Molecular Weight Distribution of (Semi-) Commercial Lignin Derivatives

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ABSTRACT

Absolute molecular weights of several commercially and semi-commercially available lignins were determined by gel permeation chromatography (GPC) with a differential viscosity detector (DV). Solubility in THF was assured by acetylation. Polystyrene molecular weight standards were used for establishing a universal calibration curve. The lignins included those from hardwood, softwood, and sugar cane bagasse; and these were isolated by the kraft or organosolv pulping process, or by steam explosion/autohydrolysis. All lignins exhibited more or less uniform distributions with weight average molecular weights (M_w) between 3,000 and 20,000; with polydispersities (M_w/M_n) between 2 and 12; with Mark-Houwink-Sakurada exponential factors (α) between 0.17 and 0.35; and with intrinsic viscosities between 0.037 and 0.08 dLg^{-1}. A significant relationship between M_w/M_n and M_w was discovered that had a correlation factor of 0.92. This relationship has the form of
$$M_w/M_n = 0.45 \ (M_w) \ 10^{-3} + 0.85.$$

INTRODUCTION

Lignin is the aromatic polymer that serves vascular plants as structural reinforcement[1,2]. In the process of papermaking, lignin is isolated in concentrated

form in amounts exceeding 50 billion pounds per year in the United States. Research of the past 25 years has demonstrated that lignins from various plant and (pulp and paper) process sources may be employed as components in both water-soluble and structural polymers and materials[3]. The advent of commercially and semi-commercially available lignin preparations from different sources creates the need for the establishment of classification criteria; and for assisting in the establishment of quality control criteria and performance specifications. While previous attempts have concentrated on both chemical structure[4,5] and on the performance of lignins as components of network polymers (polyurethanes)[6], this publication attempts to employ the recently advocated method of absolute molecular weight distribution by universal calibration[7,8,9] as classification method.

The determination of molecular weights and molecular weight distributions of lignin and lignin derivatives has long been hampered by (a) the poor solubility of many lignins in suitable organic solvents or water; and (b) by their apparent tendency to associate via hydrogen bonds and other secondary interactive forces[10-17]. However, recent advances in high pressure gel permeation chromatography (GPC), and in detectors based on differential viscometry (DV), have made it possible to determine absolute molecular weights of lignin derivatives conveniently and expediently[7,8]. Himmel et al.[7] have demonstrated that a series of commercially available molecular weight standards as well as low molecular weight lignins all fit universal calibration. Although GPC/DV continues to be limited by a full understanding of concentration, association, adsorption, and exclusion effects[7] and their relationship to the hydrodynamic behavior of lignin derivatives, Siochi et al.[8] state that "GPC/DV proves to be a reliable and a convenient tool for the determination of absolute molecular weights of lignin derivatives."

The objective of this study was to examine the absolute molecular weights of several commercial and semi-commercial lignin preparations in an effort to expose their similarities and dissimilarities.

EXPERIMENTAL

Materials

The lignins used in this study are listed in Table 1. These represent lignins that are either commercially available or that are being made available as experimental pilot materials on semi-commercial scale.

Methods

Acetylation of Lignins:

All the lignins were acetylated according to the procedure of Gierer and Lindeberg[18] with some minor changes. The lignins were freeze-dried for 24 hours before acetylation. Lignins were first dissolved in distilled pyridine before an equal amount of distilled acetic anhydride was added to the solution with continuous stirring under flowing dry nitrogen (40 mL of pyridine and acetic anhydride per gram of lignin). The reaction was carried out at 0°C for 24 hours. The acetylated lignins were recovered by precipitating the reaction mixture in 0.1 N HCl (approximately ten times the volume of the reaction mixture). The acetylated lignins were filtered and washed several times with 0.1 N HCl to remove pyridine. This was followed by washing with distilled water to remove HCl from the lignin derivatives. These derivatives were collected and freeze-dried for 24 hours and stored in a desiccator. All the lignin acetates were soluble in tetrahydrofuran (THF).

