

**STRUCTURAL CHARACTERIZATION OF KRAFT LIGNIN  
FOR ITS GREEN UTILIZATION**

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**ABSTRACT**

Laboratory-obtained kraft lignins have been studied via elemental analysis (EA),  $^1\text{H-NMR}$ , FTIR, GPC to analyse the chemical structure. The kraft lignins were subjected to oxidation with  $\text{H}_2\text{O}_2$  using  $\text{Co}(\text{salen})$  as a biomimetic catalyst at mild condition ( $80^\circ\text{C}$ , 240 min). The kraft lignins isolated from eucalyptus (EKL) and bamboo (BKL) had a low hydroxyl (oxygen) contents, a low molecular weights ( $\sim 3000 \text{ g}\cdot\text{mol}^{-1}$ ) and a uniform molar mass distribution with promising results for oxidative conversions. EKL shows a tendency to higher purity and higher functional group content in hydroxy group, methoxy group,  $\beta\text{-O-4}$  linkage than BKL. Oxidations cause depolymerization of kraft lignin, in which kraft lignin was selectively oxidized by the catalyst. Oxidation products, 2-methoxy phenol and 3-methoxy-4-hydroxy benzaldehyde, can be observed on treatment of kraft lignin. Catalytic oxidation of EKL lignin shows a higher yield of products, most likely due to the high content of  $\beta\text{-O-4}$  ether linkages, hydroxyl groups. Both structural and oxidative characteristics suggest that EKL would be a better feedstock in the production of aromatic products, as it presents higher amounts of hydroxyl functional groups,  $\beta\text{-O-4}$  linkages, and as it presents higher molecular weight and higher purity.

**KEYWORDS:** Kraft lignin, eucalyptus, bamboo, chemical structure, oxidation,  $\text{H}_2\text{O}_2$ ,  $\text{Co}(\text{salen})$ .

## INTRODUCTION

Lignin is the second most abundant renewable natural resource, exceeded only by cellulose. It consists of up to three different phenylpropanoid monomers, called *p*-coumaryl alcohol, coniferyl alcohol and synapyl alcohol that lead, respectively. These substructures are linked by many possible bonding patterns between individual units, including several types of ether ( $\alpha$ -O-4,  $\beta$ -O-4, and 4-O-5) and carbon-carbon linkages as well as different functional groups (Lebo et al. 2001).

Traditionally, lignin is usually obtained as a byproduct of pulping process. Kraft pulping (also known as sulfate pulping) is the dominant chemical pulping process in the world. It entails treatment of wood chips using strong alkali with sodium sulfide to separate lignin from the cellulose fibres. The lignin (85-93 %) and hemicellulose (56-71 %) is dissolved in kraft cooking liquor (black liquor) and is sent to a recovery system where it is burned. This recovery stage supplies much of the energy needed to operate the mill and regenerates the inorganic pulping chemicals. At the same time, novel processing methods and product concepts are required to extend the role of kraft lignin for biomass and biofuel applications. In fact, its potential as a source of valuable phenols to provide an additional value-added revenue stream for the mill is obvious (Zakzeski et al. 2010). Recently, several studies have focused on viable separation of lignin from black liquors in the pulping process to produce both a good pulp and a high-reactivity lignin. These studies have tested process integration and mill trials from an engineering and economic point of view and also leads to the opportunity to transform lignin into valuable green resource for higher value materials production (Brebun and Spiridon 2012, Nagy et al. 2010, Yang et al. 2012).

Due to the extreme complexity of lignin, novel processing methods are required to extend the role of kraft lignin for biorefinery in pulp and paper platforms. The development of new or improved catalytic processes is becoming the most promising alternative. Zakzeski et al. (2011, 2010) recently demonstrated the catalytic oxidation of lignin (Alcell lignin, soda lignin) along with several lignin model compounds using  $\text{CoCl}_2$  and molecular oxygen. Salen complexes are an important class of organometallic compounds, which have been used to catalyze a wide variety of reactions of organic substrates with oxidants like  $\text{O}_2$  and  $\text{H}_2\text{O}_2$ . They can be used as catalysts in the field of lignin and wood chemistry. In particular it was demonstrated that they were able to oxidize in high yields lignin model compounds (Haikarainen 2005). In our laboratory, salen complexes as catalysts have been successfully studied in lignin model compound conversion and delignification of kraft pulp (Zhang and Zhou 2012, Zhou et al. 2011). Motivated by the effective chemical transformations that occur during lignin model compound oxidation, we extended the biomimetic catalysts to the transformation of kraft lignin using hydrogen peroxide.

