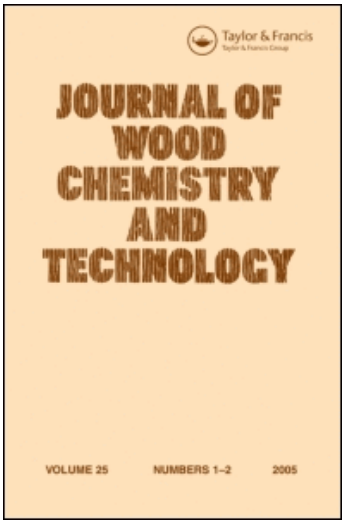

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Origin and Nature of Kraft Colour: 2 The Role of Bleaching in the Formation of the Extraction Stage Effluent Colour

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ORIGIN AND NATURE OF KRAFT COLOUR : 2 THE ROLE OF BLEACHING IN THE FORMATION OF THE EXTRACTION STAGE EFFLUENT COLOUR

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ABSTRACT

Upon chlorination and extraction, high molecular weight (>1000D) kraft lignin (KL) is degraded to a material which is structurally similar to extraction stage effluent. During bleaching there is a significant decrease in the aromaticity of KL without a concomitant decrease in colour, which would be expected if aromatic residues are the kraft chromophores. Treatment of simple sugars under conditions similar to those of kraft pulping yielded polymeric products which, on treatment with chlorine and subsequential extraction (CE), gave products with similar spectral characteristics to extraction stage effluent. It is proposed that the chromophores responsible for kraft colour are keto-enols probably derived from the degradation of carbohydrates during the kraft cook.

INTRODUCTION

The volume and colour of discharged wastewaters from pulp mills are major concerns to the kraft pulp and paper industries. Approximately 50% of the colour in kraft mill effluent is derived from the E stage[1] and more than 90% of that material has a molecular weight greater than 1000 Daltons (D)[2]. This paper examines the origin of the extraction stage colour by studying the effects of chlorination and extraction stages (CE) on precipitated kraft lignin. This paper also discusses the possible role of carbohydrates in the production of colour both in the black liquor and in CE effluent.

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It is generally considered, as first proposed by Pigman and Csellak[3], that the kraft colour is due to lignin degradation products. Gierer[4] proposed a variety of leucochromophoric (colourless) groups which can undergo condensation, auto-oxidation, and/or dehydrogenation to yield highly conjugated potential chromophores. Since then various authors[1,5] have cited these proposed structures as the actual chromophores produced during kraft pulping.

Erickson and Dence[6] used the permanganate/periodate oxidation method developed by Erickson *et al.*[7] to search for potential aromatic chromophores in the high molecular weight suspended solids present in bleach plant effluents. They found that aromatic structures in spent chlorination liquors accounted for only 2–3% of the total organic material and only 3–4% in spent extraction liquors.

Lindström and Österberg[2], using the same oxidation method, identified over 50 different aromatic structures in CE extraction liquors. They showed that in the effluents most of the organically bound chlorine is bound to non-aromatic carbon and that aromatic residues made up approximately 1% of the effluent. They also found that 75% of the chlorinated non-aromatic material had molecular weight greater than 1000 D and had a high content of carbonyl groups. These effluents were rich in carboxyl groups conjugated to double bonded carbons, or else had hydroxyl groups attached primarily to aliphatic material. Lindström and Österberg[2] found no evidence for the occurrence of native lignin structures such as β-aryl ethers and believed that the aromatic structures in the residual lignin had, to a large extent, undergone cleavage reactions during bleaching. They also stated that the remaining aromatic portion was largely condensed but they did not detail the isolation, nor the characterization, of any of these condensed materials. They argued that the presence of various hemipinic isomers was evidence of aromatic condensation during the kraft cook. However, Erickson *et al.*[7] have isolated the same hemipinic isomers from Bjorkman lignin using similar techniques. Therefore, if the colour in kraft mill discharges is due to lignin-derived materials then Gierer's proposed chromophores constitute but a minor portion of the high molecular weight materials.

Kraft mill effluents are known to contain carbohydrates. Analysis of C and E stage effluents by Pfister and Sjöström[8,9] showed that the material >1000 D contains approximately 4–6% polysaccharide material (Table 1). They also showed that C stage effluent is rich in low molecular weight compounds while E stage effluent contains primarily high molecular weight materials. Analysis of the polysaccharides present showed that they contained galactose and xylose units.

