Centrifugal washing and recovery as an improved method for obtaining lignin precipitated from South African kraft mill black liquor

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This study describes centrifugal recovery as an improved method for collection of lignin isolated from black liquor obtained from a South African kraft mill. Precipitation of lignin was achieved by utilising 6 M sulphuric acid. Recovery of the polymer was evaluated by comparing filtration straight after precipitation with centrifugal recovery and washing. Higher lignin yields were obtained with straightforward filtration recovery. However, filtration of the sample took a very long time, due to the colloidal nature of the lignin precipitate. Lignin recovery and washing utilising centrifugation reduced the recovery time at the final filtration step quite significantly. The lignin obtained was characterised by FTIR, ^{1}H- and ^{13}C-NMR spectroscopies to elucidate the heterogeneity of the sample, as well as to provide information on the syringyl and guaiacyl content of the lignin. Size Exclusion Chromatography revealed that the dispersity of the polymer was uniform and pyrolysis-GC/MS analysis provided insights and identification of typical degradation compounds that could be obtained from the lignin sample.

Introduction

Lignin has been identified as a major product that can be obtained from pulp and paper kraft mill black liquor[1,2] and its recovery has been extensively studied[3-8]. For example, industrial processes for collection of lignin from black liquor have been commercialised, namely, the Lignoboost™ process and the LignoForce™ system[9,10]. Sulphuric acid and carbon dioxide have been used successfully for precipitation of lignin from black liquor[4,5,11-13]. The method of precipitation requires lowering the pH of black liquor, which protonates the phenolic hydroxyl groups in lignin[14]. Concerns with the precipitation of lignin have been raised at the recovery step after precipitation, where filtration of the polymer has been shown to be a challenge due to its colloidal nature, and extensive studies on the filtration properties of lignin have been performed resulting in a necessity for specially designed filtration equipment to improve the filterability of lignin precipitates[4,5,15].

The objective of this work was to precipitate lignin from black liquor, followed by an improved recovery of the lignin product by an alternative method to filtration. The obtained lignin was then characterised by various techniques to ascertain its quality.

Materials and Methods

Black Liquor Characterization

Black liquor was obtained from a kraft mill whose furnish was a mixture of softwood and hardwood. Its pH was measured to be 12.90 – 13.00 and the solid content was determined based on the TAPPI 650 om-05 method. Ash content was determined based on TAPPI T 211 om-93 method. Total lignin in the black liquor was determined by UV-Vis spectrophotometry. Elemental analysis of the black liquor was also determined by CHNS/O analysis.

Lignin Precipitation from Black Liquor

Lignin was isolated by precipitation with H_2SO_4, according to the procedure described below. 100 mL of homogeneous black liquor was sampled from the bulk sample, and 6M H_2SO_4 was added to the black liquor drop-wise while stirring until pH = 9 was reached[8]. The solution was left stirring for 1 hour, followed by a further decrease in pH by addition of

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more H_2SO_4. The final pH of the solution was established at 4 and stirred for a further 1 h to ensure full particle growth. Lignin was recovered from the solution by centrifugation. The mother liquor was recovered and dissolved lignin content was determined by UV-Vis spectrophotometry. The recovered lignin was subsequently washed with acid-water a number of times (until the supernatant was clearer), each time utilizing a centrifuge to recover the washed precipitate. Finally, lignin was recovered by filtration with a Buchner funnel under vacuum suction.

Two methods of recovery of the precipitated lignin were evaluated, viz;
i)   Filtration of the precipitated lignin.
ii) Centrifugation of the precipitated lignin prior to filtration

The obtained lignin product was air-dried overnight and further dried in a vacuum oven.

Analytical Procedures

The mother liquor supernatant obtained from the initial recovery step following the precipitation was analysed for dissolved lignin by UV-Vis spectrophotometry at 280 nm. Elemental analysis (CHNS/O) of the lignin precipitate (and black liquor) was also performed. The lignin precipitate obtained was characterised by Fourier transform infrared (FTIR) spectroscopy equipped with attenuated total reflectance (ATR) sampling accessory. The structural features of the acetylated samples were studied by NMR spectrometry. $DMSOd_6$ was used as a solvent for ^{1}H-NMR, and $CDCl_3$ for ^{13}C-NMR spectra. Pyrolysis of approximately 200 µg of finely ground lignin sample was carried out for 10 s at 610 °C, followed by gas chromatography-mass spectrometry (GC/MS). The eluted compounds were identified by mass spectra comparison with NIST libraries. Size Exclusion Chromatography was used to determine the molecular weight distribution of the lignin samples. The lignin samples were subjected to acetylation in order to enhance their solubility in the mobile phase solvent[17,18]. SEC was performed on a HPLC pump with THF at a flow rate of 1 mL/min. The eluted material was detected using a multi angle laser light scattering detector in tandem with a UV detector and refractive index detectors. The chromatography media consisted of SEC-columns in an oven at 35 °C. The universal calibration curve for the instrument was based on polystyrene standards in the range 580 to 350 Daltons.