Here we report two kraft lignins, namely kraft eucalyptus lignin (EKL) and kraft bamboo lignin (BKL). We wish to present an extensive study by using FTIR,  $^1\text{H-NMR}$  and GPC to obtain a general view about the structure of isolated kraft lignin for oxidative transformation. Despite the large number of studies for the use of lignin, relatively little effort has been placed in the biomimetic catalysis from which important aromatic compounds can potentially be obtained from the conversion of kraft lignin.

## MATERIAL AND METHODS

### Lignin extraction

Eucalyptus (*E. urophylla*  $\times$  *E. grandis*, 24.5 % lignin) and bamboo (*D. brandisii*, 27.1 % lignin)

were cooked by the conventional laboratory-scale kraft method with NaOH, Na<sub>2</sub>S. All the raw materials were of China origin. The parameters used on the cooking and some data on the pulps and black liquors in these cooking series are presented in Tab. 1.

Tab. 1: Cooking conditions.

Feedstock	EA (%)	Sulfidity	AQ (%)	Liquor-to-feedstock ratio (L·kg <sup>-1</sup> )	Max. temp. (°C)	Time to max. temp (min)	Time at max. temp. (min)	Kappa number	REA (gNaOH·L <sup>-1</sup> )
Eucalyptus	17	28	0	4.0	165	120	90	17.3	11.75
Bamboo	16	25	0.5	3.6	160	100	120	16.5	10.50

Note: alkali charge on o.d. feedstock as Na<sub>2</sub>O; EA: effective alkali, AQ: anthraquinone, REA: residual effective alkali.

When the target cooking times were reached, black liquors were collected from the reaction vessel. Next DTPA was slowly added with agitation to black liquor to facilitate metal-ion removal followed by the addition of aqueous sulfuric acid (2 M) until a pH of between 2 and 3 was reached causing some of the lignin to precipitate. The solution and resulting precipitate was kept at 0°C overnight and thawed at room temperature. The precipitate was separated by centrifugation, then freeze dried and kept frozen until purification.

Detailed structural analysis of the lignin in the above samples required additional purification. The initial sample was heated in 80 % dioxane containing 0.05 M HCl at reflux for 2 hours in a nitrogen atmosphere, filtered through a medium sintered glass funnel at 0°C, and sequentially washed up with 80 % dioxane. All filtrates were collected, neutralized with solid NaHCO<sub>3</sub>, and then evaporated under reduced pressure. The liquid after rotary evaporation was slowly added to the acidic distilled water (pH 2), lignin precipitate was centrifuged and freeze-dried. The lignin sample obtained was washed with methylene chloride (three times 150 mL) and dried under vacuum with phosphorus pentoxide to give pure kraft lignin. The kraft lignin samples designated as EKL and BKL were stored in the refrigerator for testing. The moisture contents were between 2.0 % and 3.0 %.

### Lignin characterisation methods

The ash content of all the kraft lignins was calculated gravimetrically after in-furnace calcinations at 575 °C.

The acid insoluble (klason lignin) and soluble lignin of all kraft lignins was determined by the klason hydrolysis as described by Crawford and Pometto (1988). Five millilitres of the same filtrate obtained was used to determine the carbohydrate content by applying UV-vis method at 500 nm, using glucose (10-1000 g·mL<sup>-1</sup>) as standard. The purity of the kraft lignin samples was calculated from the sum of kraft and acid soluble lignin results.

A variety of different metals and elements for instance Na, K, Cu, Mn, Ni, Zn, Ca, Mg, Fe, Al and Si were measured using an inductively coupled plasma atomic emission spectrometry (ICP-AES).

Elemental analysis for C, H and N was performed with a Vario EL Elemental Analyzer 1106. Oxygen was determined by difference.

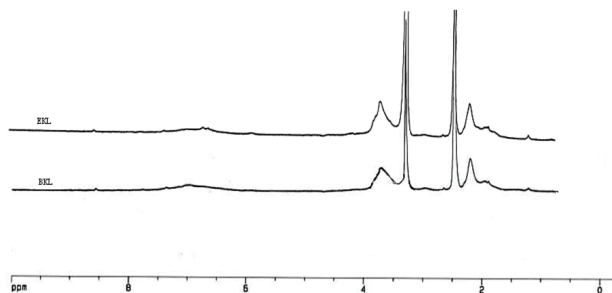


Fig. 1.  $^1\text{H-NMR}$  spectra of EKL and BKL.