TABLE 1
Analysis of Acid and Alkaline Spent Bleaching Liquors*

	C	E
Kg dissolved organic material/tonne of pulp	21.7	47
% of material >1000 D	30	80
Polysaccharides >1000 D kg/tonne	0.28	2.05
Polysaccharides as % of material >1000 D	4-5%	5-6%

* from Pfister and Sjöström[8, 9]

TABLE 2
List of Abbreviations

C	chlorinated sample
CE	chlorinated and alkali extracted sample
CEKG	chlorinated and extracted kraft cooked glucose
CEKL	chlorinated and extracted kraft lignin
E	E stage effluent
KG	kraft cooked glucose
KL	kraft lignin
PE	hydrogen peroxide bleached E stage effluent

Abbreviations used are listed in Table 2. This paper examines the effects of the CE bleaching sequence on kraft lignin (KL), kraft cooked glucose (KG), glucose and cellobiose. The products were examined by permanganate/periodate oxidation, UV-visible and NMR spectroscopic techniques. The role which carbohydrate degradation products may play in colour formation is also outlined.

RESULTS AND DISCUSSION

Permanganate/Periodate Oxidation Studies

The previous paper in the series (Ziobro[22]) used the permanganate/periodate technique to study the possible role of aromatics and carbohydrate degradation products in the origin and nature of kraft colour.

Chlorine bleaching of precipitated kraft lignin (KL) followed by alkaline extraction gave CEKL (chlorinated extracted kraft lignin). The resulting products from the permanganate/periodate oxidation of CEKL were separated by gas chromatography (Fig. 1a) and identified (Table 3). Compounds A, B, and C, which are derived from guaiacol, are not present. Therefore, the bleaching and extraction sequence has destroyed the guaiacol residues in the kraft lignin (KL). Oxidation of commercial kraft Eo effluent (Fig. 1b) yields almost identical products to those present in CEKL, as shown by the gas chromatogram for the Eo effluent. The phenol residues present in lignin survive the bleaching sequence, as demonstrated by the presence of compound D (Rt = 58.5) in both traces. The similarity of the GC traces extends to those compounds found in only trace amounts. Therefore, the chlorination and extraction of precipitated kraft lignin yields a lignin degradation product which very closely resembles the chlorinated and extracted residual lignin obtained during conventional kraft pulp bleaching.

Gierer[4] earlier proposed that catechol, hydroquinones, and quinones are the leucochromophores of kraft colour. Gellerstedt and Lindfors[11] followed the production of compounds X and Y (Table 3) during kraft cooks. No evidence was found for the presence of X and Y among the permanganate/periodate degradation products in either CEKL (Fig. 1a) or E effluent (Fig. 1b).

NMR Spectral Data

A typical NMR spectrum for *Pinus radiata* kraft lignin (Fig. 2c) is representative of a sample relatively low in carbohydrate[12]. Destruction of the aromatic portion of the lignin by CE treatment is shown by the disappearance of the fine structure of the aromatic portion of the spectra in the region of 110–160 ppm (Fig. 2b).

The oxidation of the kraft lignin is seen by the development of a very broad carbonyl peak centered at 175 ppm. The product of CE bleaching contains, as expected, less lignin but retains carbohydrates as shown by the signals in the 70–80 and 100–110 ppm regions. The spectra of E effluent (Fig. 2a) are also comparable to that of CEKL. During the CE bleaching of kraft lignin, approximately two-thirds of the material is lost, much of it aromatic. Furthermore, the similarity between the NMR spectra for E effluent and CEKL further supports the hypothesis that CEKL and CE residual lignin are structurally similar.

