

Characterization of Fractions Obtained from Two Industrial Softwood Kraft Lignins

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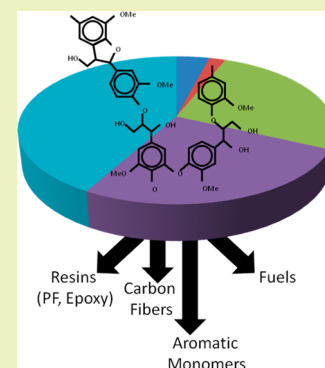
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S Supporting Information

ABSTRACT: With increasing interest in using lignin as an alternative material to petroleum-based chemicals (e.g., in the manufacture of carbon fibers or adhesives), it is becoming important to understand what properties of lignin are required to impart key features in the final product. Commercial lignins are complex, heterogeneous, macromolecular mixtures. To obtain maximum value, lignins will require classification and possibly fractionation or modification to improve properties and enable their utilization in high-value applications. To this end, the physicochemical properties of fractions derived from two industrial softwood Kraft lignins (New Bern Mill, Weyerhaeuser, U.S.A., and Backhammar Mill in Kristinehamn, Sweden) have been determined and compared to previously published data on commercially available Indulin AT lignin from MeadWestvaco.^{1,2} The fractions were obtained by successive extraction with organic solvents and analyzed using a range of techniques (e.g., DSC, ¹³C NMR, ³¹P NMR). The results showed that these industrial softwood Kraft lignins varied significantly in both the amounts of the various fractions and in the properties of the analogous fractions. These differences emphasize the issues industry faces in the utilization of industrial lignins for high-value applications where minor inconsistencies between lignin sources could pose major technical challenges.

KEYWORDS: ³¹P NMR, ¹³C NMR, Elemental analysis, Lignin, Molecular weight distribution, Thermal properties



INTRODUCTION

After cellulose, lignin is said to be the second most abundant terrestrial source of carbon. Depending on the origin, lignin can make up 20–30% of a plant source.³ In its natural form, lignin is a polyaromatic polymer composed of phenylpropanoid units with varying degrees of methoxylation. Softwood lignins, like the ones used in this study, are composed of primarily guaiacyl (G) lignin units with methoxyl groups at the C3 position and a small amount of *p*-hydroxyl (H) lignin units, which have no methoxyl groups. Softwood lignins contain virtually no syringyl (S) lignin, which have methoxyl groups at both the C3 and C5 positions.⁴ Within the plant, lignin provides structural integrity as well as acting as an antimicrobial agent, protecting the plant from diseases. Its inherent hydrophobicity also aids in providing capillary action to trees and assists the migration of water throughout the biomass.

Lignin has been investigated over the years as a possible renewable source for many applications.^{5–15} Those applications range from low-value usages, such as fuel, to high-value applications, such as fine chemicals. One of the most attractive areas of high-value lignin research deals with converting lignin into carbon fiber.^{11–13,16–18} The use of lignin as a raw material offers many benefits. Not only does it displace a nonrenewable material with a renewable biomaterial, but lignin has the potential to be produced at a lower cost than its petroleum counterparts, and very importantly, it is not dependent on the perpetually volatile petroleum market.¹⁹

With the higher value applications of lignin comes a necessity to better understand and characterize lignin. Having high lignin purity has been speculated to be crucial to the ability to form good quality lignin carbon fibers.²⁰ Additionally, the processability of lignin, in particular for carbon fiber production, has been shown to depend on its chemical structure, which in turn depends on the source of the lignin and how the lignin is isolated from the source.^{21–24} A number of studies over the years have shown that Kraft lignin is generally structurally heterogeneous and that its exact composition depends on the isolation method used.^{25–27} Recently, the nature of the lignin (e.g., hardwood vs softwood, ultrafiltered vs not) has been shown to have a direct impact on the spinnability and thermal behavior of lignin fibers, spun with the intent of using them for carbon fiber formation.^{10,11} However, to our knowledge, there have been no studies to date to link the chemical and thermal properties of softwood lignins to fiber properties. Due to this necessity for more complete comprehension, fractions were produced from two industrial softwood Kraft lignins. These lignins and fractions were extensively characterized for molecular weight, contamination, and chemical functionality, which are all properties highly important for applications in carbon fiber production.