Results and discussions

Black liquor analysis

After repeatability and reproducibility studies on the sample, the moisture content of the black liquor was around 85%. This is typical of black liquors obtained prior to evaporation steps, *i.e.* weak black liquor. The inorganic material in black liquor was calculated to be 9%, and the total lignin content to be around 50%. The results obtained from elemental analysis (C – 15.97, H – 7.97, O -46.45, S - 0.55) show deviation from typical data obtained from literature compared with the sample in this study[8]. The major difference is observed on the carbon and oxygen content, whereby these two elements are usually found in more or less equal quantities. The black liquor sample in this experiment shows oxygen content that is approximately three times that of carbon.

Lignin characterisation

Lignin yield

The lignin yield obtained from precipitation experiments was approximately 83% on a dry weight basis. The method used to determine lignin precipitation in black liquor gives a reasonable estimate of the concentration, as other organics found in black liquor could also be absorbing at 280 nm, however it is known that lignin is the predominant material absorbing at that wavelength[5]. Close to 10% of the lignin presumed to be contained in the original black liquor sample was unaccounted for, and this source of error can be attributed to the organic matter that absorbs with lignin at the same wavelength, as well as losses incurred in transferring the sample to and from the centrifuge tubes. Centrifugation was selected for this study due to its efficiency, as filtration was onerous. Samples that were filtered straight after precipitation showed a higher lignin yield (93%), however, filtration of the sample took as long as an entire day to accomplish for only 100 mL of black liquor utilised for precipitation. Stepwise centrifugal washing of the precipitate, prior to filtration in the final step, on the other hand, was achieved in less than 2 hours. Centrifugation of the sample allows for a better separation of the colloidal liquid that forms as a result of lignin precipitation from black liquor. Furthermore the centrifuge also assists in rapid removal of the mother liquor during the stepwise washing.Elemental analysis of the precipitated lignin sample showed the following data; C - 66.80%, H - 6.27%, N - 0.20%, S - 4.82%, O -

18.84%. The CHO ratio of the precipitated lignin was compared with the data reported in the literature for different wood species, and it was observed that the obtained lignin was closely related to that of Eucalyptus species. In the case of this study the information about the wood source utilised in the mill was not provided.

FTIR

Characterisation of the structure of lignin by FTIR confirmed the presence of aromatic rings of lignin at the following main absorption bands; ν_{max}/cm^{-1} 1598, 1512, 1423, 915. Vibration bands in infrared spectroscopy may also assist in recognizing the syringyl (S) and guaiacyl (G) units for a given lignin. The absorption bands observed at ν_{max}/cm^{-1} 1325, 1112, 820 represent syringyl, and ν_{max}/cm^{-1} 1265 represents guaiacyl. The lignin obtained in the current study is represented by more syringyl type features than guaiacyl. With knowledge that hardwoods contain more S-units than G-units, it can be stated that 'FTIR data obtained showed more absorption bands in favour of S-units, thus the mixture of wood species utilised in the mill, and therefore the black liquor utilised in this study, had more hardwood than softwood species'.