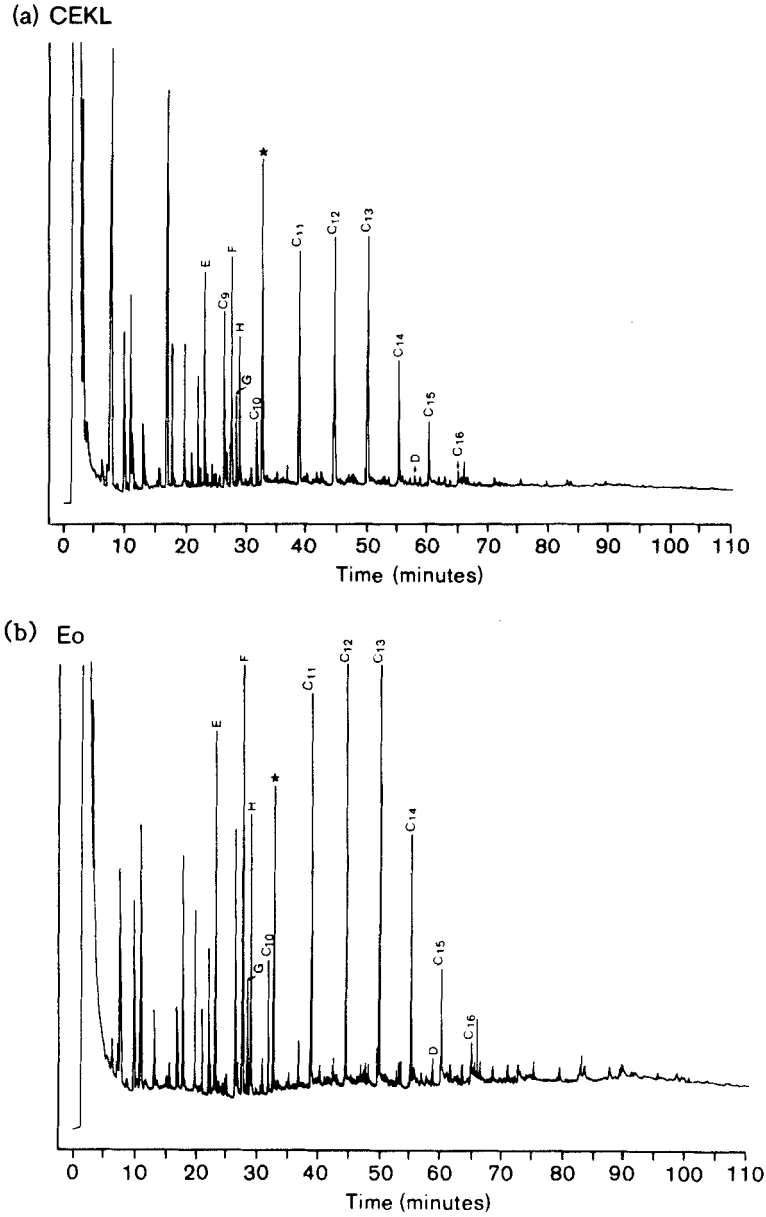
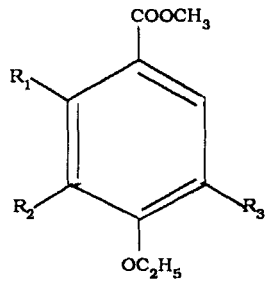


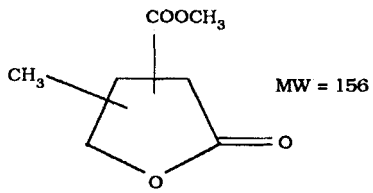
FIGURE 1. Gas chromatogram of the products resulting from the permanganate/periodate oxidation of (a) chlorinated and extracted kraft lignin CEKL and (b) extraction stage effluent E.

TABLE 3
Identification of Oxidation Acids



	COMPOUND	Rt
A	R_1 = H, R_2 = H, R_3 = OCH_3	73.6
B	R_1 = $COOCH_3$, R_2 = H, R_3 = OCH_3	90.0
C	R_1 = H, R_2 = $COOCH_3$, R_3 = OCH_3	97.5
D	R_1 = H, R_2 = H, R_3 = H	58.5
X	R_1 = H, R_2 = H, R_3 = OC_2H_5	ND
Y	R_1 = H, R_2 = $COOCH_3$, R_3 = OC_2H_5	ND

C_x Methyl ester of linear acid of chain length



E, F, G, and H
Exact position of the functional groups and double bond cannot be determined by mass spectrometry.

