane/HCl. For comparison the two models based on the gel degradation theory are also plotted (molecular weight of repeat unit=200[7,9].)

these lignins, however, did not show the progressive increase expected to occur during a gel degradation process. The data of Pla[14], on similar samples produced by the successive extraction technique, do show this trend.

The results are so far in good qualitative agreement with what one expects from the degradation of a crosslinked network: the heterogeneity of the sols, the skewed shape of the refractive index chromatograms, and most importantly, the trend of the

increasing sol molecular weight with solubilization. The correlation of the molecular weight data of Table 2 with the Szabo and Goring model of delignification[8] and that of Bolker and Brenner[9], however, still remains to be examined.

The plot in Figure 2 indicates that neither of the two models correlates with the experimental results. The molecular weights of the isolated lignins are higher than the predictions of both models. Qualitatively, the experimental sigmoidal shaped curve accords with the two-gel model of Szabo and Goring, but this agreement is probably not meaningful. Quantitative agreement of the two-gel model has been reported[8] for both kraft[3] and sulfite[4] delignification when conducted by continuous extraction.

Lignin Associative Interactions

To account for the widespread disparities reported between molecular weights and distributions of lignins, associative effects have been proposed. Such associative interactions among lignin components have been found to occur during gel permeation chromatography in different mobile phases[25-27]. Conclusions on extensive hydrogen bond formation between free hydroxyl groups in dioxane lignins have also been reported by Hatakeyama[28] and Bogomolov *et al.*[29]. Thus, any association between lignin molecules in solution would cause an increase in their molecular weight values, which in turn might account for the discrepancies observed in Figure 2.

In order to explore this possibility, four of the isolated dioxane lignins were quantitatively acetylated with acetic anhydride in pyridine (as described by Hatakeyama *et al.*[28]). The molecular weights of the acetylated samples were then re-evaluated by GPC/LALLS. Essentially no changes were observed in the

Table 3

Molecular Weights of Various Dioxane Lignins Before and After Acetylation

Delignification Sample, Time (h)	Molecular Weights Before Acetylation (g mol^{-1})			Molecular Weights(a) After Acetylation (g mol^{-1})		
	$\bar{M}_w \cdot 10^{-4}$	$\bar{M}_n \cdot 10^{-4}$	$\bar{M}_w/\bar{M}_n$	$\bar{M}_w \cdot 10^{-4}$	$\bar{M}_n \cdot 10^{-4}$	$\bar{M}_w/\bar{M}_n$
DL 2.0	1.87	1.02	1.83	0.96	0.34	2.83
DL 3.0	2.47	1.45	1.70	2.76	1.29	2.14
DL 4.0	3.92	2.78	1.41	5.75	3.10	1.85
DL 6.0	4.81	2.89	1.66	6.40	2.70	2.37

(a) Average of two runs, dn/dc used: 0.1854 mL g^{-1}, second virial coefficient: 5×10^{-5} mol mL g^{-2}

chromatograms of the acetylated samples compared to those of their non-acetylated counterparts. Their unimodal and broad character was uniformly retained, together with their maximum elution volumes. The intensity of scattered light, however, was found to change and gave the new set of molecular weight values shown in Table 3.

If association within the original lignin solutions does occur, one would expect a decrease in both weight and number average molecular weights after acetylation (assuming that acetylation fully destroys all association complexes). The $\bar{M}_n$ values of Table 3 do exhibit such a trend, except for one sample, while the $\bar{M}_w$ values show the opposite. A sample calculation in which it was assumed that large highly functional molecules associate preferentially to smaller ones, has indicated that the polydispersity ratio of a polymer in which no association occurs should be higher than its counterpart where association operates: i.e., the breadth of the size distribution will be wider in the sample that shows no association. The results in Table 3 agree with this concept; the $\bar{M}_w/\bar{M}_n$ invariably increased after acetylation.

A factor that causes additional complications, however, is that on acetylation the molecular weight per C_9 unit in lignin will increase by incorporation of acetyl groups on each previously free hydroxyl position. This increase is expected to be substantial, because the NMR work of Lenz[30] has shown that, in a variety of lignin preparations, there is at least one free hydroxyl proton per C_9 unit. These opposing effects preclude drawing any definite conclusions concerning the presence or absence of association in the dioxane lignins described in Tables 2 and 3.

Lignin Recondensation Reactions

Another parameter that requires examination is the possibility of lignin self-condensation reactions occurring during the experiment. Such reactions would certainly cause the molecular weights of the isolated sols to be higher than those predicted by any gel degradation model. Evidence favoring the occurrence of condensation reactions in lignin model compounds under acidolysis conditions has been reported by Lundquist and Ericsson[31].

