# Fractional Precipitation of Softwood Kraft Lignin: Isolation of Narrow Fractions Common to a Variety of Lignins

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ABSTRACT: In a manner similar to crude oil, technical lignins need refining if their potential as reactive polyphenols of well-defined molecular weight polymers and oligomers is to be actualized. In this paper, we demonstrate that a continuum of narrow fractions can be isolated by the incremental addition of a nonpolar solvent (hexanes) in a polar (acetone) solution of softwood wood kraft lignin. Three distinct commercial samples of softwood kraft lignin were used to examine the validity of the developed protocol using detailed chromatographic and quantitative functional group analytical methods. It was shown that all samples contain a common relatively monodisperse fraction of a polyphenolic material that can be isolated from the different lignins in yields ranging between 10 and 20% w/w. The versatility of the developed fractional precipitation protocol was further validated by creating artificial physical mixtures of the examined lignins in different proportions and isolating from them precisely calculated fractions of nearly identical molecular weight distributions and composition. Overall, the fractional precipitation approach described here offers the possibility that representative specific narrow fractions, common to a variety of softwood kraft lignins, can be isolated irrespective of the manufacturing details of the pulping process. As such, the otherwise known heterogeneous kraft lignin material, whose composition is relatively unpredictable due to manufacturing variations in making pulp, may now offer consistently homogeneous lignin streams with significant commercial ramifications.

KEYWORDS: *Kraft lignin, Fractionation, Functional groups,* [31]*P NMR, Molecular weight*
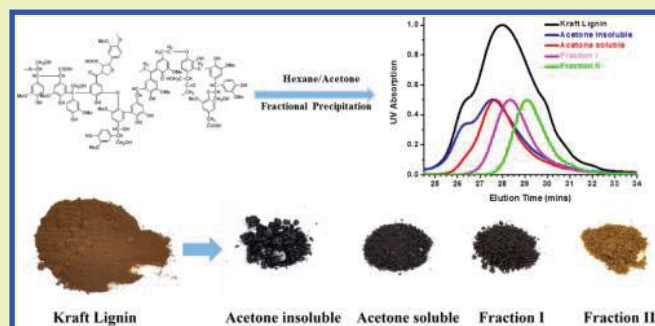
■ INTRODUCTION

Next to cellulose, lignin is the second most abundant material on earth, with a branched and irregular chemical structure composed of a phenyl propane (C_6–C_3) unit as the main building block.[1] Native lignins are originally formed by a complex natural enzymatic lignification processes (involving radical coupling reactions) utilizing three primary structural units, i.e., p-hydroxylphenylpropane (H), guaiacyl (G), and syringyl (S), whose contents significantly vary among different plant species.[2,3] Because the replacement of petrochemically based feedstocks with sustainable alternatives is becoming increasingly important, technical lignins (those produced as byproducts from the industrial processing of wood) represent a promising renewable feedstock for aromatic chemicals, polymers, adhesives, etc.[4–8]

There are, however, significant challenges associated with the utilization of technical lignins as petrochemical feed stocks due to their variable nature, functionality, reactivity, and heterogeneity. This is because during the widely used industrial kraft pulping process, native lignin structures can be altered significantly by fragmentation and condensation. The most abundant aryl alkyl ether linkages, such as β–O–4, are susceptible to fragmentation resulting in the formation of

large amounts of phenolic hydroxyl groups.[9] New linkages, such as enol ethers and stilbenes are also generated. Furthermore, quinone methide intermediates can induce additional carbon–carbon linkages.[10,11] As such, kraft lignins are inherently heterogeneous, of high polydispersity, and have complex and variable functional group distributions depending on the process variables used during the pulping process.[12] In order to solve the technical issues associated with the inherent heterogeneity of technical lignins, a variety of lignin fractionation methodologies have been proposed in the literature. These efforts that have offered relatively homogeneous lignin fractions have aided our understanding of its composition,[13–18] various details of the manufacturing processes,[19–22] and its utility as phenolic compounds.[23–25]

Overall, lignin fractionation methodologies can be viewed as lignin purification efforts addressing contamination issues. For example, during ultrafiltration, the removal of carbohydrate impurities was demonstrated, which further facilitated subsequent melt spinning efforts.[26,27]

**Table 1. Origin, Manufacturing Details, and Molecular Weights of the Kraft Lignins Used in This Effort**

lignin source	wood source	delignification type	pulp type aim	target kappa	H factor	active alkali	M_n (×10³)	M_w (×10³)	PDI
KL1	Southern pine	Kamyr continuous	bleachable grade	22	1500−1600	undisclosed	2.4	15	6.1
KL2	Southern pine	Kamyr continuous	liner board	32−35	600	20−22%	1.5	15	10
KL3	Norway spruce	Kamyr continuous	undisclosed	undisclosed	undisclosed	undisclosed	2.2	9.9	4.5

Scheme 1. Flow Chart of a Practical Fractional Precipitation Scheme Developed for Softwood Kraft Lignin
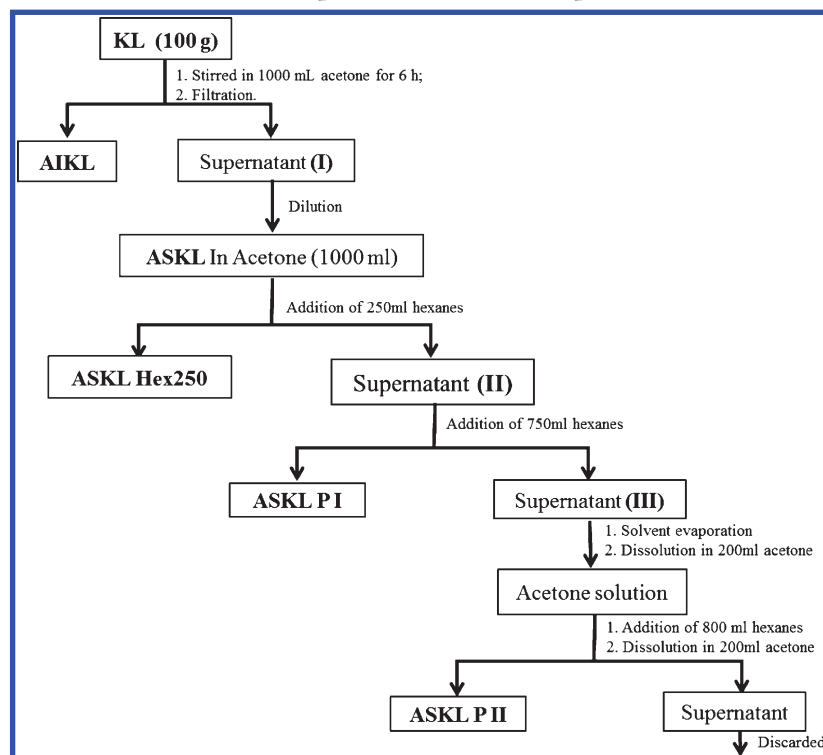
To date, three different fractionation approaches have been applied that include sequential organic solvent extraction (most frequent), selective precipitation at reduced pH values, and membrane ultrafiltration.[20,26−29] Mörck et al. adopted a series of solvents to extract both softwood and hardwood kraft lignins in an order of an increasing Hildebrand Solubility Parameter,[29] and Thring et al. extracted Alcell hardwood lignin into fractions with solvents of increasing hydrogen-bonding capability[20] in both cases with remarkable results. Major limitations, however, are imposed by the sequential solvent extraction approach because only a limited set of available solvent types exist offering only limited possibilities of fractionation. This limitation was attempted to be rectified by inserting solvent mixtures between two successive extraction steps with two different solvents.[12,30] Furthermore, the highly branched, compacted (due to aromatic π−π interactions), and the entangled structure of lignin coupled with solvent diffusion considerations dictate the use of extended and repeated extraction sequences that impose further economic limitations.