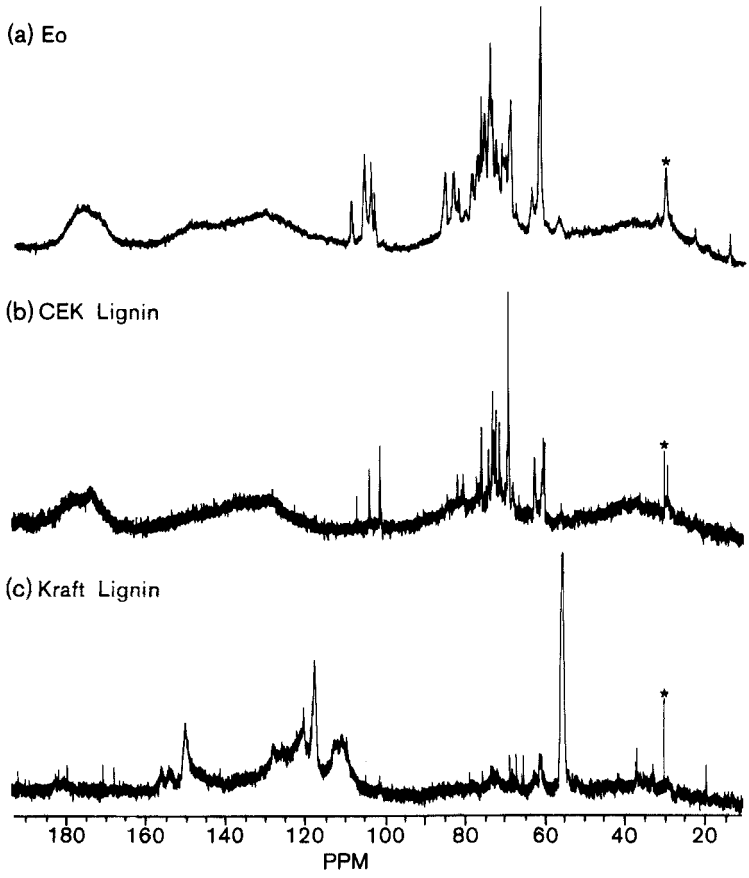


FIGURE 2. NMR spectra of (a) extraction stage effluent Eo, (b) chlorinated and extracted kraft lignin CEKL, and (c) kraft lignin KL.

The dealkylation of guaiacol units by chloronium ions to produce methanol is seen in the disappearance of the methoxyl signal at 55.9 ppm (Fig. 2c and 2b). Pfister and Sjöström[8] found that 5.95 kg methanol was produced per ton of pulp.

These results obtained on the KL and CEKL samples support the statement by Lindström and Österberg[2] that the bulk of the native lignin structure is destroyed during the chlorination and extraction bleaching sequences. Furthermore, it is doubtful if any of Gierer's proposed leucochromophores would survive a CE bleaching sequence.

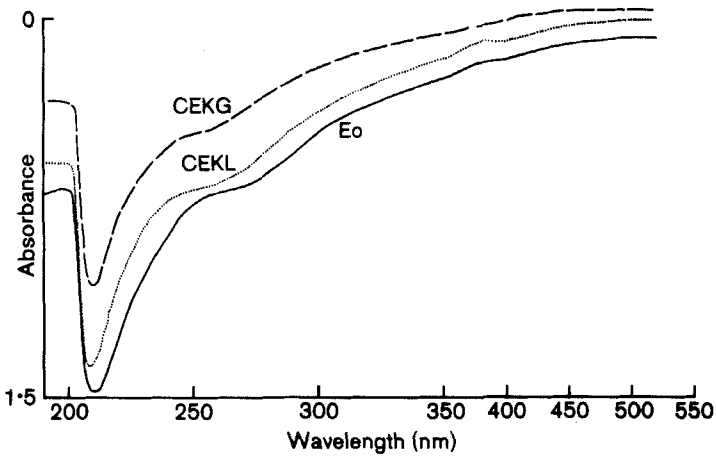


FIGURE 3. UV-visible absorption spectra for CEKG, CEKL, and E effluent.

Carbohydrate Degradation

Another possible source for the coloured high molecular weight products present in CE effluent is from the alkaline polymerisation of wood carbohydrates and the reaction of these products with chlorine and alkali. To test this hypothesis glucose was cooked under kraft conditions and the high molecular weight components (>1000 D) were subsequently chlorine bleached and alkaline extracted.

The "kraft cooking" of glucose (KG) yielded 7% polymer, which was readily obtained by adjustment of the cooking liquor to pH3 with the addition of 3 M sulphuric acid. During bleaching, kraft glucose (KG) consumed about half the chlorine (0.71 g Cl_2/g substrate) to form chlorinated extracted kraft glucose (CEKG) as did precipitated kraft lignin (1.42 g Cl_2/g substrate) to form CEKL.

The UV-vis absorption curves of CEKG to CEKL and E effluent are compared in Fig. 3, and the absorptivities at three selected wavelengths, 465 nm (colour), 280 nm (phenols), and 254 nm (aromatics), and the ratio of 280/254 nm are summarised in Table 4.