Received: September 16, 2014

Revised: November 21, 2014

Published: November 24, 2014

MATERIALS AND METHODS

Two industrial softwood Kraft lignins (SKLs) were used for this work. The first SKL was primarily southern pine obtained from the New Bern Mill belonging to the Weyerhaeuser Company, U.S.A. (WY SKL), and the second SKL was Norwegian spruce from the Backhammar Mill in Kristinehamn, Sweden (BH SKL). New Bern produces a bleached fluff pulp, and the Backhammar mill produces an unbleached linerboard. Both lignins are softwood Kraft lignins, which are similarly isolated from black liquor via acidification with CO₂ to a pH of approximately 10. The lignin was filtered and washed further with H₂SO₄ to displace the sodium ions on the lignin.^{30,31}

The solvents for the fractionation process were purchased from Integra Chemical, and all were 99 plus grade. Deuterated solvents (CDCl₃ and DMSO-*d*₆) were purchased from Sigma-Aldrich and had a purity of 99.9%.

Solvent Fractionation Process. The SKLs were fractionated according to the process outlined by Morck et al.²⁵ Ash content data, measured at 725 °C, was provided by Weyerhaeuser. Unfractionated BH SKL had an ash level of 0.89 wt %, and unfractionated WY SKL contained 0.30 wt %. Because both unfractionated SKLs had very low ash content, the acid and water washing steps were omitted. In comparison, the ash content of Indulin AT was reported by Weyerhaeuser to be 11.5 wt % using the same method. The large difference in purity between the lignins reported in this paper and those for Indulin AT are likely to have an impact on the properties of the fractions. Prior to fractionation of the SKLs, the lignins were dried overnight at 105 °C, and then 500 g of oven-dried lignin was added to 2.5 L of the respective solvent while stirring. After addition, the suspensions were stirred at room temperature for an additional 30 min. The slurry was then filtered. The undissolved material was then resuspended in an additional 2.5 L of the same solvent. This suspension was stirred for an additional 30 min before being filtered. The undissolved material was washed in the filter with an additional 1 L of solvent. The remaining undissolved material was dried thoroughly and ground into a fine powder (when necessary).

The dissolved filtrates were combined, and the dissolved material was recovered by removing the solvent under reduced pressure using a Heidolph Laborata 4001 rotary evaporator. The recovered material was then further dried overnight in a vacuum oven under reduced pressure and a temperature of 50 °C. The fractions were then ground and stored in a desiccator until further use.

The solvents involved in the fractionation exhibit a range of solvation properties (Table 1). Previous work has shown that the

Table 1. Hildebrand Solubility Parameters and Polarity Indices for Solvents Used in Fractionation Process

solvent	δ (cal ^{1/2} cm ^{-3/2})	polarity index
dichloromethane	9.93	3.1
<i>n</i> -propanol	11.97	4
methanol	14.28	5.1

solubility of lignin increases as the hydrogen bonding capability of the solvent increases and as the Hildebrand solubility parameter approaches 11. Lower molecular weight fractions of the lignin (F1 and F2) are soluble in a broader range of solvents. This enabled the selective isolation of the NB and WY F1 and F2 fractions in solvents with lower Hildebrand solubility parameters, such as dichloromethane and *n*-propanol. Additionally, it was previously found that when hydroxylated solvents (such as water and low alcohols) are added to low hydrogen bonding-capable solvents with a Hildebrand solubility parameter δ value greater than 9, the overall lignin solubility in the mixture is greater than the individual solvents. Typically, the hydrogen bonding capability of the mixture is also greater than the individual solvents. Because the solubility of lignin will be affected by both molecular weight and chemical structure, this broad range of solvents allows the production of fractions of increasing molecular weight and differing chemical functionality.

Molecular Weight Determination. The lignin samples were all acetylated to allow for dissolution in tetrahydrofuran (THF) for gel permeation chromatography (GPC) analysis. A total of 100 mg of dry lignin samples were acetylated by stirring with 1 mL of acetic anhydride and 1 mL of pyridine at room temperature for 24 h. After 24 h, the reaction was quenched by the addition of ethanol. The acetylated lignins were then isolated by removing the solvent and reagents in a vacuum oven. The dry samples were then dissolved in THF for molecular weight analysis using an Agilent 1200 series liquid chromatography system equipped with ultraviolet (UV) detector. The dissolved sample was filtered through a 0.45 μ m membrane filter prior to injection. A total of 20 μ L of the sample was automatically injected. GPC analyses were completed using a UV detector on a 4-column sequence of Waters Styragel columns (HR0.5, HR2, HR4, and HR6) at 1.00 mL/min flow rate. Polystyrene standards were used for calibration. WinGPC Unity software (version 7.2.1, Polymer Standards Services USA, Inc.) was used to collect data and determine molecular weight profiles.