The work described in this effort embarks from our view that economical and industrially feasible processes for lignin fractionation are essential for consistently delivering homogeneous reactive polyphenols of well-defined narrow molecular weight polymers and oligomers based on lignin. Consequently, we developed a novel fractionation methodology that is used for synthetic polymers but largely neglected for technical lignins best described as fractional precipitation.[28,38]

■ EXPERIMENTAL SECTION

Materials and Chemicals. Three industrially produced softwood kraft lignins were used in this work, all using carbon dioxide technologies to precipitate the lignin from industrial streams known as "black liquors" designated as KL1, KL2, and KL3. More details related to the nature of the wood used and some of the kraft process variables are shown in Table 1. Prior to use, all lignins were air-dried and then thoroughly dried in a vacuum oven set 40 °C for at least 48−72 h. The hexanes used were of technical grade and purchased from Fisher Scientific (N320), and the acetone was purchased from Sigma-Aldrich (reagent grade). Both solvents and all other reagents were used as received.

NMR Analyses. NMR spectra were acquired using a Bruker 300 MHz spectrometer equipped with a Quad probe dedicated to ³¹P, ¹³C, ¹⁹F, and ¹H acquisitions. Hydroxyl content analyses were determined using a quantitative ³¹P NMR procedure developed in our laboratory.[31−33] An accurate weight (about 40 mg) of a dried lignin sample was introduced into a vial. To this sample, 500 μL of an anhydrous pyridine/CDCl₃ mixture (1.6:1, v/v) was added, and the lignin was allowed to dissolve. Then, 200 μL of an endo-N-hydroxy-5-norbornene-2, 3-dicarboximide (e-NHI) solution (9.23 mg/mL serving as internal standard) and 50 μL of chromium(III) acetylacetonate solution (5.6 mg/mL serving as a relaxation reagent) were added. The solutions of the internal standard and relaxation reagent were both prepared using an anhydrous pyridine/CDCl₃ mixture (1.6:1, v/v). Finally, 100 μL of the phosphitylating reagent (2-chloro-4,4,5,5-tetramethyl-1,2,3-dioxaphospholane) was added, and the mixture was vigorously shaken, transferred into an the NMR tube, and subjected to immediate ³¹P NMR analysis.

GPC. GPC measurements were carried out using a Waters GPC instrument equipped with UV (set at 254 nm) using tetrahydrofuran

(THF) as the eluent at a flow rate of 1.0 mL/min at 35 °C. An injection volume of 50 μL and a sample concentration of 1 mg/mL were used. Three ultra styragel linear columns (Styragel HR 1, Styragel HR 5E, and Styragel HR 6) were linked in series. A series of narrow polystyrene standards (820, 2330, 3680, 13200, 30000, 44000, 570000, 5185000 Da) were used for calibration. Prior to GPC analyses, all samples examined in this work were subjected to a fast room-temperature acetobromination derivatization procedure developed in our laboratory.[34] Five milligrams of a dried lignin sample were mixed with 2 mL of glacial acetic acid/acetyl bromide mixture (92:8, v/v). The mixture was then stirred at room temperature for 2 h. Finally, the solvent and excess acetyl bromide were quickly and thoroughly removed at room temperature using a rotary evaporator connected to a cold trap-protected high vacuum pump. The resulting derivatives were highly soluble in THF.[34]

Detailed Fractional Precipitation of KL1. KL1 (100 g) was incrementally (1/2 h) dispersed into acetone (1000 mL) under vigorous agitation, and the resulting suspension was kept under moderate stirring for another 12 h at room temperature. The acetone insoluble fraction from KL1 (AIKL1) was isolated by filtration using a Whatman filter paper under vacuum and was further rinsed with 200 mL of acetone. The supernatant acetone solution was transferred into a 3 L glass jar, and its volume was made up to 1.00 L with acetone. An aliquot of hexanes (as specified in the text below) was added slowly to generate a suspension of lignin. This suspension was stirred for about an hour to allow the lignin fraction to coagulate and completely attach itself onto the inner walls of the container. The resulting supernatant and precipitate were separated by decanting the supernatant into another 3 L glass jar for the ensuing fractional precipitation stage. The precipitation and separation steps described above were repeated by adding fresh hexanes in eight sequential aliquots as follows: 100 mL in five portions resulting in five fractions, 200 mL in two portions resulting in another two fractions, and finally, 600 mL in one portion resulting in a final fraction. After each step, the coagulated gummy material left in the container (after decantation) was rinsed with a 100 mL of the solvent mixture that had resulted up to that stage. After evaporation of the solvents, the isolated fraction was then air-dried, followed by vacuum drying in an oven set at 40 °C for 12 h. In general, solvent losses were kept to a minimum by ensuring that the suspensions and the supernatants were kept in sealed flasks and that whenever possible decantation was used instead of vacuum filtration.