Gel Permeation Chromatography:

Narrow distribution polystyrene standards were obtained from Polymer Laboratories and American Polymer Standards Corporation. These standards were dissolved in HPLC-grade THF, and they were used for constructing the

TABLE 1

List of Lignin Preparations

(Semi-) Commercial Designation	Plant Source	Process Type	Producer (Company) Name and Location
Indulin AT	Softwood (Pinus Sp.)	Kraft	Westvaco Corp., Charleston, S.C.
Indulin[1]	Hardwood (Species Mix)	Kraft	Westvaco Corp., Charleston, S.C.
Eucalin	Hardwood (Eucalyptus)	Kraft	ENCE Madrid, Spain
ALCELL Lignin	Hardwood (Species Mix)	Organosolv (ethanol)	Repap Technologies Valley Forge, PA
Organocell Lignin[1]	Softwood (Picea Sp.)	Organosolv (methanol/alkali)	M/D Organocell, Munich, Germany
Lignin, O-Acetyl	Hardwood (Species Mix)	Organosolv (ethanol)	Aldrich Chem. Co. Milwaukee, WI
Angiolin X[1,2]	Hardwood (L.tulipifera)	Steam Explosion (Stake Tech.)	B-REAL, Floyd, Virginia
Sucrolin	Sugar cane bagasse	Autohydrolysis	C.G. Smith Sugar, Merebank, RSA
HSPA-Bagasse[1,3]	Whole bagasse	Steam Explosion (Stake Tech.)	H & C Sugar, Aieya, HI
HSPA-Pith[1,3]	Bagasse-pith	Steam Explosion (Stake Tech.)	H & C Sugar, Aieya, HI
HSPA-Leaf[1,4]	Bagasse-leaves	Steam Explosion (Stake Tech.)	H & C Sugar, Aieya, HI

[1]Experimental sample
[2]Unregistered designation
[3]Process conditions involved 1.5 min at 220°C and isolation using aq. alkali followed by acid precipitation.
[4]Process conditions involved 2.33 min at 220°C; (isolation as in footnote #3).
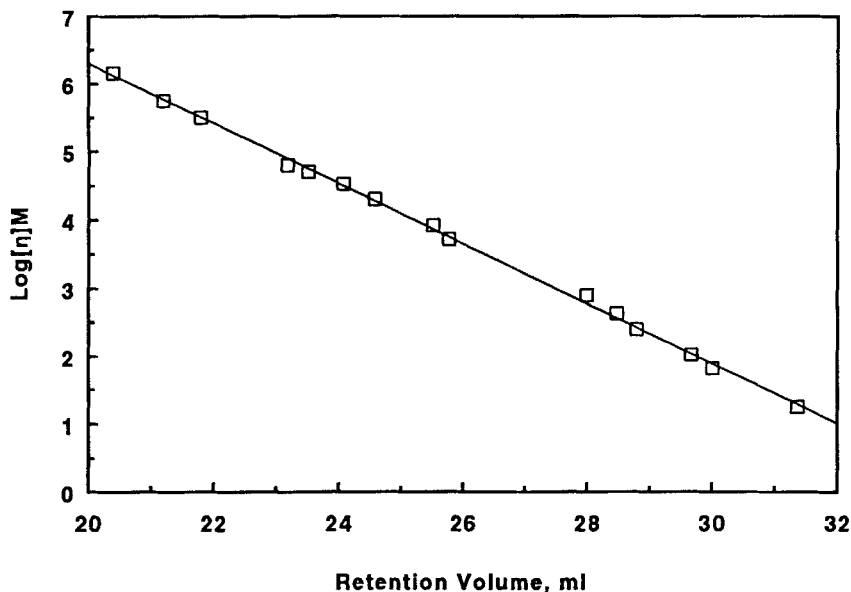
Figure 1. Universal Calibration Curve obtained with Waters Ultrastyragel columns using narrow distribution polystyrene standards in THF.

universal calibration curve (log $[\eta]M$ versus retention volume) (Figure 1). Molecular weights were determined using the Viscotek Differential Viscometer, Model 100, in series with the Waters 410 Refractive Index detector, three Waters Ultrastyragel columns with pore diameters of 10^3 Å, 10^4 Å and 10^6 Å, and a Waters 510 HPLC pump. Samples were introduced via the Waters U6K injection port at a flow rate of 1 ml/min. Data collection was performed with a personal computer interfaced to the detection and injection systems. Data manipulations were handled with the Unical software package 2.71 provided by Viscotek. Lignin solutions were prepared carefully in HPLC-grade THF to ensure accurate concentrations which ranged from 3-6 mg/mL. The lignin acetate solutions were injected within 5 minutes of dissolution, except where indicated. Concentrations of polystyrene standards were molecular weight dependent, ranging from 0.01 to 5 mg/mL.