Differential Scanning Calorimetry. Differential scanning calorimetry (DSC) was done to measure the glass transition (T_g) of the lignins using a TA Instruments DSC Q200. Lignin samples were dried overnight in a vacuum oven before approximately 5 mg was weighed into T Zero aluminum pans and sealed hermetically. All samples were run with a gas flow of 50 mL/min at a heating and cooling rate of 10 °C/min. The lower temperature was set to -75 °C for each sample, but the upper temperature depended on the degradation temperature of the sample. Indeed, the lower molecular weight samples typically degraded at a lower temperature as compared to the high molecular weight samples. An initial DSC scan was done in order to observe the onset of degradation. From that data, the upper temperature, which occurred before this onset of oxidation, was determined for each sample. New samples were prepared according to the above procedure for the DSC scans, which were used to obtain the T_g (s) for the lignins. For each run, two heating and cooling cycles were recorded with measurements being done on the second cycle. The glass transition was calculated using TA Instruments Universal Analysis 2000 software, which calculates the T_g at 1/2 ΔC_p for the transition. Three replicates were obtained for each sample.

Thermal Gravimetric Analysis. Thermal gravimetric analysis (TGA) was done using a TA Instruments TGA50. Lignin samples of about 15 mg were analyzed for weight loss in platinum pans using air as a purge gas. The temperature was ramped to 105 °C (with data collection off) and held for 1 min to eliminate any moisture acquired during sample transfer. The data collection was then turned on, and the samples were heated at a rate of 15 °C/min to 1000 °C.

Carbohydrate Analysis. Sugar analysis was performed by converting the polysaccharide components to monomers by hydrolysis with sulfuric acid. The sugar stream was then separated via high performance anion exchange chromatography and pulsed amperometric detection (HPAEC/PAD). The amounts of individual sugars were calculated by comparing to peak integrations obtained for known standards.

Total Sulfur Analysis. Total sulfur was measured using the ASTM D1552-90 standard test method, using a Leco S632 sulfur analyzer.

Elemental Analysis. Elemental analysis was performed according to ASTM D5373-02 method using a Carlo-Erba elemental analyzer.

³¹P NMR of Lignins. The ³¹P NMR spectra of the lignin samples were collected using a Bruker 400 MHz DMX NMR spectrometer. The samples were first dried under vacuum for 24 h at 40 °C and then phosphorylated according to the literature.²⁸ Specifically, 30 mg of lignin was accurately weighed into a 2 mL vial. The internal standard cyclohexanol (10.85 mg/mL) and relaxation agent chromium(III) acetylacetonate (5.0 mg/mL) were added, followed by 0.5 mL of a solvent of pyridine/CDCl₃ (1.5/1 v/v). The mixture was then reacted with 50 μ L 2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane (TMDP). The spectra were recorded with a 25 s pulse delay and 128 scans at room temperature.

¹³C NMR of Lignins. The ¹³C NMR spectra were recorded using a 500 MHz Avance spectrometer, operating at a ¹³C frequency of 125.66 MHz. Samples were prepared according to the literature.²⁹ The spectra

were recorded using a ^{13}C 90° pulse width of 15 μs , 1.4 s relaxation delay, and 40,000 total scans at room temperature.

RESULTS AND DISCUSSION

Lignin purity and chemistry are extremely important for the production of high performance carbon fibers from lignin. The best performing lignin-based carbon fibers have been produced using a solvent purified/fractionated Kraft lignin.³⁰ Through solvent purification/fractionation, the requisite properties required for fiber spinning and subsequent thermal processing are obtained albeit not fully understood. Various methods exist to purify/fractionate lignins including solvent fractionation,^{1,25–27,31–33} ultrafiltration,^{34–37} and combinations thereof.^{38,39} For the purpose of this study, the well-established solvent fractionation protocol of Morck et al.²⁵ was chosen. This sequential extraction of isolated lignin with solvents of increasing Hildebrandt solubility parameter (Figure 1) produce

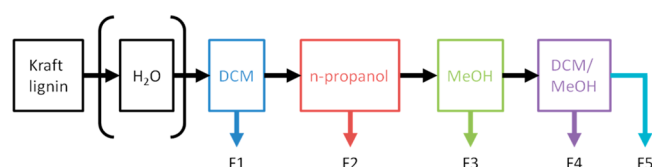


Figure 1. Solvent fractionation schematic, using the method described by Morck et al.²⁵ From left to right, the undissolved portion is dissolved in the following solvent. Specifically, the water-washed lignin is first washed with DCM, CH_2Cl_2 (blue), to produce the F1 fraction. The insoluble lignin is then washed with *n*-propanol, $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$ (red), to produce the F2 fraction, then washed with MeOH, CH_3OH (green), to yield the F3 fraction, and finally DCM/MeOH in a 70/30 v/v ratio (purple) to produce the F4 fraction, and the remaining insoluble fraction (F5). Note that for the samples herein the water wash was omitted, as indicated by the brackets.