In order to shed some light on the matter, at least with respect to dioxane/HCl conditions, the lignin isolated early in the process (i.e., after 0.5 h of delignification) was recooked under standard conditions for various lengths of time. These experiments were aimed at answering the question: do the isolated lignin fragments further degrade during a batchwise process according to the requirements of the gel degradation theory? The results in Table 4 suggest that the answer is negative. The recooking of the early sample, DL 0.5, for various lengths of time ranging from 1.0 to 7.0 hours caused a monotonic increase in its molecular weight.

Table 4

Molecular Weights Obtained on Recooking an Early Dioxane Lignin Sample

Sample Recooking Time (h)[a]	$\bar{M}_w \cdot 10^{-4}$ ($g\ mol^{-1}$)[b]	$\bar{M}_n \cdot 10^{-4}$ ($g\ mol^{-1}$)[b]	$\bar{M}_w/\bar{M}_n$
0.0	1.14	0.66	1.71
1.0	1.60	1.20	1.26
2.5	1.70	1.20	1.40
4.0	2.30	1.80	1.20
7.0	4.90	3.00	1.60

(a) Sample recooked was the one isolated at 0.5 hrs of delignification shown in Table 2, DL 0.5.
(b) dn/dc used: 0.1854 mL g^{-1}, second virial coefficient: 5×10^{-5} mol mL g^{-2}.

The chromatograms from this last series of experiments are shown in Figure 3. The refractive index response seemed to narrow somewhat as recooking became more extensive. At the same time, the LALLS response progressively intensified. Figure 4 summarizes the fractionation exhibited by the chromatograms of the recooked samples. The chromatograms show that the sample contained a variety of distinct species during the early stages of the recooking process. As the recooking time increased, however, the distributions became smoother, while new species appeared in the high molecular weight region. Thus, distinct species seemed to condense together giving rise to larger molecules of a variety of sizes, which, at the 7.0 hour recooking time, resulted in a smooth curve tailing towards the high molecular weight end of the distribution. Such behavior is qualitatively very similar to the changes expected within sols approaching the gel point during polyfunctional gelation, or approaching the degelation point during network degradation[1]. During

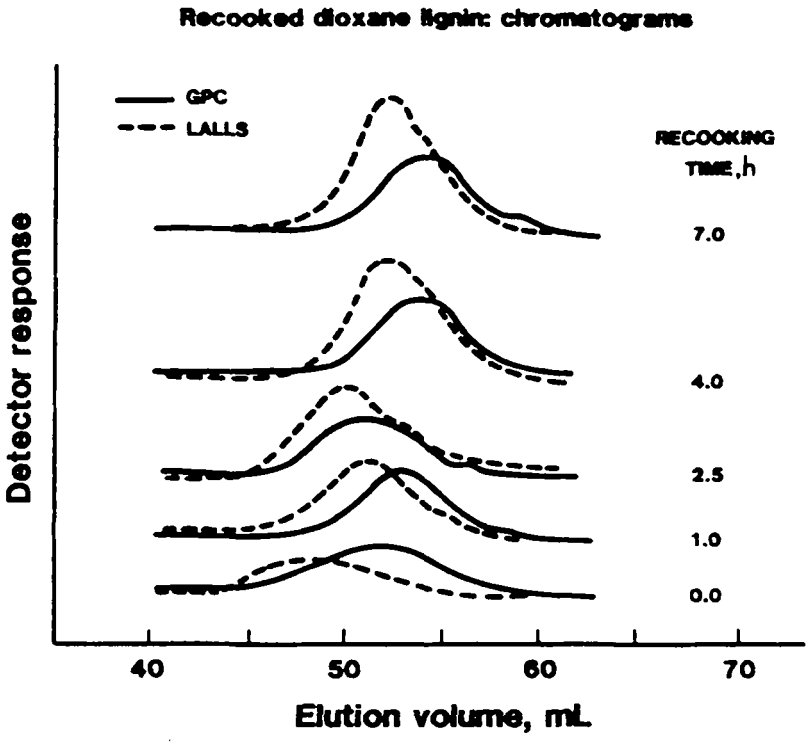

FIGURE 3. GPC/LALLS outputs of the recooked dioxane lignins of Table 4.

polymerization before the gel point, the high molecular weight tail of the species distribution should become progressively more pronounced at the expense of the lower molecular weight species. It seems, therefore, that the recooking of an early fraction (DL 0.5) of dioxane lignin initiates gelation.