2A

2B
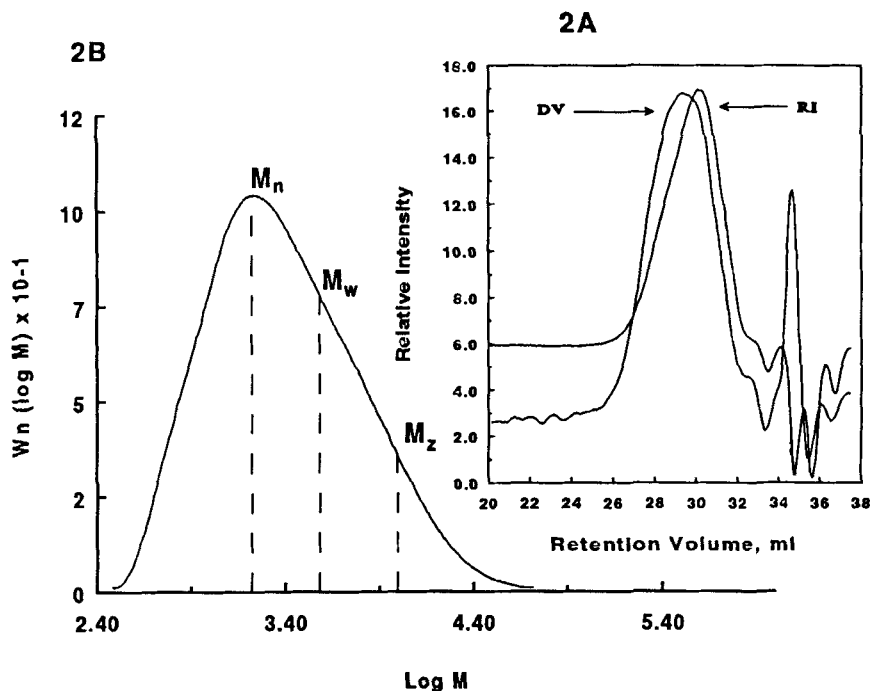
Figure 2. A) Dual chromatograms (RI and DV) showing the elution of Acetylated Eucalin from the GPC system. B) Molecular weight distribution of Acetylated Eucalin.

RESULTS AND DISCUSSION

Concentration (refractive index, RI) and differential viscosity (DV) signals obtained with the gel permeation chromatography (GPC) system using a typical lignin acetate are shown in Figure 2A. The RI trace appears to lag behind the DV trace for two reasons. Firstly, the two detectors are in series with the RI detector being last, so there is a real time lag between the traces. Furthermore, this offset is accented by the differential response of the two detection systems. The DV detector is most sensitive to high molecular weight molecules while the RI detector is sensitive to concentration. This differential response accents the time

lag and accounts for the dissimilar shapes of the two traces. These are substantially identical to those reported earlier by Himmel et al.[7] and Siochi et al.[8]. Calculations in terms of absolute molecular weights using the universal calibration curve (Figure 1) were computed by the Viscotek Unical 2.71 software. The Unical software relies upon a prior calibration with polymer standards of known molecular weight. The elution of polymer standards that span above and below the hydrodynamic range of the unknowns serves to establish the hydrodynamic "response" of the GPC columns. For our purposes, the hydrodynamic response is defined as the straight line relationship between elution volume and hydrodynamic volume. The hydrodynamic volume is the product of the molecular weight and the intrinsic viscosity. At a discrete value of hydrodynamic volume, there is a corresponding and discrete value of elution volume. When an unkown sample elutes, the molecular weight is unknown, but the elution volume and intrinsic viscosity are measured directly. Because the hydrodynamic response of the columns has been established with known standards, the Unical software back calculates the molecular weight of the unknown. Additional discussion of this issue can be found in reference 7. These calculations resulted in molecular weight distributions (Figure 2B) along with quantitative information regarding number, weight, and viscosity average molecular weights; polydispersity (M_w/M_n); Mark-Houwink-Sakurada (MHS) constants, intrinsic viscosity, etc.