lignins with discrete chemical and physical properties that have been extensively reported in the literature, thereby enabling a comprehensive comparison of the findings presented herein. The resulting fractionation yields for both SKLs are shown in Figure 2. As previously mentioned, the lignins are both softwood and were extracted from black liquor in essentially identical manners. Despite this, and the fact that softwood lignins, which unlike hardwood lignins, reportedly do not significantly vary between species, there are major differences in the solubility.^{40,41} Notably, WY SKL contains a much larger amount of the lower molecular weight fractions (F1 and F2)

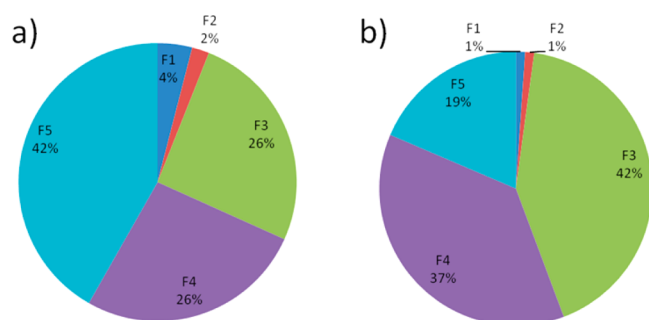


Figure 2. (a) Fractionation yields (% of starting material) for Fraction 1 to Fraction 5, starting from WY SKL and (b) starting from BH SKL. The associated error is ± 0.1 wt %. The values are rounded in the figure for clarity (see text for numbers reported to the correct significant digits).

(Figure 2). The amount of WY SKL F1 is 4 times the amount of BH SKL that is soluble in the same solvent and almost twice that of the previously reported Indulin AT SKL F1.² Similarly, WY SKL also contains 2 times the amount of *n*-propanol-soluble lignin (F2) when compared to both BH SKL and Indulin AT SKL. Another notable difference is the amount of F5 lignin, the insoluble material remaining at the end of the sequential solvent fractionation process (Figure 1). BH SKL and Indulin AT SKL have a much lower F5 yield (18.6 and 25.0 wt %, respectively) when compared to WY SKL (41.8%). These results suggest that the composition of industrial softwood Kraft lignins differs significantly from one source to another. It appears that the differences in the Kraft cooking conditions, e.g., Kappa, sulphidity, etc., contribute significantly to the differences in the lignin properties. It is known that the source black liquors obtained from the two mills differ with respect to targeted end Kappa numbers. The Backhammar lignin is derived from black liquor obtained by pulping to a Kappa of approximately 40,⁴² whereas the New Bern black liquor is from Kraft pulping to a Kappa of 28–32. It is also quite possible that the more severe pulping conditions used at New Bern result in a black liquor containing a more condensed higher molecular weight lignin. This may explain the greater yield of the NB F5 fraction compared to the BH F5 lignin.

Prior research²⁵ shows that as the polarity of the solvent used for extraction increases so does the molecular weight of the extracted lignin. However, because the solubility of the lignin fractions will depend both on molecular weight and on chemical functionality, one should not be surprised if there are minor discrepancies in the trend of increasing molecular weight from F1–F5 (Table 2). GPC analysis of the lignin fractions follows this expected trend for both Indulin AT SKL and WY SKL. For the BH SKL, the F2 lignin had a greater relative \overline{M}_w (2390 Da) than the F3 fraction (1890 Da). Even after acetylation, both the WY SKL and BH SKL F5 fractions had minimal solubility in all solvents (e.g., THF) and alkali. Most was removed during filtration. As a result, the molecular weight for the F5 fractions is most likely not representative of the entire fraction and should be used cautiously (Table 2). Along with the increase in molecular weight from F1–F5, the polydispersity also increases. The GPC analysis further confirms what was observed from the results of the solvent fractionation. The unfractionated SKLs themselves show significant differences in molecular weight, as well as the molecular weight distribution (Figure S1, Supporting Information). The unfractionated WY SKL has a relative weight-average molecular weight (\overline{M}_w) of 6900 Da, which is almost twice that of the unfractionated BH SKL \overline{M}_w of 3830 Da. As previously mentioned, although WY SKL has a substantially greater amount of the low molecular weight F1 fraction, it also has a substantially larger amount of the high molecular F5 fraction, which provides evidence for the higher polydispersity of WY SKL (4.6). Additionally, having 41.8% of F5 largely explains WY SKL having a much higher relative \overline{M}_w than BH SKL.