$^1\text{H-NMR}$  spectroscopy of acetylated kraft lignin provides improved spectral resolution of key lignin functionality (Lundquist 1998). The acetylated kraft lignin samples (~100 mg) were measured in  $\text{DMSO-d}_6$  (450  $\mu\text{L}$ ) and the spectra were recorded with a 400 MHz Avance Bruker spectrometer using standard Bruker sequences. A less tedious method for methoxyl determination of lignin that involves the use of  $^1\text{H-NMR}$  uses the theoretical ratios between aromatic and methoxyl protons of guaiacyl and syringyl. These ratios can actually be measured from the  $^1\text{H-NMR}$  spectra of acetylated lignins. Aromatic and methoxyl protons occur between 6.4-7.1 and 3.5-4.1 ppm respectively, see Fig. 1. From these ratios (x) the %  $\text{OCH}_3$  was calculated from the equation %  $\text{OCH}_3 = 28.28436 - 19.750047 \times$  submitted by Aberu and Freire (1995). The area of the OH signal (phenolic at 2.3 and aliphatic at 2.0 ppm) was related to the area of the methoxyl signal at 3.5-4.1 ppm. Methoxyl signal is used as internal standard for the OH group calculation (Faix et al. 1992). The kraft lignin samples were acetylated with acetic anhydride and pyridine before the use (Thring et al. 2002).

For molecular weight determination the acetylated kraft lignin was measured in tetrahydrofuran using Agilent 1100 GPC.

FTIR spectra of unacetylated kraft lignins were obtained using a Bruker Equinox 55 FTIR spectrometer. Background spectra were collected before every sampling. The absorption bands were assigned as suggested by Nada et al. (1998).

### Typical reactions

Reactions were conducted in a 200 mL Parr stainless steel autoclave. The temperature was monitored using a thermocouple, and stirring was conducted using a magnetic driver equipped with an impellor at 750 rpm. Reactions were conducted as follows (unless noted otherwise): Into a 0.50 g kraft lignin sample was added  $\text{Co}(\text{salen})$  (0.75 g), along with 30 %  $\text{H}_2\text{O}_2$  (17.0 mL) and 100 mL deionized water. The autoclave was then sealed and heated to 80°C over about 5 min. After a designated reaction time (240 min), the autoclave was cooled to 18-20°C, vented, and the sample was taken. The autoclave was thoroughly rinsed with deionized water.

Products and residual substrate were separated from the aqueous mixture by three sequential extractions using trichloromethane (60.0 mL). Prior to conducting reactions, extraction efficiencies of the potential reaction components (i.e. 2-methoxy phenol, vanillin, 4-hydroxy-3-methoxy phenyl ethanone, etc.) using trichloromethane or diethyl ether were determined. Extraction efficiencies were generally higher when trichloromethane was used, compared to diethyl ether. Distinct organic phase was formed when both of these solvents were combined with aqueous mixture, and the bottom trichloromethane phase was collected and analyzed using a Shimadzu GC/MS-QP2010 unit or a LC/MS-2010EV unit, and products were identified and compared with pure standards when available.

## RESULTS AND DISCUSSION

## Composition analysis results

Tab. 2 shows the klason lignin, acid soluble lignin, carbohydrate, ash of kraft lignin samples. Both the kraft lignin samples are very different both in their lignin and in their ash content. The data in Tab. 2 clearly showed that the purified samples had different amounts of lignin as the following (in wt %): 97.57 % in EKL, 90.14 % in BKL. The EKL lignin recovered from black liquor was much higher in lignin content than the BKL.

Tab. 2: Purity, elemental analysis results and formulae of kraft lignins.

Sample	Klason lignin (%)	Acid soluble lignin (%)	Carbohydrate (%)	Ash (%)	Purity (%)	C (%)	H (%)	N (%)	O (%)	Empirical formula	C <sub>9</sub> formula	C <sub>10</sub> formula
EKL	88.70	8.87	0.81	0.84	97.57	56.38	6.49	1.32	36.81	C <sub>4.70</sub> H <sub>6.49</sub> O <sub>2.30</sub>	C <sub>9</sub> H <sub>12.43</sub> O <sub>4.40</sub>	C <sub>10.0</sub> H <sub>13.81</sub> O <sub>4.89</sub>
BKL	87.02	3.12	3.32	5.35	90.14	65.28	5.69	0.39	28.64	C <sub>5.44</sub> H <sub>5.69</sub> O <sub>1.79</sub>	C <sub>9</sub> H <sub>9.41</sub> O <sub>2.96</sub>	C <sub>10.0</sub> H <sub>10.46</sub> O <sub>3.29</sub>

Tab. 3: ICP-AES results.