The results obtained with fifteen different lignin samples are summarized in Table 2. Values for M_n range between 1,200 and 2,600 g/mole; and those for M_w lie between 3,000 and 20,000 g/mole. Polydispersities (M_w/M_n) fall between the range of 2 and 12; and Mark-Houwink-Sakurada (MHS) exponential factors (α) are in the range of 0.17 and 0.35. Intrinsic viscosity values fall in the range of 0.037 and 0.08 dLg^{-1}, and these are slightly above those reported by Siochi et al.[8] for hydroxypropyl lignin derivatives. Molecular weight and dispersity ratios are substantially in agreement with those reported by Himmel et al.[7] and Siochi et al.[8] using identical instrumentation and experimental technique. After

TABLE 2

Absolute Molecular Weights of (Semi-) Commercial Lignin Preparations

LIGNIN TYPE	# on Fig. 4	M_n x10^{-3}	M_w x10^{-3}	M_w/M_n	Log K	α (MHS)	$[\eta]$ dlg^{-1}
KRAFT							
-Indulin AT	1	2.2	19.8	9.0	-2.22	0.29	.079
-Indulin	2	1.3	3.7	2.9	-2.14	0.26	.053
-Eucalin	3	1.7	3.9	2.3	-2.38	0.33	.060
-Curan[1]	4	1.8	14.2	8.1	-2.33	0.29	.056
ORGANOSOLV							
-Organocell	5	2.3	10.8	4.7	-2.08	0.24	.066
-Alcell-OAc [2]	6	1.8	4.1	2.3	-2.17	0.21	.037
STEAM EXPLOSION							
-Angiolin X	7	2.0	11.3	5.8	-2.43	0.35	.072
-Sucrolin[3]	8	1.7	19.3	11.4	-1.88	0.18	.066
-Bag.[4] (3.8)[5]	9	1.6	12.4	7.7	-2.06	0.25	.077
-Bag. (4.0)	10	2.1	14.3	6.8	-2.07	0.24	.065
-Bag.Pith (3.8)	11	1.8	10.7	6.0	-1.99	0.24	.076
-Bag. Pith (4.0)	12	2.6	16.7	6.4	-2.07	0.23	.067
-Bag. Leaf (3.9)	13	2.1	10.7	5.2	-1.97	0.22	.075
-Bag. Leaf (4.1)	14	1.7	13.5	7.9	-1.78	0.17	.069
-Bag. Leaf (4.3)	15	2.3	18.5	8.1	-1.86	0.18	.065

[1] Aldrich product #37,095-9
[2] Aldrich product #37,102-5
[3] Aldrich product #37,107-6
[4] HSPA Bagasse
[5] Numbers in parentheses refer to the steam explosion severity factor, Log R$_0$
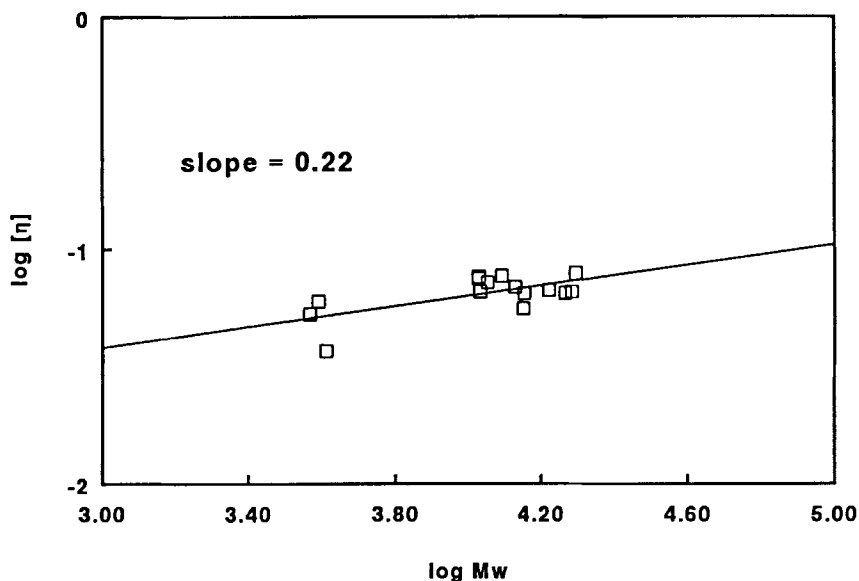
Figure 3. Mark-Houwink-Sakurada plot of $[\eta]$ versus M_w for the 15 lignin acetate samples listed in Table 2.