Practical Fractional Precipitation Procedure of Softwood Kraft Lignin. The following methodology was developed as a means to adapt the previously described detailed fractionation to one that may be scaled industrially. The following procedure is based on the detailed molecular weights and ^{31}P NMR analyses accumulated from the fine precipitation procedure applied on KL1. Scheme 1 shows the steps developed that were applied to all lignins and their mixtures (see text).

A dry portion (100 g) of a lignin sample or a physical mixture of lignins was initially extracted with acetone (1000 mL) in a manner identical to that described in the section titled Detailed Fractional Precipitation of KL1 affording an insoluble solid residue (AIKL) and a supernatant (**I**).

The volume of the supernatant (**I**) was subsequently adjusted to 1.00 L with acetone prior to subsequent fractional precipitations using hexanes. During this practical setup, the first suspension was produced when 250 mL of hexanes was slowly added to the acetone supernatant (**I**) solution and kept under stirring until the gummy precipitate completely attached itself onto the inner walls of the container. This fraction (designated as ASKL Hex250) was then isolated by decanting the resulting supernatant (**II**) to another clean flask and subsequently washed with a solvent mixture (100 mL) of acetone and hexanes of the same composition as the solvent mixture used to precipitate it (which was 4:1 in this step).

To the supernatant (**II**), 750 mL of hexanes were added slowly under stirring to afford the second gummy residue designated as ASKL PI which was also isolated and washed with a fresh acetone/hexane (1/1) mixture and dried in a vacuum oven at 40 °C.

The resulting supernatant (**III**) was fully dried on a rotary evaporator and then redissolved with 200 mL of acetone. To this solution, 800 mL of hexanes was slowly added to generate a third fraction designated as ASKL PII. ASKL PII was washed with a mixture of acetone and hexanes at a ratio of 1/4 and dried in a vacuum oven. The final supernatant was found to contain less than 3% of lignin fragments of low molecular weight and therefore was not investigated but discarded.

Identical procedures were also applied to mixtures of the three available softwood kraft lignins. One mixture was composed of 70% KL1 and 30% KL2 and designated as sample [70]KL1[30]KL2, and the second mixture was composed of 30% KL1 and 70% KL2 and designated as [30]KL1[70]KL2. The third mixture was composed of equal amounts of the three available lignins and was designated as [33]KL1[33]KL2[33]KL3 (see footnote b in Table 3).

■ RESULTS AND DISCUSSION

Detailed Fractional Precipitation of Softwood Kraft Lignin. Theoretically, fractional precipitation may offer an infinite number of polymer fractions with the use of a continuous solvent gradient that involves two miscible organic solvents, one being a good solvent for a given polymer solution and the other being a poor solvent.[28] During this work, an effort was made to resolve the inherent heterogeneity of technical lignins by fractional precipitation with the aim to arrive at a technically feasible scheme that eventually may offer ways of refining this valuable technical resource. While acetone seems to be a good polar solvent for certain components of softwood kraft lignin, it offers a significant amount of a solid insoluble residue termed as acetone insoluble kraft lignin (AIKL). Good solvents for lignin such as dimethyl sulfoxide and N,N-dimethylformamide were not selected for this work due to their relatively high cost and boiling points. Hexanes were selected because they represent common nonpolar laboratory/industrial organic solvents miscible with acetone. During our endeavors to fully exploit and comprehend the methodology of fractional precipitation, a detailed effort was undertaken to fractionate lignin KL1 (Table 1). More specifically, KL1 was initially extracted with acetone to offer an acetone insoluble fraction (AIKL1) and a supernatant. The supernatant was quantitatively collected, diluted to a specific constant volume (1L), and then subjected to detailed fractional precipitation by the incremental addition of hexanes (Experimental Section). Every lignin fraction collected was designated as "N Hex", where "N" is the number of the total accumulated volume of hexanes in milliliters (mL) used for the particular fractionation step. Interestingly, the first two fractions, 100 Hex and 200 Hex obtained from the first two additions of 100 mL of hexanes to the acetone supernatant, were not fully soluble in acetone any longer after being dried. These are important considerations that require attention and further exploration as to the origin of these phenomena. In our efforts to arrive at a practical fractionation protocol that offers softwood kraft lignin fractions of consistent and reproducible characteristics, we thus excluded the fraction originating from the addition of 250 mL of hexanes (Figure 1). All subsequent fractions were fully soluble in acetone after dryness. All fractions including AIKL were then subjected to detailed characterization using GPC and quantitative ^{31}P NMR analyses.

Yields of Fractions. The yield for each fraction upon the addition of 100 mL aliquot of hexanes was found to vary significantly with each addition of hexane in the acetone solution (Figure 1). Overall, we observed a monotonic increase in the mass of lignin fraction collected up until the volume
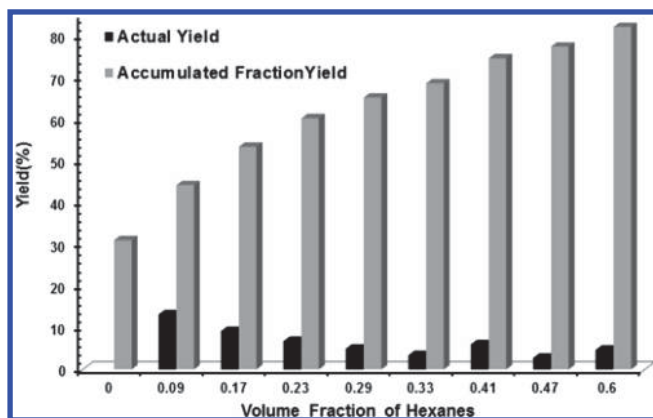
Figure 1. Yield of lignin fractions upon the addition of hexanes in an acetone solution (see Experimental Section, detailing the fractional precipitation of KL1) of ASKL.

Figure 2. Normalized and superimposed GPC chromatograms of lignin fraction from the fine fractional precipitation procedure of KL1.

fraction of hexanes reached 0.6. Beyond this point, only minor alterations in the actual yield of individual fractions were observed.