The fractions for both WY and BH SKL show a strong positive correlation between relative molecular weight and glass transition temperature (T_g) (Figure 3). Similar to other reported SKLs,⁴³ unfractionated BH SKL has a T_g of 151 °C. However, the unfractionated WY SKL shows unique thermal properties. Despite having a higher relative molecular weight (~ 6900 Da), unfractionated WY SKL has a lower T_g (122 °C) than unfractionated BH SKL, which is a counterintuitive and surprising discovery. This anomaly has been explained by the

Table 2. Average Relative Molecular Weights (\overline{M}_w , \overline{M}_n) and Polydispersity ($\overline{M}_w/\overline{M}_n$) of Lignin Fractions^a

fractions	\overline{M}_w (Da)	\overline{M}_n (Da)	$(\overline{M}_w/\overline{M}_n)$ (Da)	fractions	\overline{M}_w (Da)	\overline{M}_n (Da)	$(\overline{M}_w/\overline{M}_n)$ (Da)
WY SKL ^b	6900	1500	4.6	BH SKL ^b	3830	960	4.0
WY SKL F1	611	380	1.6	BH SKL F1	882	420	2.1
WY SKL F2	1620	650	2.5	BH SKL F2	2390	720	3.3
WY SKL F3	2070	740	2.8	BH SKL F3	1890	460	4.1
WY SKL F4	5960	1150	5.2	BH SKL F4	6240	1490	4.2
WY SKL F5 ^c	3330	930	3.6	BH SKL F5 ^c	7030	1710	4.1

^aError in the molecular weights and in the polydispersity is ± 10 and ± 0.1 Da, respectively. ^bUnfractionated. ^cF5 fractions were only partially soluble in THF after acetylation, so GPC results would not be representative of the entire fraction.

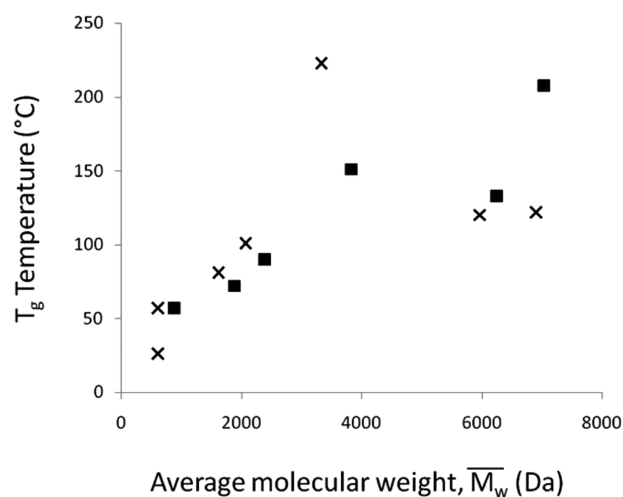


Figure 3. Correlation between the average relative molecular weight of the lignin samples studied here and their measured T_g . The data for the WY SKL and its corresponding fractions are shown using X, whereas the BH SKL and its fractions are represented by black filled squares. The error associated with the T_g is ± 1 °C and that of the average molecular weight is ± 10 Da.

high amount of relatively low molecular weight lignin in WY SKL, which acts as a plasticizer and lowers the observed T_g of the unfractionated WY SKL.⁴⁴

Analysis of the thermal stability of the lignin fractions via TGA showed that the major degradation occurred between 500 and 600 °C (Table 3), a temperature which is slightly higher than for some other softwood lignins reported in the literature.^{45,46} However, complete decomposition occurred within the typical range of 500–950 °C, in agreement with literature reports.^{7,46,47} A comparison of the data in Tables 2 and 3 suggests that there appears to be no correlation between molecular weight and thermal stability. Recent work⁴⁵ has suggested that the thermal stability of lignin is related to both molecular weight and chemical composition. Our data suggests that perhaps chemical composition is more important than the molecular weight for thermal behavior. Certainly, it would appear that solubility in the various organic solvents used may

play a role. The F5 fraction for the BH SKL had lower maximum degradation temperatures compared to the F1–F3 counterparts. For the WY SKL F5, the trend is much less clear. Ropponen et al.⁴⁶ also analyzed solvent extracted fractions for thermal stability, and their results indicated that the insoluble fraction for softwood Kraft lignin was less thermally stable. This was in contrast to the insoluble material obtained during fractionation of hardwood Kraft and organosolv lignin, which was deemed to be higher in inorganic content. As a result, those insoluble fractions underwent degradation at a higher temperature than their soluble counterparts. For the samples investigated here, the inorganic content of both WY SKL and BH SKL was very low, less than 1.00 wt % ash (error ± 0.02 wt %).