Sample	Element content (ppm)										
	Na	K	Cu	Mn	Ni	Zn	Ca	Mg	Fe	Al	Si
Eucalyptus	420	690	1.4	23	0.7	3.9	1400	80	20	17	10
Bamboo	7.1	1900	5.3	18	0.9	9.2	430	260	74	46	8.1
EKL	8900	24	8	0.8	1.2	1.4	18	11	38	2.9	29
BKL	5100	51	2	0.5	< 0.5	0.9	89	34	23	2.8	9.4

As shown in Tab. 2, particularly notable is the low ash content of EKL lignin. In most demanding lignin applications, low ash levels are generally required. EKL lignin came very close to meeting this specification, while BKL lignin did not correspond (Toledano et al. 2012). The low purity of BKL lignin is related to the high ash and carbohydrate values due to the nature of bamboo (Stenius 2000).

The data in Tab. 2 show that carbon content increases from EKL to BKL. The nitrogen content of the EKL lignin is higher than that of BKL. Compared to BKL, EKL shows a high oxygen content possibly due to oxidation. Based on elemental analysis, the empirical, C<sub>9</sub>, C<sub>10</sub> formulae of the different kraft lignins are calculated using values in Tab. 2. The C<sub>9</sub> formula of EKL is different to that of BKL. Worth noting, though not surprising, is that the monomeric units of these kraft lignins have greater contents of oxygen than coniferyl alcohol (C<sub>10.0</sub>H<sub>12</sub>O<sub>3</sub>) (Boerjan et al. 2003), possible reasons for this discrepancy are interpreted that partial lignin was oxidized during extraction at elevated temperature and hemicellulose fractions were present in the kraft lignin.

As shown in Tab. 3, ICP-AES indicated that eucalyptus, bamboo, EKL and BKL contain low silica content. Sodium, potassium, copper, manganese, nickel, zinc, calcium, magnesium, iron and aluminum were also detected. The procedure used in the determination of ash content of sample is based on heating the acid insoluble residue sample at 575°C to a constant weight. If there is char formation of carbohydrate residue during the heating process, the value of the ash that is recorded will be inflated (Mousavioun and Doherty 2010) and it is therefore expected since sample BKL has high carbohydrate content (see Tab. 2).

### Molecular weight and functional groups of kraft lignin

Tab. 4 summarises all main data of kraft lignins obtained by GPC for molecular weight and by  $^1\text{H-NMR}$  for functional groups.

GPC data shows that  $M_w$ ,  $M_n$ , PD results of  $\text{H}_2\text{SO}_4$  precipitated kraft lignins are consistent with the Nagy'research data of  $\text{CO}_2$  precipitated kraft lignins ( pH 10.5:  $M_w$  2939,  $M_n$  1694, PD 1.73; pH 9.50:  $M_w$  2979,  $M_n$  1795, PD 1.66) (Nagy et al. 2010), while on the other hand, shows significantly smaller values than Indulin AT lignin extracted from pine wood with the kraft method ( $M_w$  19800,  $M_n$  2200, PD 9.0) and Organocell lignin from spruce wood with ethanol ( $M_w$  10800,  $M_n$  2300, PD 4.7) (Glasser and Jain1993). It is noteworthy that PD of EKL and BKL samples are similar, with values between 1.60 and 1.70, which confirms the uniform character of the kraft lignins obtained from  $\text{H}_2\text{SO}_4$  precipitation. The greater molar weight values were observed in EKL lignin than BKL, one explanation is that there are different structural characteristics in lignin between wood and nonwood. This assumption is supported by the different formula (Tab. 2) and functional group value (Tab. 4) observed for these kraft lignin samples. Differences in the molecular weight distributions could cause marked variations in the performance of the polymer.

Tab. 4: Molecular weight and functional group content of kraft lignin.