NMR

Further structural characteristics of lignin were determined by ^{1}H and ^{13}C NMR spectra. The observed ^{1}H spectrum was typical of lignin, whereby chemical shifts of δ_H/ppm 8.58 belong to the syringyl unit directly attached to phenolic protons; δ_H/ppm 7.79 – 6.73 represent syringyl and guaiacyl units aromatic protons; the broad peak at δ_H/ppm 3.94 – 3.64 methoxy groups of lignin; δ_H/ppm 2.30 – 2.00 represents the benzyl protons; and aliphatic protons are represented by chemical shifts at δ_H/ppm 1.24 – 0.81[19,22]. Furthermore, the signal detected at δ_H/ppm 6.73 usually assigned to syringyl unit aromatic protons, also confirmed the assumption that the obtained lignin had higher syringyl content than guaiacyl[20]. There was a multiplet signal at δ_H/ppm 3.9 – 3.64, which depicted a significant number of methoxy protons, representing ~ 33% of the total number of protons. These methoxy protons represent the syringyl and guaiacyl units of lignin.The precipitated acetylated lignin sample was also analysed by ^{13}C NMR to further elucidate any additional structural features. The signal detected at δ_C/ppm 172.45 represented aliphatic carbonyl carboxyl carbons. The aromatic region of the

spectrum was indicated by peaks at δ_C/ppm 149.98, 136.74, 124.42 that represented etherified and non-etherified carbons of the syringyl and guaiacyl units in the lignin samples. The signal at δ_C/ppm 56.48 was representative of the methoxy groups in syringyl and guaiacyl units. The signal at δ_C/ppm 21.50 represented saturated hydrocarbons that were found on the side chains of the lignin molecules[20,21].

Py-GC/MS

Py-GC/MS was used to evaluate the degradation products that could be obtained from the precipitated lignin. The structures of the pyrolysis products were determined using gas chromatographic retention times, mass spectrometry data, and identified using a NIST library. The retention times and resulting products are shown in Table 1. The other products that were obtained from lignin pyrolysis, such as furans, aromatic hydrocarbons, and long chain acids are also shown in Table 1 (peak nos. 1, 2, 3, 27 and 28). Major lignin phenolic compounds belonging to the guaiacol and syringol families were obtained between *ca* 15 – 30 mins (peak no. 5 - 26). The chromatogram showed 7 major peaks belonging to guaiacol (6), 2-methyl-5-methoxyphenol (8), 4-ethylquaiacol (13), acetovanillone (15), 4-methylguaiacol (17), syringol (17), trans-isoeugenol (23) moieties. From Table 1, it can be observed that most of the lignin compounds obtained display a guaiacol characteristic and are intact (6, 8, 9, 13, 16, 18, 20), whereas only two syringol type compounds were clearly observed (17 and 26). Since syringol compounds are larger than their guaiacol counterparts, the data shows that there is a probability that the syringol compounds were broken down (resulting in the loss of the other methoxy group) and detected as guaiacol compounds. The hydrocarbon, peak 27, coincides with the information reported earlier that the lignin obtained in this study could originally be from a mixture of hardwood and softwood cook.

Size Exclusion Chromatography

Molecular weight distribution of the acetylated lignin sample was determined by SEC. The resulting chromatograms were acquired by three different methods, that is, assuming 100% mass recovery in the columns, refractive index increment (dn/dC) of 1.65 $cm^{-3}.g^{-1}$, and dn/dC of 1.80 $cm^{-3}.g^{-1}$. The dn/dC of 1.80 $cm^{-3}.g^{-1}$ belongs to polystyrene standards, and it has been shown that lignin and polystyrene standards display similar patterns throughout a wide range of molecular weights[19,22]. In their study on the accurate