To better understand the chemical composition of the generated fractions and their potential effect on the lignin properties, the carbohydrate contents were determined. It is known that during Kraft pulping, some of the lignin molecules dissolved in the black liquor still have carbohydrate molecules attached to them. During lignin precipitation from black liquor, some of these carbohydrates are precipitated and recovered along with the lignin. Because some are covalently bound, they cannot be easily removed during the washing process. The low quantities of glucose and mannose observed among the fractions demonstrates the sensitivity of glucomannans to the Kraft process. They are dissolved very quickly in the process and not observed to a large extent in the lignin. Galactose and arabinose are observed to a much greater extent in the lignin fractions and indicate their higher stability to the harsh cooking conditions. The carbohydrate concentrations for the WY and BH SKL fractions are shown in Figure 4; similar trends are observed for both WY SKL, BH SKL, and Indulin AT SKL fractions.^{1,2} The F1 fraction contained virtually no sugars, while F5 had the greatest level for both lignins. However, there is no positive linear correlation between relative average molecular weight and carbohydrate content because the F4 fractions, which are among the highest relative molecular weight for both lignins, contained the second lowest level of sugar contamination. Because the insoluble F5 fraction does contain the largest amount of carbohydrates and these fractions are

Table 3. TGA Analysis of SKLs Fractions^a

fractions	dW/dT (max) (°C)	T (90%) (°C)	fractions	dW/dT (max) (°C)	T (90%) (°C)
WY SKL F1	543	220	BH SKL F1	566	271
WY SKL F2	571	253	BH SKL F2	571	288
WY SKL F3	535	275	BH SKL F3	570	277
WY SKL F4	501	274	BH SKL F4	570	331
WY SKL F5	534	278	BH SKL F5	542	306

^adW/dT is the derivative weight peak, and T (90%) is the temperature at which 10% of the weight loss occurred (error ± 1 °C).

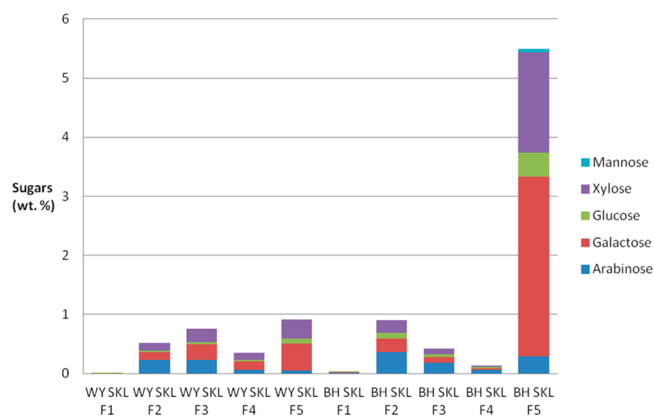


Figure 4. Carbohydrate weight percent for the SKL fractions by sugar type. The typical error is ± 0.05 wt %.

hypothetically the highest molecular weight, we can speculate that perhaps both molecular weight and sugar contamination affect the propensity of lignin to dissolve in certain solvents.

To gain further insight into the chemical nature of the fractions, elemental analysis was performed. The data shown in Table 4 indicate that overall the percentages of each element is fairly uniform across the fractions, with the exception of WY SKL F1 and F2. The lower carbon content in WY SKL F1 suggests the presence of a higher amount of another element, such as O or S. Likewise, the higher carbon content in WY SKL F2 suggests the potential presence of less O or S in these fractions.

Given the elemental analysis data above, the total sulfur content was measured, as shown in Table 5 and Figures S2 and S3 of the Supporting Information. Previous work⁴⁸ showed that the lower molecular weight fractions contained the highest concentrations of sulfur. Sulfur analysis of the solvent fractionated WY SKL and BH SKL was consistent with this, with the F1 fractions containing 7.98 and 2.41 wt % sulfur, respectively. Helander et al.⁴⁸ speculated that the sulfur is covalently bound to the small molecular weight lignin fragments. While this still may be true for the most part, attempted dissolution of the F1 fraction in acetone yielded a powder, which after filtration, washing, and drying resulted in the FT-IR spectrum shown in Figure S2 of the Supporting Information. This spectrum confirms the presence of elemental sulfur. In addition, this sulfur analysis showed that there was a large difference in the distribution of total sulfur of the overall lignin among the fractions (Table 4). Despite only accounting for 4% of the overall lignin, the WY SKL F1 fraction contained 14.9% of the total sulfur. The F5 fraction (41.8% of the total isolated Kraft lignin—not 41.8% of the lignin extracted from the black liquor) contained only 32% of the total sulfur for WY SKL. BH SKL, on the other hand, followed more of a linear

Table 5. Total Sulfur Content in Lignin Fractions and Percentage of Overall Sulfur^a

fractions	total S in fraction (wt %)	% of overall sulfur	fractions	total S in fraction (wt %)	% of overall sulfur
WY SKL F1	7.98	14.9	BH SKL F1	2.41	1.55
WY SKL F2	2.73	2.55	BH SKL F2	1.92	1.21
WY SKL F3	2.16	25.8	BH SKL F3	1.77	44.2
WY SKL F4	2.01	24.8	BH SKL F4	1.66	36.5
WY SKL F5	1.65	32.0	BH SKL F5	1.51	16.6