close inspection of this data, one is struck by the compactness of the lignin acetate molecule in THF. This point is represented graphically in Figure 3 where log $[\eta]$ is plotted against log M_w for all 15 samples. The MHS exponent from Figure 3 is equal to 0.22, which approaches the low end of the published range of this parameter for various lignins[10]. The average value of the experimentally determined MHS exponents from Table 2 is 0.26 ± 0.05. While the data is somewhat scattered, the low slope of the fitted line indicates that the hydrodynamic volume of the lignin acetates is not strongly dependent upon the molecular weight. In other words, as the molecular weight rises, the probability of finding a branch point in the molecule also rises. As a result, the hydrodynamic volume, and thus the intrinsic viscosity, of the lignin acetates increases less dramatically with molecular weight than would be the case for a
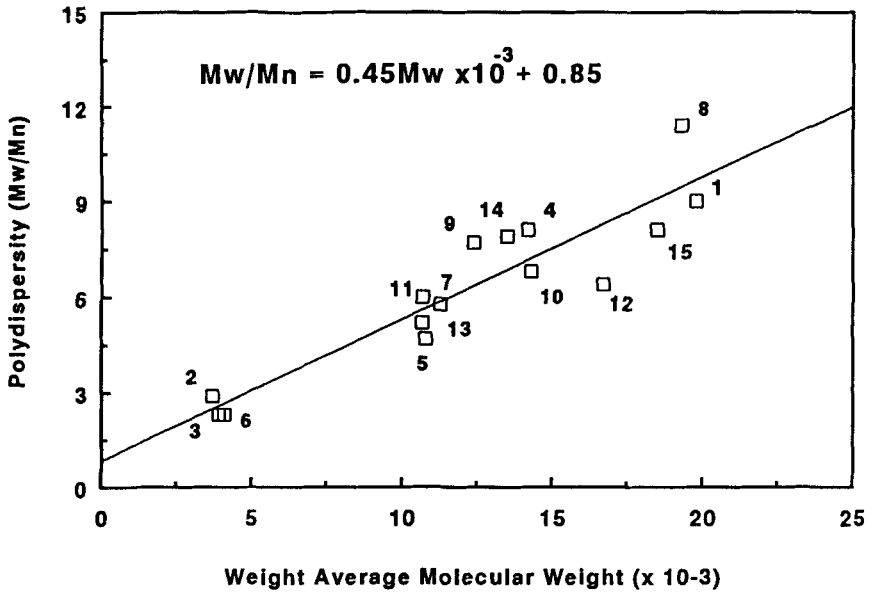
Figure 4. Relationship between polydispersity of lignin acetates with their respective weight average molecular weight.

linear coil molecule. This information suggests that these lignin acetates are highly compact spherical molecules in THF. This is apparently a general quality of lignin acetates in THF because, from light scattering, Merkle et al. have found that organosolv spruce lignin acetate is more compact in THF than in acetone and trifluoroethanol[19]. The data of Table 2 suggest that a significant relationship exists between the dispersity (M_w/M_n) of a lignin sample and its weight average molecular weight (M_w) (Figure 4). This relationship takes the form of

$$M_w/M_n = 0.45 \, (M_w) \, 10^{-3} + 0.85 \qquad (1)$$

with a correlation factor (R) of 0.92. Although it is not necessary for all lignins to conform with this relationship, the high correlation factor represents somewhat