Table 1—Products generated from lignin pyrolysis.
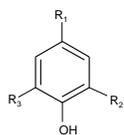
Peak no.	Ret. Time	Base m/z	R1	R2	R3	Name
1	3.75	91.05				Toluene [#]
2	5.55	96.05				3-Furaldehyde, Furfural [#]
3	11.18	94.05				Phenol
4	13.90	108.1			CH3	2-methyl-phenol
5	14.69	107.1	CH3			p-Cresol
6	15.06	109.1		OCH3		2-methoxy-phenol
7	17.36	122.1	CH3	CH3		2,4-dimethyl-phenol
8	18.38	123.1			OCH3	2-Methoxy-5-methyl-phenol *
9	18.94	138.1	CH3		OCH3	Creosol
10	19.35	110.1		OH		Catechol
11	21.31	140.1	OH		OCH3	1,4-Benzenediol, 2-methoxy
12	21.47	124.1	CH3		OH	1,2-Benzenediol, 4-methyl
13	21.98	137.1	CH2CH3	OCH3		Phenol, 4-ethyl-2-methoxy
14	22.50	124.1	CH3	OH		1,2-Benzenediol, 4-methyl
15	23,16	150.1	O=CCH3	CH3		4-Hydroxy-3-Methoxyacetophenone
16	23.49	138.1			OCH3	2-methoxy-3methyl-phenol *
17	24.44	154.1		OCH3	OCH3	Phenol, 2,6-dimethoxy
18	24,63	164.1	CH2CH=CH2	OCH3		Eugenol
19	24.77	151.1	O=CCH3	OCH3		Apocynin
20	24.95	137.1	CH2CH2(CH3 or OH)	OCH3		Phenol, 2-methoxy-4-propyl or Homovanillyl alcohol
21	25.58	164.1	CH=CHCH3	OCH3		Phenol, 2-methoxy-4-(1-propenyl)-, (Z)
22	25.88	164.1	CH=CHCH3	OCH3		trans-Isoeugenol
23	27.55	168.1	O=COH		OCH3	3-Hydroxy-4-methoxybenzoic acid
24	29.97	167.1	CH3	OCH3	OCH3	Benzene, 1,2,3-trimethoxy-5-methyl [+]
25	31.10	180.1	O=CCH3	OCH3	OCH3	3',5'-Dimethoxyacetophenone [+]
26	33.60	194	CH2CH=CH2	OCH3	OCH3	4-allyl-2,6-dimethoxy phenol[+]
27	45.77	55.1				cis-Vaccenic acid [#]
28	52.02	239.2				Dehydroabietic acid [#]

Smaller aromatic hydrocarbons, and furan compounds, and other compounds that can be obtained from lignin.

* R1 group represents hydrogen.

+ The OH group is not present in these compounds.

measurement of the dn/dC of lignin, Contreras et.al[23], found the dn/dC of *Eucalyptus globulus* lignin to be 0.165 $cm^{-3}.g^{-1}$. The molecular weights and distribution calculated from the three methods were then compared (Table 2). The number average molecular weight (M_n), and the weight average molecular weight (M_w) calculated from both the abovementioned dn/dC values showed a close relation with each other, with a difference of 16500 and 17200 $g.mol^{-1}$, respectively. A large difference in the averages is observed where 100% mass recovery in the columns was assumed, with a close to 50000 $g.mol^{-1}$ difference across the three methods. These lower values for M_n and M_w displayed by this method confirmed that less than 100% of the mass injected was recovered in the columns. The dn/dC for polystyrene standards would be a more suited reference, for the reason that the 'true' origin of the species of lignin sample in this study was not provided, as well as different species would differ by location even though they might be from the same *genus*. Therefore, it can be proposed that *ca* 82% of the mass was recovered in the columns from our SEC system. The dispersity (replacing polydipersity index) for the lignin sample was

Table 2—Size exclusion chromatography results for acetylated lignin sample

Method	Mn (g.mol^{-1})	Mw (g.mol^{-1})	Mz (g.mol^{-1})	Polydispersity (cm^{-3}.g^{-1})	
				Mw/Mn	Mz/Mn
100% mass recovery	1.48E+05	1.54E+05	1.60E+05	1.03 (± 0.058)	1.07 (± 0.106)
dn/dC 0.165	1.98E+05	2.06E+05	2.14E+05	1.03 (± 0.058)	1.07(± 0.106)
dn/dC 0.180	1.82E+05	1.89E+05	1.96E+05	1.03 (± 0.58)	1.07(± 0.106)

observed to be Đ = 1.036 cm^{-3} g^{-1}. Dispersity is the ratio of M_n and M_w to measure of the spread of the molar-mass in a polymer[23]. The Đ value obtained for the sample studied showed that the lignin polymer displayed a close to uniform structure, and falls in the narrow polymer range. Lignins with a narrow molecular weight distribution are preferred in case of valorising the polymer.

Conclusions

This study demonstrated that the overall process of centrifugal washing and recovery of lignin was more efficient straightforward filtration. Characterisation of the lignin samples showed predominance of syringly moieties, indicating that more hardwood than softwood was utilised during the pulping process. SEC data revealed high molecular weight averages in the lignin sample; whereby Đ = 1.036 cm^{-3}.g^{-1} of the lignin sample fell in the narrow molecular weight region, revealing uniformity in the polymer. Thus, the centrifugal method of recovery of the precipitated lignin also provides a sample that is a good prospect for further modification. Py-GC/MS analysis provided identification of potential compounds that could be obtained through pyrolysis of the sample. Such products provide a scope for valorisation of lignin in future studies.

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