This conclusion is further strengthened by the observation that, at the end of the recooking periods totalling 4.0 and 7.0 hours, respectively, a small amount of gelatinous insoluble substance appeared. It was not possible to accurately quantify it,

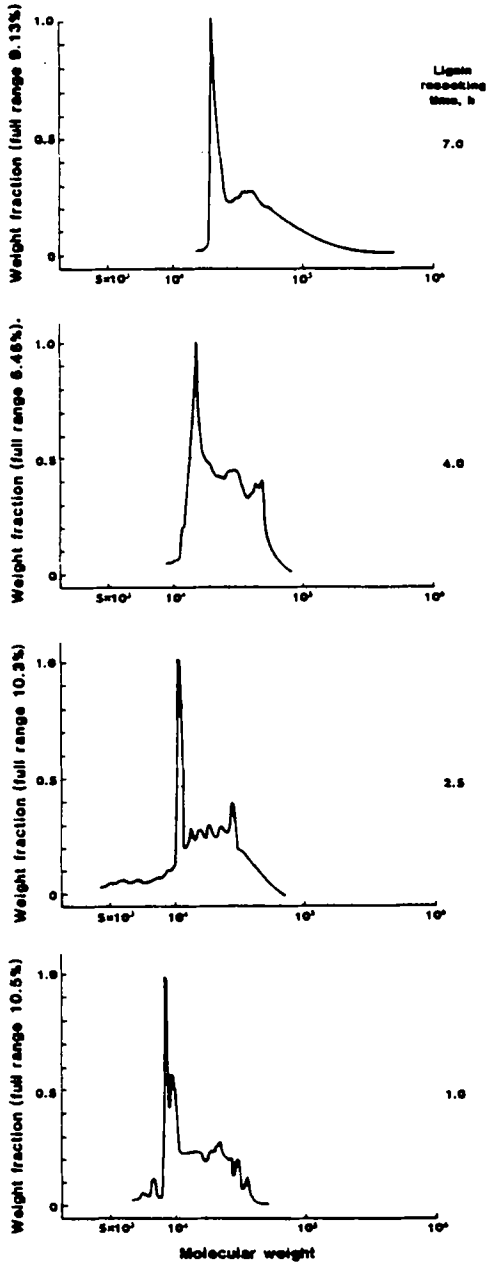

FIGURE 4. The fractionation of four of the recooked dioxane lignin samples of Table 4.

however, due to the small scale on which these experiments were done. The appearance of a gel from totally soluble starting materials almost unequivocally supports the conclusion that gelation took place, thus rendering fruitless any attempts to rationalize the observed increase of the molecular weights on the basis of associative effects. The reactive nature of dioxane lignins has also been confirmed by Soviet chemists during the past decade[29,32-34].

It might be argued that, in the present experiments, the phenomenon of recondensation was observed on only a small fraction of the total lignin isolated from wood: these experiments were done on sample DL 0.5 (Table 2) which represents only 11.1% w/w of the total lignin that wood contains. Therefore, lignin fractions isolated during later stages of the original delignification experiments were recooked, and Table 5 shows the results. The sample taken for recooking was DL 3.0 (of Table 2) which represented 37.6% w/w of the lignin present in wood. Its molec-

Table 5

Changes in Molecular Weights on Recooking a Middle Dioxane Lignin Sample[a]

Sample Recooking Time (h)	$\bar{M}_w \cdot 10^{-4}$[b,c] (g mol^{-1})	Second Virial Coefficient (mol mL g^{-2})[b]
0	2.47	[d]
1	4.84	-0.709×10^{-3}
2	4.95	-0.541×10^{-2}
4	5.13	-0.862×10^{-3}

(a) Sample recooked was the one isolated at 3 hrs of delignification shown in Table 2 representing $W_S = 0.376$.
(b) Measured by the static LALLS technique.
(c) dn/dc used: 0.1854 mL g^{-1}.
(d) Not determined.

ular weight ($\bar{M}_w$) doubled after one hour of recooking, while more extended treatment (2 and 4 hours) gave a much smaller increase in the molecular weight. When a late lignin fraction, sample DL 6.0, representing 74.9% w/w of the lignin in wood, was recooked for an additional 15 hours, its weight average molecular weight increased from 4.81×10^4 g mol^{-1} to 1.3×10^5 g mol^{-1}.

The molecular weights in Table 5 were determined by the static low angle laser light scattering technique, thus allowing for the determination of the second virial coefficients of the lignins. The significant feature of these new physicochemical data is that the values thus determined are all negative. A negative second virial coefficient is rather unusual and can be attributed to polymer aggregation. Such a negative value was also reported by Kolpak et al.[19] in their studies of a medium-kappa kraft lignin, and was rationalized by invoking aggregation. Gupta and Goring[35], on the other hand, reported a zero second virial coefficient in their early studies of alkali lignins. Thus, the possibility of association in the lignins in solution finds support in this new set of results.

These additional recooking experiments clearly indicate that the recondensation of dioxane lignin proceeds throughout the process and is not a property of only the early lignin fraction. This conclusion, however, is in direct contradiction to the results of Adler et al.[36], Felicetta and McCarthy[37], Yean and Goring[4] and Nokihara et al.[38], in which the molecular weights of recooked lignosulfonates showed a marked decrease.