Kraft cooked glucose (KG) was the most intensely coloured material and also has high absorptivities at 280 and 254 nm. The absorbance at 280 nm is to be anticipated since phenol was detected among the permanganate/periodate

TABLE 4
Absorptivities

	465 nm Lg^{-1} cm^{-1}	280 nm Lg^{-1} cm^{-1}	254 nm Lg^{-1} cm^{-1}	280/254
KL	0.517	11.6	12.5	0.928
CEKL	0.513	7.57	9.88	0.766
KG	2.84	20.0	23.7	0.840
CEKG	1.34	14.7	18.7	0.786
E	1.67	15.6	19.8	0.788
PE	0.496	16.8	23.7	0.709

oxidation products. Furthermore, various workers[13, 14, 15, 16] have isolated a variety of aromatic and phenolic compounds from alkaline and kraft cooking of sugars. KG has a ratio of 286/254, intermediate between that for KL and the bleached products. The effect of the CE bleaching sequence is seen by the decrease in the ratio of the absorptivities at 280/254 showing the destruction of any substituted phenolic residues. Upon bleaching of KG, colour was decreased over 50% while the absorptivities due to phenols and aromatics decreased about 30%. The bleaching of KL caused decreases in the absorptivities at 280 nm and 254 nm but did not affect color.

If the chromophores of kraft black liquor are lignin related, then CE bleaching should decrease the absorptivities at all of the wavelengths measured. Instead the absorptivity for colour (465 nm) remains constant while those at 280 nm and 254 nm decrease. There is also a decrease in the ratio of absorptivities 280/254 showing that the CE bleaching sequence is destroying substituted phenols.

Bleaching of E effluent with hydrogen peroxide causes a decrease in colour greater than 70%, as seen in Table 4 and in Fig. 4. However, there is an increase in the absorptivities at 254 nm and 280 nm. If kraft colour was due to the aromatic portions of lignin then a corresponding decrease would be expected as well. Peroxide bleaching also decreases the absorbance at 207 nm in E effluent.

Therefore, the UV-visible data further support the notion that the chromophores responsible for kraft colour are not lignin related. They may therefore be derived from carbohydrate degradation products attached to kraft lignin, or associated with it.

Though CEKG, CEKL, and E effluent (Fig. 3) have some similar UV-visible absorption spectra characteristics, they are structurally quite different, as seen

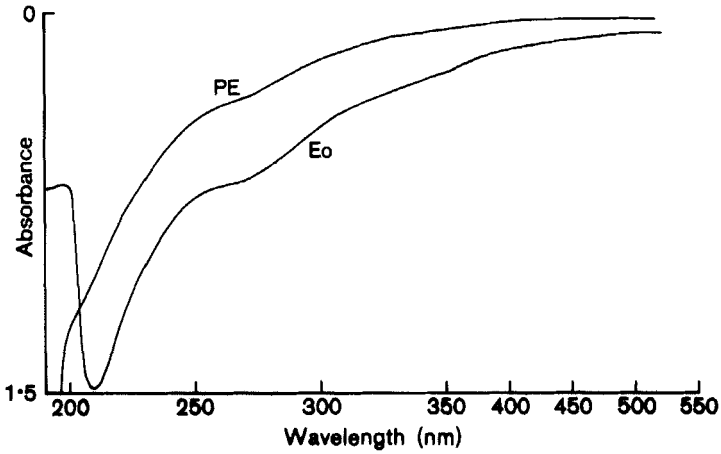


FIGURE 4. UV-visible absorption spectra for E effluent (E) and hydrogen peroxide bleached E effluent (PE).

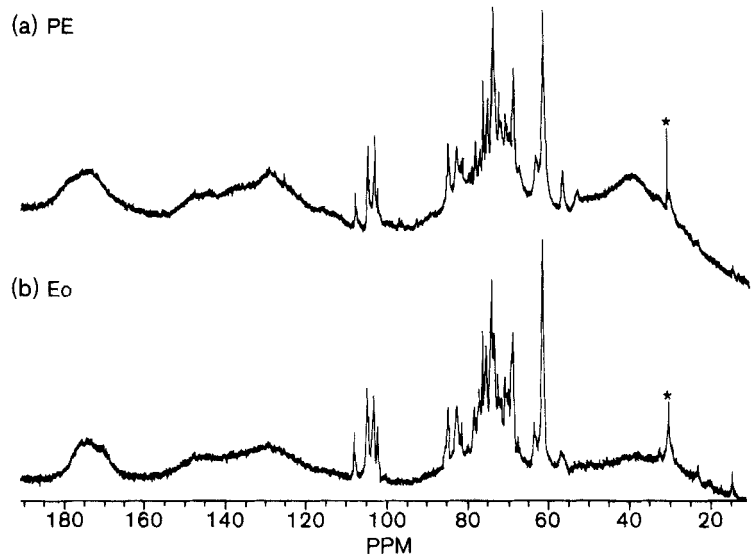


FIGURE 5. NMR spectra of (a) hydrogen peroxide bleached E effluent PE and (b) E effluent Eo.