Sample	Mw (g·mol <sup>-1</sup> )	Mn (g·mol <sup>-1</sup> )	PD	Methoxyl	Phenolic	Aliphatic	Total OH
				(%) (3.5-4.1) ppm	OH (%) (2.4-2.1) ppm	OH (%) (2.1-1.6) ppm	
EKL	3031	1843	1.6	20.08	2.37	4.45	6.82
BKL	2720	1576	1.7	16.73	2.10	3.18	5.28

Note: Mw: weight-average molecular weight, Mn: number-average molecular weight, PD: polydispersity.

Tab. 4 lists the content of methoxyl, phenolic OH, aliphatic OH and total OH, which are based on  $^1\text{H-NMR}$  studies. The methoxyl content of kraft lignins increases from BKL to EKL lignin. This increase is not related to molecular weight but related to the insolubility of syringal dominated lignin macromolecule in the hardwood (eucalyptus) (Lebo et al. 2001). Also, with the lower methoxyl content, BKL is likely possesses vacant sites that are desirable for lignin functionalisation. EKL lignin has more phenolic and aliphatic OH groups compared to BKL lignin. Hydroxyl group content of lignin plays a crucial role in determining its solubility and reactivity characteristics due to the deprotonation and the activation of the aromatic ring (Malutan et al. 2008).

### Infrared spectroscopy

Fig. 2 shows FTIR spectra of kraft lignins. It is clear that the two kraft lignins showed structural similarities, but differences in structure with SA lignin (Sigma Aldrich lignin), which is attributed to the different lignin sources and the different extraction methods (Tan et al. 2009, Zakzeski et al. 2010).

On the other hand, it is seen from Fig. 2 that the absorption of the band of C=O groups at  $1725\text{ cm}^{-1}$  is stronger in case of EKL than BKL. This can be attributed to the method used in the pulping process and the raw material used (eucalyptus, bamboo) (Macleod 1990).

FTIR shows that a band at  $620\text{ cm}^{-1}$  is shared by both spectra in the case of the two kraft lignins, indicating the presence of sulfur, which was potentially incorporated in the lignin due to the use of sodium sulfide in the kraft pulping process (Tan et al. 2009).

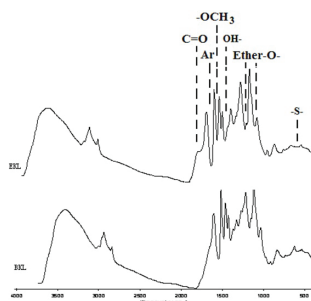


Fig. 2: FTIR spectra of EKL and BKL, measured on KBr discs.

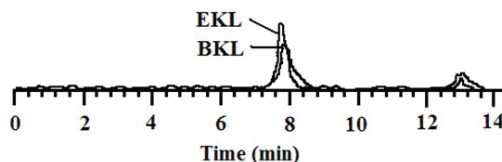


Fig. 3: Total ion chromatograms of EKL and BKL sample for GC-MS detection.

### Lignin oxidation

The oxidation of the kraft lignins in  $\text{H}_2\text{O}_2$  using Co(salen) catalyst was investigated. Any possible products are depicted in Fig. 3, which displays the differences in the total ion chromatograms between the EKL and BKL sample for GC-MS detection. Two peaks appeared near 7.7 min (2-methoxy phenol) and 12.9 min (3-methoxy-4-hydroxy benzaldehyde) that increased in abundance with sample from BKL to EKL, which suggests that kraft lignins were selectively oxidized by the catalyst. Most likely, EKL lignin contains more hydroxyl functional groups (Tab. 4) that are susceptible to oxidations to produce 3-methoxy-4-hydroxy benzaldehyde and contains more  $\beta$ -O-4 linkages (Fig. 2: ether-O-) that, if successfully cleaved, would potentially result in 2-methoxy phenol.

## CONCLUSIONS

The results of the kraft lignin analysis coupled with the GC-MS evidence obtained during the oxidation provide insight regarding the kraft lignin transformations. The  $\beta$ -O-4 linkages present in the kraft lignin, if successfully cleaved would potentially result in low molecular weight aromatic product 2-methoxy phenol, which indicate the reason that more 2-methoxy phenol was detected as a result of the oxidation for EKL sample. Similarly, phenolic functional groups played a crucial role in determining reactivity characteristics of a lignin, benzyl and other alcohol functionalities were susceptible to oxidation to form aldehydes. These oxidations proceeded at higher rates under catalytic conditions for EKL sample.

Nevertheless, the combination of aqueous oxidation and Co(salen) catalyst proved suitable for kraft lignin transformations.

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