A possible explanation for the contradiction between the present experimental results and those in the literature arises from closer examination of the chemistry of the respective delignification processes. Felicetta and McCarthy[37] and Yean and

Goring[4] delignified wood in bisulfite sulfurous acid solutions. The resulting lignin preparations were dialyzed and recooked in the same medium or in water at low and high concentrations. The molecular weights measured always gave numbers lower than the starting preparation. Our experiments, however, are chemically different from theirs. The dioxane lignins of Table 2 were prepared and, without prior dialysis, were recooked in a medium which is chemically different from that of the previous studies. The presence of sulfonic groups on the benzyl carbons would probably result in partial stabilization[39] of the lignin species, consequently minimizing condensation. The absence of sulfonic groups in the dioxane preparation would have the opposite effect.

In any event, the possibility of irreversible condensation reactions occurring during a batchwise acidic sulfite pulping process was also accounted for by Nokihara et al.[38]. They observed that the molecular weight of soluble lignosulfonates, at nearly complete delignification, decreased further with additional cooking to a value of about 5000 g mol^{-1}. Further cooking resulted in an increase of the molecular weight.

The experimental procedure of Nokihara et al.[38] is really the only one that can be compared to ours, because their experiments were performed batchwise, and they did not dialyze the soluble products prior to molecular weight evaluation. Dialysis of a lignin preparation, as performed by Felicetta and McCarthy[37] and Yean and Goring[4], would remove a substantial fraction of the low molecular weight material. It is possible that such a dialyzed sample may be less susceptible to condensation on recooking, due to the absence of smaller sized species. When such species are present, they may serve as bridges to connect two larger fragments. This concept is supported by the absence of low molecular weight peaks in the chromatograms of Figures 1 and 3.

The demonstrated sensitivity of dioxane lignin preparations to recondensation during the cook renders the present results unsuitable for testing the gel degradation theory. The functions that relate sol fraction, degree of reaction, and molecular weights of the solubilized product cannot be applied to dioxane lignins because of this serious limitation. Nevertheless, in principle, a delignification reaction which causes only the random cleavage of specific bonds in the lignin network may lead to the determination of previously inaccessible architectural network characteristics through the use of the gel degradation equations. Accordingly, future efforts in this area of lignin research should be directed toward the development of a delignification process which will fully comply with the requirements of the gel degradation theory.

EXPERIMENTAL

Materials

Black spruce sawdust, pre-extracted for over 50 hours with a 1:1 acetone:ethanol mixture, was stored at -10°C until used. Immediately prior to use, it was dried in a vacuum oven at 35°C for 48 hours. The fat-extracted, dry sawdust contained 27.1% Klason lignin and 0.3% acid soluble lignin. The dioxane used in the delignification experiments was always freshly distilled from sodium, and kept under a positive dry nitrogen pressure.

The method of Pepper *et al.*[16]; was essentially followed for preparing the dioxane lignin fractions. Delignification was allowed to proceed for each of the time intervals specified in Table 1. The procedure was then repeated with fresh wood and reagents for subsequent longer times.

Elemental analyses and methoxy contents reported in Table 1 were determined by Schwarzkopf Microanalytical Laboratories, Woodside, N.Y. The Klason lignin contents were determined by the Analytical Services Division of the Pulp and Paper Research Institute of Canada, Pointe Claire, Québec. Ultraviolet absorption coefficients were measured on a Pye-Unicam SP8-150 UV/visible spectrophotometer at 280 nm in THF solutions ranging in concentration from 5 to 30 x 10^{-3} g/L.

The dioxane lignins were acetylated according to the modification by Hatakeyama et al.[28] of the Brauns[40] technique.

For the recooking experiments, approximately 100 mg of dioxane lignin was dissolved in 10 mL (1% w/v) of the dioxane: H_2O:HCl mixture (90:8:1.8) under dry nitrogen. The solution was then recooked at 97-99°C for the required time. At the end of each recooking period, as specified in Tables 4 and 5, the solution was concentrated and the lignin was precipitated in 150 mL of distilled water.

For instrumental analyses, a solution of known concentration (usually 2.5 x 10^{-3} g/mL) of the dried lignins in distilled THF was filtered through a 0.5 μm Millipore filter (Waters Associates). These solutions were prepared and stored at -4°C, at least 24 hours prior to measurements. Samples were prepared from this clean stock solutions and appropriately diluted for their refractive index determination, GPC/LALLS chromatography, and UV absorption measurements. Molecular weights were determined by using a GPC with a broad range of μ-styragel columns, coupled in series to a KMX-6 Chromatix Low Angle Laser Light Scattering Photometer. The design and operational of the instrument have been discussed in the literature[41].

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