Because our work was focused on developing an understanding toward arriving at a practical protocol, it is worth noting here that sometimes hexanes in more than 100 mL were used in order to obtain a practical yield (see section titled Detailed Fractional Precipitation of KL1). For example, less than 5% in yield was obtained for the last fraction by using 600 mL of hexanes. The supernatant solution was continuously diluted so that the precipitation of lignin molecules became increasingly less efficient. Such additions are considered uneconomical in terms of solvent usage. Therefore, the fractional precipitation process was terminated at a total addition of 1500 mL hexanes. During our work, the final supernatant was not used because literature accounts have documented the possibility of it containing very high sulfur contents (>20%).[35,36] Overall, the accumulated yield of lignin during the fine precipitation efforts described here was nearly 80% (Figure 1). However, the generalized fractionation procedure to be discussed next involves final concentration and precipitation steps that significantly reduce the solvent usage and increase the fractionation yield up to 95%, which is in close agreement with earlier reported solvent extraction fractionation processes.[37]

Molecular Weight Characteristics of Fractions. During this work we used acetobromination as the preferred method of derivatization[34] in order to minimize intermolecular and intramolecular lignin interactions because such interactions have been shown to offer inconsistent data.[34,36] When the GPC chromatograms of the detailed fractions of KL1 were normalized to unity and superimposed (Figure 2), a clear trend became apparent. The chromatographic peaks progressively shift from low elution volumes to higher ones upon successive additions of hexanes. Table 1, among others, details the molecular weight information for the three examined starting lignins and indicates, as anticipated, that the polydispersity index (PDI = M_w/M_n) for KL1 is 6.1. The data displayed in Figure 2 shows that upon addition of hexanes the extreme heterogeneity of the starting kraft lignin, KL1, is dramatically reduced, and highly monodisperse fractions of lignin can be obtained ranging from 1.5 to 1.1 (note that the 200 Hex fraction is suggested to be discarded due to its peculiar insolubility behavior after drying). This is a significant advance over earlier solvent extraction efforts where the reported
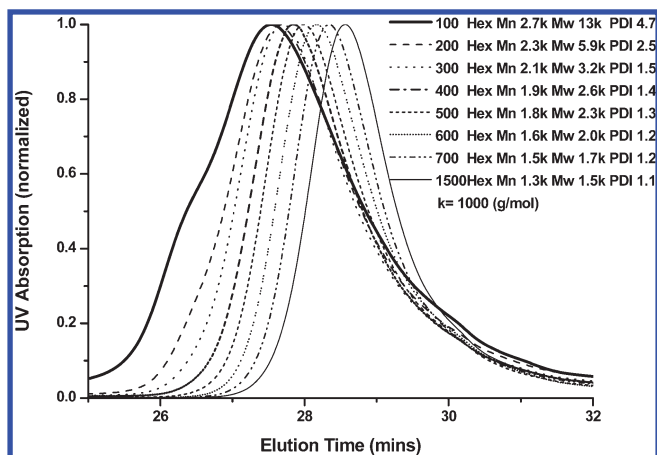
polydispersities are usually higher than 2[20,21] with the notable exception of some extraction processes using solvent mixtures.[12] The rationalization we offer for the fact that such highly uniform fractions of softwood kraft lignin can be created by fractional precipitation is because this process offers the ability to gradually alter the polarity of the environment the lignin molecules are solvated with and form a condition of complete dissolution. As such, theoretically, as the polydispersity of lignin fractions approaches unity, the finer is the selection of the solvent gradient.

Evidently (and in our view of commercial significance), the PDI of the examined lignin fractions drops quickly from 11 (for AIKL) to 4.7 and 2.5 for the first two fractions collected with the addition of 100 and 200 mL Hex, respectively (Figure 3).
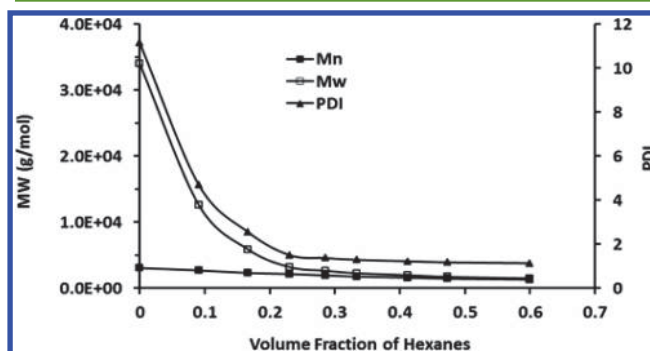
Figure 3. M_n, M_w, and PDI of fractions as a function of volume fraction of hexanes. AIKL is to be at 0% v/v of hexanes.

The PDI is then observed to decrease much slower, approaching 1.1 as the hexanes concentration was increased (Figures 2 and 3). The resulting uniformly narrow molecular weight distributions of the later fine fractions resulting from the detailed fractional precipitation are clearly demonstrated in the data of Figure 2.

It is also of value to note that the glass transition temperatures for the starting KL1 was determined to be about 148 °C and that of its acetone insoluble counterpart (AIKL) was about 180 °C, while the initial acetone soluble fraction (before any detailed fractionation) was about 110 °C. As anticipated, these data are in accord with the progressively decreasing molecular weight and PDI information presented and discussed in this section.

Table 2. Yield and Functional Group Information for All Fractions Obtained during the Fractional Precipitation of KL1 as a Function of Volume Fraction of Hexanes

	fraction information		OH content (mmol/g)[a]				
name	volume fraction of hexanes	yield of fraction (%)	aliphatic OH	condensed PhOH	noncondensed PhOH	total PhOH	COOH
AIKL1	0	31.0	3.28	1.75	1.83	3.58	0.44
100 Hex	0.09	13.2	2.35	1.96	2.04	4.00	0.52
200 Hex	0.167	9.2	2.30	2.17	2.35	4.52	0.59
300 Hex	0.231	6.8	2.18	2.16	2.33	4.49	0.57
400 Hex	0.286	5.0	1.95	2.07	2.34	4.41	0.58
500 Hex	0.333	3.4	1.87	2.12	2.44	4.56	0.60
700 Hex	0.412	6.0	1.81	2.18	2.58	4.76	0.64
900 Hex	0.474	2.8	1.72	2.25	2.93	5.18	0.71
1500 Hex	0.600	4.7	1.60	2.22	3.03	5.25	0.72

[a]Obtained by quantitative ^{31}P NMR.