of a surprise. It would have been expected that molecular weight parameters are significantly influenced by chemical factors, such as depolymerization and repolymerization leading to greater variation. Additional variation may also result from topochemical effects that must arise from this collection of lignin sources[20,21]. However, a positive relationship between polydispersity (M_w/M_n) and M_w does agree with Flory's gelation theory, which in reverse applies to the process of delignification[20-25]. It is interesting to note that the bagasse lignin acetates show a general correlation between polydispersity and the severity of steam explosion, log R_0. Log R_0 is a measure of the severity of steam treatment that accounts for the variables of time, temperature and pressure[26]. Higher values of log R_0 correlate to more severe treatments and therefore to more extensive degradation. For example, bagasse leaf lignin acetates show an increase in polydispersity as steam explosion severity increases (Table 2). As above, this is in agreement with the treatment of delignification as the statistical process of degelation. In other words, the polydispersity of the sol increases as the extent of network degradation rises. Note that all bagasse samples follow this trend except for whole bagasse (numbers 9 and 10 in Table 2). While the polydispersity of the whole bagasse samples does not rise with log R_0, the M_w increases which is generally consistent with statistical degelation.

Association and "aging" phenomena have been reported repeatedly for lignin preparations, especially in aqueous systems[8,12]. The effect of aging in THF-solution has been examined with two lignin preparations, and the results are summarized in Table 3. The molecular weight data is essentially constant for the Eucalin sample as are the M_n and [η] for the Indulin AT lignin acetate. However, the weight average molecular weight of Indulin AT exhibits a 16% reduction after 3 days, and a 23% reduction after 9 days. This steady reduction in M_w suggests that lignin acetate associations are being disrupted with time. At first glance, this change may seem excessive. However, in light of the results reported by Siochi et. al[8], a 23% change over 9 days is minimal and arguably encouraging.

TABLE 3

Lignin Acetate Molecular Weights as a Function of Time in THF Solution

Lignin Acetate	Days	M_n x10^{-3}	M_w x10^{-3}	M_w/M_n	α (MHS)	$[\eta]$ dLg^{-1}
INDULIN AT						
	1	2.20	19.8	9.0	0.29	.079
	3	2.10	16.6	7.9	0.24	.077
	9	2.10	15.2	7.1	0.27	.075
EUCALIN						
	1	1.65	3.85	2.3	0.33	.060
	3	1.60	3.90	2.4	0.30	.060
	9	1.65	3.75	2.3	0.28	.056

Examination of the GPC/DV data from reference 8 shows that hydroxypropylated lignins may show M_w changes in excess of 40% after 4 hours of aging in THF. Curiously, the time dependent behavior reported in reference 8 occurs as molecular weight increase or decrease, without any obvious pattern. Furthermore, the hydrodynamic volume (as judged by the product of experimentally determined M_n and $[\eta]$) of hydroxypropylated lignins also appears to be more variable than that of the acetylated lignins shown here[8,9]. This comparison suggests that the associative properties of lignin derivatives may depend upon the nature of their derivatization, hydroxypropylation compared to acetylation. Nevertheless, a 23% change in M_w after 9 days aging is not excessive in the opinion of the authors. The message from this discussion is that awareness and caution are still in order when discussing GPC of lignin derivatives.

The lignins included in this study represent commercial or semi-commercial materials with known isolation history. Not included in this series

was a hardwood organosolv lignin preparation with unknown isolation and separation protocol. This lignin preparation, however, had a dispersity that was approximately half of that predicted for its molecular weight according to Equation 1. This suggests that lignins exist that have dispersities which are at variance to the relationship of Equation 1 owing most probably to their method of isolation and/or purification.

CONCLUSIONS

Acetylated lignins from kraft and organosolv pulping, and from steam explosion/autohydrolysis and isolated from different plant sources exhibit a significant linear relationship between dispersity (M_w/M_n) and M_w with a slope of 0.45 dispersity per 1,000 M_w.

Steam explosion lignin acetates generally exhibited a positive relationship between polydispersity and severity of steam explosion, which is in agreement with the modeling of deliginification as the statistical process of degelation. Otherwise, the nature of delignification (Kraft versus steam explosion, etc.) had no obvious affect on molecular weight distribution.

A slight time dependent association was evident from changes in M_w of one sample. Other molecular weight parameters such as M_n, [η], and the MHS exponent were essentially constant.

The results suggest that GPC/DV represents a convenient and rapid method for classifying lignins according to their molecular weights.

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