^aSee Figures S2 and S3 of the Supporting Information for further details. (Error ± 0.03 wt %).

trend with the proportion of sulfur being evenly distributed among the fractions (Figure S3, Supporting Information). North American mills typically use a much lower sulfidity as compared to their European counterparts⁴⁹, and it is noted that using higher sulfidity in the Kraft process leads to better delignification kinetics and may explain why the sulfur is more evenly distributed in the Backhammar fractions.⁵⁰

Additionally, ³¹P NMR^{29,51} was done in order to calculate the concentrations of various hydroxyl groups within the fractions (Figure 5). In general terms, the results indicate an increase in

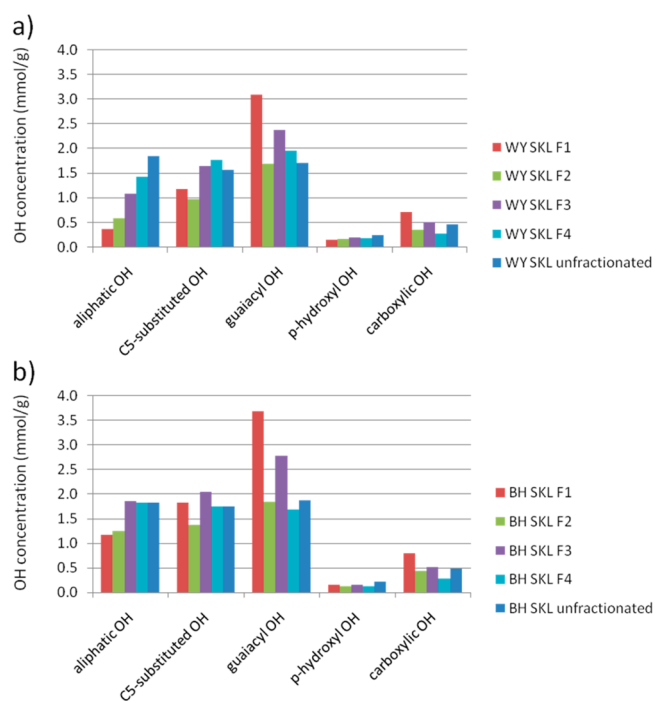


Figure 5. Concentration of the various OH moieties obtained from ³¹P NMR analysis: (a) WY SKL and fractions and (b) BH SKL and fractions. The error is ± 0.05 mmol/g.

Table 4. Elemental Analysis for Lignin Fractions^a

fractions	%C	%H	%N	fractions	%C	%H	%N
WY SKL	65.0	5.6	0.05	BH SKL	65.3	5.8	0.03
WY SKL F1	57.7	5.4	0.01	BH SKL F1	68.3	6.1	0.02
WY SKL F2	70.6	5.5	0.03	BH SKL F2	65.7	5.9	0.15
WY SKL F3	66.3	5.9	0.16	BH SKL F3	67.0	6.0	0.03
WY SKL F4	65.0	5.6	0.11	BH SKL F4	64.5	5.8	0.04
WY SKL F5	63.6	5.6	0.07	BH SKL F5	65.3	5.6	0.04

^aErrors are $\pm 0.2\%$ for C, $\pm 0.1\%$ for H, and $\pm 0.01\%$ for N.

Table 6. Integration of ^{13}C NMR Spectra^a

fractions	aliphatic COOR	$\text{C}_{\text{Ar-O}}$	$\text{C}_{\text{Ar-C}}$	$\text{C}_{\text{Ar-H}}$	aliphatic C–O	methoxyl OCH_3	aliphatic C–C
WY SKL F1	0.04	0.88	1.67	3.59	0.53	0.89	1.45
BH SKL F1	0.00	0.83	1.62	3.68	0.42	0.94	1.37
WY SKL F2	0.01	0.94	1.72	3.46	0.38	0.89	1.22
BH SKL F2 ^b	0.03	0.8	1.6	3.7	0.3	0.51	0.32
WY SKL F3	0.01	1.20	1.79	3.13	0.33	0.79	0.69
BH SKL F3	0.03	1.12	1.72	3.28	0.34	0.73	0.31
WY SKL F4	0.02	1.27	1.82	3.03	0.25	0.84	0.31
BH SKL F4	0.01	1.25	1.79	3.08	0.15	0.71	0.18

^aThe assignments are as follows ⁴⁵: aliphatic COOR = 175–168 ppm; $\text{C}_{\text{Ar-O}}$ = 162–140 ppm; $\text{C}_{\text{Ar-C}}$ = 140–123 ppm; $\text{C}_{\text{Ar-H}}$ = 123–102 ppm; aliphatic C–O = 98–58 ppm; methoxy OCH_3 = 58–54 ppm, and aliphatic C–C = 49–0 ppm. ^bThe integrals reported for BH SKL F2 represent the average of integrals taken from two different ^{13}C NMR spectra obtained for three different samples. The associated errors are from left to right: 0.01, 0.3, 0.1, 0.4, 0.1, 0.09, and 0.09.