Table 3. Yields for Each Fraction Described in the Fractionation Scheme of Figure 1 Resulting from Three Different Softwood Kraft Lignins and Yields of the Same Fractions Once Physical Mixtures of the Three Lignins Were Created

	yields for each fraction (wt %)								
				^{70}KL1^{30}KL2		^{30}KL1^{70}KL2		^{33}KL1^{33}KL2^{33}KL3[b]	
fraction designation	KL1	KL2	KL3	actual	estimate[a]	actual	estimate[a]	actual	estimate[a]
AIKL	32 ± 2	72 ± 3	30	48 ± 1	44	61	61	49	45
ASKL Hex250	31 ± 2	3.7 ± 0.3	29	19 ± 1	23	9.0	12	18	21
ASKL PI	21 ± 1	11 ± 0.5	25	19 ± 1	18	15	14	19	19
ASKL PII	15 ± 1	9.6 ± 0.6	12	13 ± 0.5	13	12	11	12	12

[a]Estimated yields were calculated as the weight average yields based on the weight percentages of the individual fractions previously obtained for KL1, KL2, and KL3. For example, the estimated yield of ASKL PI of ^{30}KL1^{70}KL2 can be calculated as 21 × 30% + 11 × 70% = 14. [b]For brevity purposes, the notation used here ^{33}KL1^{33}KL2^{33}KL3 actually represents 33.3 wt % for each lignin

Table 4. Functional Group Contents Obtained by Quantitative ^{31}P NMR Analyses for Initial Lignins and the Obtained Fractions

lignin ID	sample ID	aliphatic OH (mmol/g)	noncondensed phenolic OH (mmol/g)	condensed phenolic OH (mmol/g)	total PhOH (mmol/g)	COOH (mmol/g)
KL1	KL	2.37	1.99	2.52	4.51	0.67
	AIKL1	2.31	2.24	2.40	4.64	0.54
	ASKL1 Hex250	2.34	2.24	2.23	4.47	0.53
	ASKL1 PI	1.74 ± 0.07	2.27 ± 0.06	2.68 ± 0.11	4.94 ± 0.16	0.65 ± 0.06
	ASKL1 PII	1.29	2.10	3.89	5.99	0.77
KL2	KL2	2.58	1.72	2.09	3.81	0.46
	AIKL2	3.02	1.68	1.80	3.48	0.47
	ASKL2 Hex250	2.70 ± 0.08	2.05 ± 0.01	2.12 ± 0.08	4.17 ± 0.08	0.42 ± 0.02
	ASKL2 PI	2.17 ± 0.04	2.30 ± 0.04	2.68 ± 0.04	4.98 ± 0.08	0.43 ± 0.01
	ASKL2 PII	1.64 ± 0.04	2.18 ± 0.08	3.34 ± 0.19	5.52 ± 0.19	0.52 ± 0.03
KL3	KL3	2.31	1.93	2.41	4.34	0.62
	AIKL3	3.13	1.77	1.73	3.50	0.38
	ASKL3 Hex250	2.12	1.92	1.93	3.85	0.48
	ASKL3 PI	1.87	2.88	2.35	5.23	0.67
	ASKL3 PII	1.33	3.43	1.83	5.25	0.73

To better understand the fractional precipitation process, we plotted the molecular weights of the individual fractions of KL1 as a function of the volume fraction of hexanes (Figure 3). As such, one observes that both M_n and M_w of the individual fractions progressively decrease by increasing the hexanes concentration in the acetone solution, but M_w tends to decrease at a faster rate than M_n. Consequently the polydispersity index (PDI), calculated from the ratio of M_w and M_n, progressively decreases.

As such, the potential of the fractional precipitation approach is demonstrated here. The data is indicative of the fact that it is possible to obtain well-defined lignin fractions by the appropriate adjustment of the volume of hexanes into an acetone solution of softwood kraft lignin.

Functional Group Analyses. Detailed quantitative ^{31}P NMR analyses of all lignin fractions are shown in Table 2. Compared to AIKL, all fractions collected from the fractional precipitation are of lower aliphatic hydroxyl group content and of higher phenolic hydroxyl content (for both condensed and noncondensed phenolic OH forms). Similar phenomena have been previously reported and rationalized on the basis of the kraft process chemistry. This involves the formation of new phenolic hydroxyl groups and elimination of aliphatic hydroxyl groups while degrading native lignin into relatively small molecular weight kraft lignins.[13]

It is likely that the AIKL fraction may represent a group of lignin molecules that are closer to the native lignin molecules likely containing more aryl alkyl ethers. Detailed ^{13}C and two-

dimensional (2D) NMR analyses currently pursued for these samples in our laboratory may eventually shed light on these hypotheses. It is, however, important to point out that the yield of AIKL was about 70% (Table 3) for KL2, while it was about 30% for KL1. These large yield differences may be ascribed to the different way the wood was processed. For KL1, Table 1 shows that a bleachable grade pulp was aimed for, while for KL2, a linerboard material was to be manufactured. The associated kraft pulping delignification intensity as manifested in the H factors (Table 1) is much higher for KL1 than KL2. Consequently, this may explain why KL2 showed such a higher yield of AIKL compared to KL1. Furthermore, this is also reflected in the functional group differences reported in Table 4 for AIKL1 and AIKL2. The more intensive degree of delignification in KL1 resulted in AIKL1 containing about 33% more total phenolic OH than AIKL2. Such comparisons cannot be made for KL3 because the manufacturing details for it have not been disclosed.

Efforts to rationalize the functional group information presented in Table 2 with the hydrophobicity of the precipitation medium can now be made. Overall, it is apparent that as the amount of hexanes is enriched in the acetone/hexanes mixture, and the lignin fractions that precipitate out contain progressively lower aliphatic OH groups but higher total phenolic OH and COOH groups.

In fact, the plot of Figure 4a shows a linear relationship being applied for the ratio of aliphatic OH/phenolic OHs (condensed or noncondensed) as a function of volume fraction of hexanes in acetone. Similar linearity is also apparent for the number average molecular weight (Figure 4b). One needs to note that the molecular weights reported here are only relative because they were determined by using a calibration curve from polystyrene standards. Despite this, the linear relationship of Figure 4b between the number average molecular weight and the ratio of aliphatic hydroxyls to phenolic hydroxyl groups may indeed reflect an intrinsic correlation between the two. Despite the fact that no detailed molecular rationalization can be made at this time, it is envisaged that this empirical correlation may offer a better handle and understanding of the fractional precipitation of softwood kraft lignin using the binary system acetone/hexane.

Toward a Generalized Fractional Precipitation of Softwood Kraft Lignin. The effort described so far that demonstrated an understanding of the detailed fractional precipitation of softwood kraft lignin into a continuum of fractions (using KL1) can now be expanded and generalized. It is now possible to embark at developing a fractionation scheme of softwood kraft lignin with the minimum of steps. The fact that a continuum of narrow fractions can be isolated offers the possibility that representative specific narrow fractions, common to a variety of softwood kraft lignins, can be isolated irrespective of the manufacturing details of the pulping process. The significance of developing such a process rests with the fact that to date kraft lignin is viewed as a heterogeneous material. Its composition is relatively unpredictable because manufacturing variations in making pulp result in variable lignin streams that are usually incinerated. Creating the foundations for isolating a consistently homogeneous lignin stream from any lignin feedstock would thus offer a new way of refining lignin with significant commercial ramifications.

Our work was thus focused at arriving at an isolation practical protocol that will allow one to prepare softwood kraft lignin fractions that not only possess good homogeneity (narrow
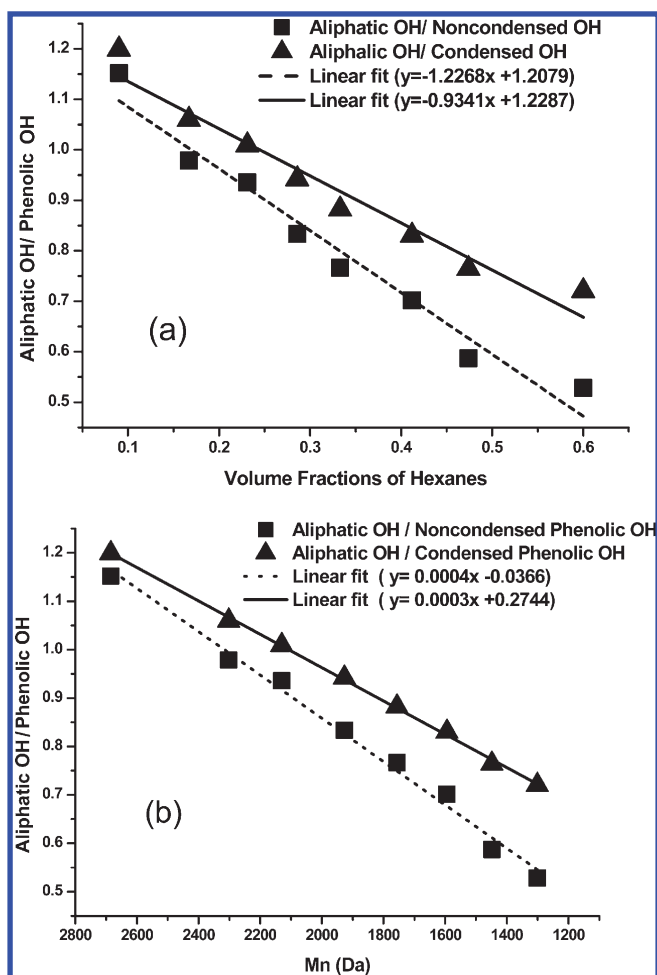
Figure 4. Plots of functional groups present on the various isolated fractions from KL1 as a function of hexanes/acetone volume fraction (a) and number average molecular weight, M_n (b).

polydispersity) but also are reproducibly produced in good yields from a variety of lignin streams and mixtures of kraft lignin.

The practical procedure developed is shown in Scheme 1. Using any of the three lignins described in Table 1, one may initially isolate the AIKL fraction via a simple acetone extraction step. The resulting acetone supernatant once diluted to 1.00 L and upon the slow addition of 250 mL of hexanes has a fraction appear (designated as ASKL Hex250) that needs be discarded. This is due to its peculiar insolubility in acetone once dried. The developed procedure showed that once ASKL Hex250 is removed and upon another addition of 750 mL of hexanes to the supernatant a consistent and reproducible kraft lignin fraction is produced that is designated ASKL PI. Ensuing work and data in this paper demonstrates the consistency and significance of this fraction. The remaining supernatant once dried and redissolved in 200 mL of acetone and upon the addition of 800 mL of hexanes offered the lignin fraction designated as ASKL PII.

Yields of Fractions Emerging from the Application of Scheme 1. Table 3 shows that each individual fraction significantly varies among the three different softwood kraft lignins we examined. This is to be anticipated because different pulping processes were used to delignify the wood, and as such, the lignins were degraded to different degrees resulting in variable initial kraft lignins (Table 1). As already noted, the

yield of AIKL in KL2 (low intensity pulping of wood creating liner board) was as high as 72 ± 3%, while the same fraction for the bleachable grade pulp KL1 was 32 ± 2%. In contrast, the fraction to be discarded (ASKL Hex250) in KL1 was about 31%, while in KL2, originating from the low intensity pulping process, was only about 4%. The common useful fraction among all lignins (ASKL PI) was about 21% and 25% for KL1 and KL3, respectively, and only 11% for KL2 for the lignin emerging from the low intensity pulping process. Overall, Table 3 shows that the proposed fractionation procedure may offer a total yield of lignin that is about 95%.

In an effort to further explore the universality of the devised practical fractionation protocol described in Scheme 1, we created physical mixtures of the examined technical lignins, KL1, KL2, and KL3 and subjected these mixtures to the proposed fractionation scheme. We then measured yields of the various fractions produced and compared them to the calculated yield estimates based on the yields of fractions obtained when each lignin was used individually (Table 3). Three physical mixtures of the starting lignins were created: mixture (a) containing 70 wt % of KL1 and 30 wt % of KL2, mixture (b) containing 30 wt % of KL1 and 70 wt % of KL2, and mixture (c) containing equal amounts of KL1, KL2, and KL3 (33.3 wt % of each). An examination of the yield data of Table 3 reveals that the calculated estimates for nearly all fractions are relatively close to those experimentally obtained from the mixtures. One important practical consideration that was found to significantly affect the accuracy and reproducibility of our yields is the way the initial acetone lignin solution is created. During our work, we determined that it was beneficial to add the initial lignin (100 g) incrementally, over a period of half an hour. This allowed it to slowly disperse into acetone (1000 mL) under vigorous agitation followed by moderate stirring for another 6 h at room temperature. This procedure was found to offer consistently reproducible fraction yield data. Adding the acetone into solid lignin under agitation was found to be undesirable because the lignin was not dissolved evenly.

The fact that both binary and ternary mixtures offered yield data consistent with the calculated values lends support to the universality of the proposed approach and adds confidence that reproducible fractions can be isolated from different softwood kraft lignins irrespective of their manufacturing details.