aliphatic hydroxyl groups from F1–F5. The concentration of C5-substituted phenolic units does not show any specific trends between the fractions. However, the F2 fraction for both lignins had the lowest concentration of this condensed phenolic moiety. Carboxylic acid concentration was highest in the F1 fractions. Similarly, the F1 fraction contained the highest amount of guaiacylphenolic content for both SKLs with WY SKL F1 having 3.10 mmol/g and BH SKL F1 having 3.68 mmol/g. This is to be expected, given that these fractions have the lowest molecular weight. The F3 fractions also had high concentrations of guaiacyl phenolic groups. The *p*-hydroxyphenyl lignin unit concentration was consistently low between the fractions as one would expect in softwood-based lignin. Overall, the WY and BH SKL show similar trends in the various functional groups.

Finally, ^{13}C NMR experiments were performed to further provide more detailed chemical analysis of the lignins and reveal subtle differences between the WY and BH SKL fractions in terms of types of moieties and relative amounts. The subtle differences become less pronounced for fractions F3 and F4, suggesting that the lignin composition becomes more uniform as the number of steps in the organic solvent extraction procedure increases (Table 6 and Figure S4 of the Supporting Information), in agreement with literature findings.^{45,52} In addition, the data show that the number of carbon atoms per aromatic ring for a number of different moieties is similar for a given WY and BH SKL fraction, with the exception of the F2 fraction, which displays less methoxyl content. This is consistent again with the elemental analysis. What is also interesting is the difference in carbon content between the fractions. As shown in Table 6, the F1 and F2 fractions have significantly more aliphatic C–O, methoxyl, and aliphatic C–C content. Perhaps this increased aliphatic content is correlated to the lower T_g temperatures found for fractions F1 and F2, although the lower molecular weight may be more of a contributing factor. In any case, this is in agreement to previous findings by Saito et al.,⁴⁵ who suggested that the presence of more aliphatic carbon atoms means that there is more potential for free volume expansion and hence a lower T_g .

Overall, we can clearly see that the two SKLs used in this study are similar in some areas yet very different in others. The fractionation data shows that WY SKL has larger amounts of both high and low molecular weight fractions when compared to BH SKL. Further analysis of these fractions both highlights these differences between the two lignins and the heterogeneity of each lignin itself, which likely comes about from differences in Kraft cooking conditions, e.g., Kappa values. The fractions

follow the trend of increasing molecular weight from F1–F5 with the increasing polarity of the solvent used for extraction. Similarly, the T_g of these fractions follows this trend by increasing in temperature as the molecular weight increases from F1–F5. The thermal stability of these fractions does not follow the molecular weight. The BH SKL F5 fraction actually has the lowest thermal stability of the fractions from that lignin. This suggests that thermal stability is tied closely to the chemical nature of the lignin. Overall, the percentage of carbon in the fractions did not vary significantly. The levels of nonlignin components in these fractions were also analyzed, and these results did show some clear differences. The sulfur levels were highest in the F1 fractions, and the carbohydrate levels were the highest in the F5 fractions. NMR analysis showed differences in chemistry such as an increasing level in aliphatic OH groups from F1–F5. Both WY and BH F1 possess the largest concentration of guaiacyl phenolic moieties. They also have the highest concentration of aliphatic C–C and C–O bonds.

This detailed analysis of two SKLs demonstrates that SKLs can have major differences, both physically and chemically. The heterogeneity within each lignin and between industrial lignins of similar background highlights the fact that different lignins may be better suited for certain markets than others. For example, a low T_g and high aliphatic hydroxyl content leads to a better performance in lignin epoxy resin applications.^{53–55} For phenol–formaldehyde resins, a lignin with a low T_g and high phenolic hydroxyl content is desirable.^{53,54,56} Similarly, it is speculated that polydispersity and thermal properties (T_g , T_d) are key for the successful incorporation of lignin into carbon fiber.³⁰ Therefore, modification or fractionation of the lignin may be necessary to impart key physical and chemical attributes for the desired application.

■ ASSOCIATED CONTENT

📄 Supporting Information

Molecular weight distributions of the fractions studied here, as well as the sulfur analysis of the samples. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

The authors acknowledge support from Weyerhaeuser and NSERC through the Lignoworks Network. We acknowledge the various facilities at Weyerhaeuser, where some of the analyses were conducted. S.K.S. thanks CFI for funding of the NMR spectrometer used in this study.

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