Chromatograms of Individual Fractions. The data of Figure 5 shows the size exclusion chromatograms of all individual fractions that emerge from the devised fractionation scheme depicted in Figure 1. The comparison of these three sets of chromatograms offers qualitative evidence as to the fact that the proposed fractionation scheme offers fractions of similar molecular weight distribution among the three different examined lignins (KL1, KL2, KL3; Table 1). For example the chromatograms of the initial KL1, KL2 and KL3 (Figure 5a, 5b and 5c respectively) are broad as anticipated (see Table 1 for their specific molecular weight information).

For all three lignins, a bimodal molecular weight distribution is apparent for their AIKL fractions. These fractions show the highest average molecular weight and an apparent secondary peak located in the high molecular weight end of the distribution. Furthermore, all AIKL values show a low-intensity but very broad shoulder at the very high molecular weight end of the chromatograms. Similar features were also apparent in the work of Ropponen et al.[12] despite the fact that their solvent
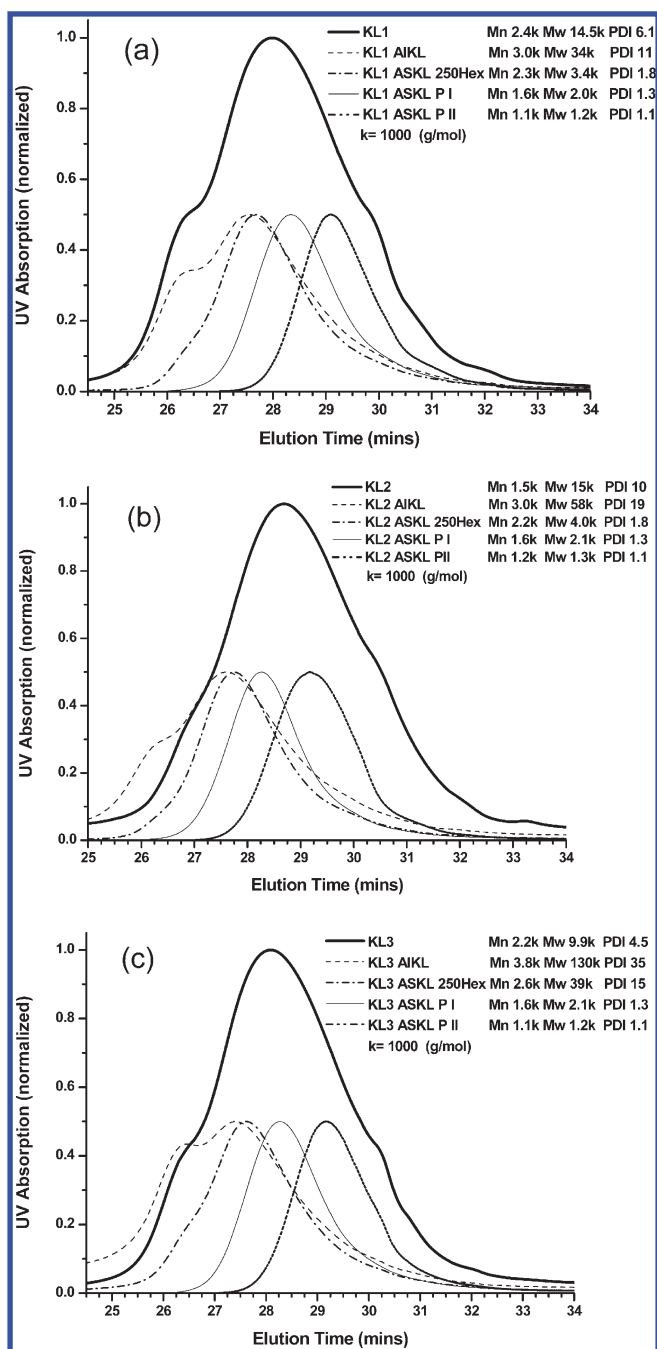
Figure 5. Overlay of normalized GPC chromatograms of KL1 (a), KL2 (b), and KL3 (c) and their fractions.

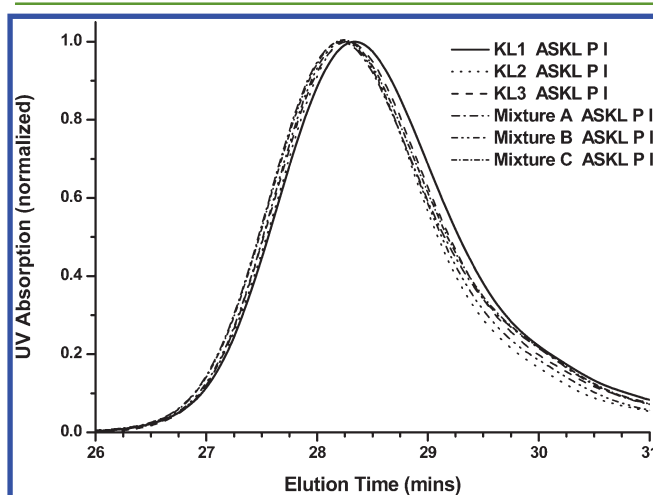selection and their chromatographic elution solvent were different from ours.

Subsequent fractions obtained by fractional precipitation show that all fractions are progressively becoming uniform as one moves from AIKL to ASKL PI and ASKL PII.

Fractions designated ASKL Hex250 are seen not to contain an apparent high molecular weight shoulder; however, they still possess a secondary peak (at an approximate elution volume of 26.6 ML) in the high molecular weight end of their distributions similar to that of AIKL albeit of considerably lower intensity. Finally, fractions ASKL PI and PII are seen to be always of the lowest molecular weight and monodisperse for all three lignins KL1, KL2, and KL3.

Functional Group Analyses and Data Trends Obtained From the Application of Scheme 1. Overall, the hydroxyl content analyses of the fractions as obtained from quantitative ^{31}P NMR analyses are listed in Table 4.

Selected reported data is also associated with very low standard deviations testifying to the reproducibility of the developed fractionational precipitation procedure outlined in Scheme 1. For all three kraft lignins, KL1, KL2, and KL3, the aliphatic hydroxyl contents of the fractions show a consistent descending order in the sequence of the isolation process, i.e., AIKL > ASKL Hex250 > ASKL PI > ASKL PII. The total phenolic hydroxyl contents, however, show an opposite trend (AIKL < ASKL Hex250 < ASKL PI < ASKL PII). Similar trends were also apparent and reported during kraft lignin fractionation efforts using ultra filtration.[35] Overall, these data and their agreement with literature trends[13] point to the possibility that the nature and abundance of the functional groups present in softwood kraft lignin fractions is directly related to the molecular weight of the fraction as already pointed out by the data of Figure 4b.
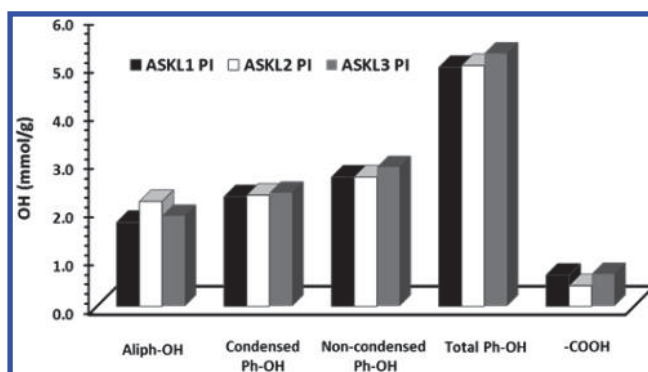
Common Fraction ASKL PI. The power of the fractional precipitation approach becomes apparent in the data of Figure 6 where fraction ASKL PI, obtained from the three different

Figure 7. Comparison of hydroxyl group contents of the ASKL PI fraction from different kraft lignin samples obtained by the application of the procedure outlined in Scheme 1.

This practical procedure demonstrates that it is possible to arrive at a consistent homogeneous fraction originating from different softwood species that have been subjected to different kraft pulping conditions. It is to be noted, however, that the actual description of the "practical" fractionation scheme presented in Scheme 1 does not represent a final commercial flow chart but simply an embarkation point, whose details need to be closely examined from a technical and financial point of view.

Elemental Analyses of Fractions. Two of the examined industrial technical lignins (KL1 and KL2) and selected fractions were subjected to heavy metal analyses. Because sulfur content is an important technical variable associated with the quality and future utility of a given kraft lignin, this was also measured. The data of Table 5 does not show consistent and

Figure 6. Normalized and superimposed GPC chromatograms of KL1, KL2, and KL3 and their mixtures: mixture A = ^{70}KL1^{30}KL2, mixture B = ^{30}KL1^{70}KL2, and mixture C = ^{33}KL1^{33}KL2^{33}KL3.

Table 5. Sulfur and Metal Analyses for Two Initial Softwood Kraft Lignins and Selected Fractions

sample ID	S (w/w %)	Na (w/w %)	Fe (mg/kg)	Mn (mg/kg)	Cu (mg/kg)
KL1	1.64	0.12	50.2	25.7	1.07
ASKL1 PI	1.32	0.011	15.0	ND	<1.00
AIKL1	1.49	0.32	121	80.7	2.32
KL2	1.75	1.37	112	37.5	2.24
ASKL2 PI	1.08	0.077	10.7	<1.00	<1.00
AIKL2	2.07	1.97	152	54.8	3.26

softwood kraft lignins, and the three physical mixtures (Table 3) are normalized and superimposed. As per the overall objectives of our work, the fractional precipitation approach depicted in Scheme 1 shows that lignin fractions of nearly identical narrow molecular weight distributions (without a high molecular weight shoulder or tail) can be obtained from all three different kraft lignins. Notably, this is irrespective of the processing details of which the wood has been subjected. Creating binary and/or ternary physical mixtures of industrial kraft lignins and subjecting them to the fractionation procedure of Scheme 1 offers the consistent common fraction ASKL PI with an identical molecular weight distribution.

It is of extreme significance to note that all the ASKL PI fractions have shown exceptional similarity in their molecular weight characteristics and are also shown to be very close in their hydroxyl group contents (Figure 7) irrespective of their different industrial kraft processes and wood origins.

conclusive variations on the sulfur contents among the different fraction and the two lignins examined. This somewhat correlates with variable literature accounts as well.

For example, Mörck et al. reported that a sulfur content of 2.7% was present in a lignin fraction obtained from an industrial softwood kraft black liquor using an organic solvent fractionation procedure.[29] Mikaela et al., however, reported sulfur contents as high as 27% in a low molecular weight fraction obtained via ultra filtration.[35] Interestingly, the last authors have reported dramatic reductions in sulfur contents by using a nonpolar organic solvent extraction of the starting lignin prior to ultrafiltration.[35]

During this work we determined that the sulfur contents for the "common fraction" ASKL PI obtained from KL1 and KL2 were 1.32% and 1.08%, respectively. These figures are lower than the sulfur contents of the starting nonfractionated materials (20% and 38% less for KL1 and KL2, respectively). Furthermore, they compare well with the data obtained with organic solvent fractionation data as reported by Mörck et al.[29]

In relation to metal contents measured (sodium, iron, manganese, and cooper), the data of Table 5 points out to the fact that the fractional precipitation procedure that affords the fraction ASKL PI, beyond refining a kraft lignin stream, also removes inorganic substances such as heavy metals. Notably, the iron content of ASKL PI is seen to be dramatically reduced compared to the starting lignins (KL1 and KL2). Iron tends to form strong complexes with catechols present in technical lignins. As such, one tentative rationalization that may be offered for this observation is that the catechol content of this fraction (ASKL PI) could be significantly reduced, thus accounting for its reduced iron binding capacity. In contrast to this observation, however, the data of Table 5 shows that the AIKL fraction tends to encapsulate a significant amount of the heavy metals as evidenced by the increases reported in it for all metals measured.

■ CONCLUSIONS

Starting from a state of complete dissolution in a polar solvent, lignin molecules can be precipitated upon gradual additions of a selected miscible but nonpolar solvent. In this way, the molecular composition of each lignin fraction can be manipulated by adjusting the solvent mixture along an almost continuous solvent gradient. In this work, acetone and hexanes were used as the polar and nonpolar solvents, respectively. A number of aliquots of hexanes when slowly added into an acetone extract of a technical kraft lignin offered a series of well-defined lignin fractions. The knowledge accumulated from this detailed fractionation effort was then used to devise a practical fractional precipitation procedure by unifying fractions of similar molecular weights and distributions. As such, two homogeneous fractions (ASKL PI and PII) of narrow molecular weight distributions were afforded in combined yields ranging from 20% to 37% by weight. The developed fractionation procedure was shown to afford a nearly identical fraction from three different softwood kraft lignins irrespective of their manufacturing details. The validity of the procedure when examined with artificial physical mixtures of technical lignins offered data in accordance with predicted calculated values.

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Notes
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