by their NMR spectra (Fig. 6b, 6c, and 5b respectively). NMR shows that KG derived materials are just random polymers which give broad, nondistinct signals. The NMR spectra of E and CEKL show the remains of the lignin structures after a CE bleaching sequence. Upon bleaching with hydrogen peroxide no major structural differences between PE and E are distinguished though there is a 70% reduction in colour (Fig. 5a and b). Therefore, decolorisation may involve minor structural changes in the chromophores to cause decolorisation. Since the chromophore is only a minor component in the polymer, it is not possible to detect the changes.

Hypothesis

It is proposed that during the kraft cook the "peeling" reactions are terminated by the presence of lignin fragments attached to the sugars. Kleinert[17] proposed that during kraft cooking lignin could be bound to sugars via ether linkages. Recently, Gierer and Wännström[18] have isolated such lignin-carbohydrate complexes. The termination of the "peeling" reaction could leave a terminal keto-enol.

The presence of keto-enols was first proposed by Bennett *et al.*[19] as one of the groups which can complex with calcium to cause precipitation of the high molecular weight dissolved solids in kraft effluent.

A few of the proposed chromophoric structures and their calculated λ max. are summarised in Fig. 7. The extension of the conjugation and/or the addition of various substitutents to the enone give rise to an entire family of compounds. The observed broad spectral curve could be a summation of the spectra of a family of related compounds with the proposed parent structure. All of these compounds would have molar absorptivities greater than 10,000.

The substitution of chloride groups for hydroxyl groups would cause a hypsochromic (blue) shift ranging from 12 to 50 nm depending upon the site of substitution. Furthermore, the colour change observed upon pH adjustment of E effluent may be due to the charge stabilization by H^+ of the carbonyl groups, which would disrupt the conjugation of the chomophores. Oxidation of the proposed chromophores by hydrogen peroxide should destroy the absorbance at 207 nm. This decrease in absorbance at 207 nm is observed when Eo effluent is bleached by hydrogen peroxide (Fig. 4).

To test the hypothesis that kraft effluent colour is carbohydrate derived, α-glucose and cellobiose were chlorinated and extracted. Glucose consumed 0.188 g chlorine/g substrate while cellobiose used 0.200 g chlorine/g substrate during the chlorination stage. In Fig. 8 the NMR spectra are compared for

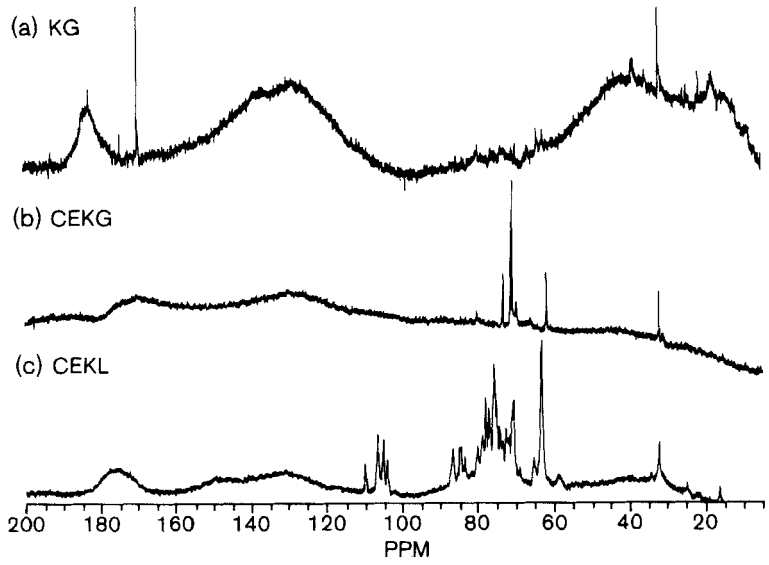


FIGURE 6. NMR spectra for (a) kraft cooked glucose KG, (b) chlorinated extracted kraft cooked glucose CEKG, and (c) chlorinated and extracted kraft lignin CEKL.

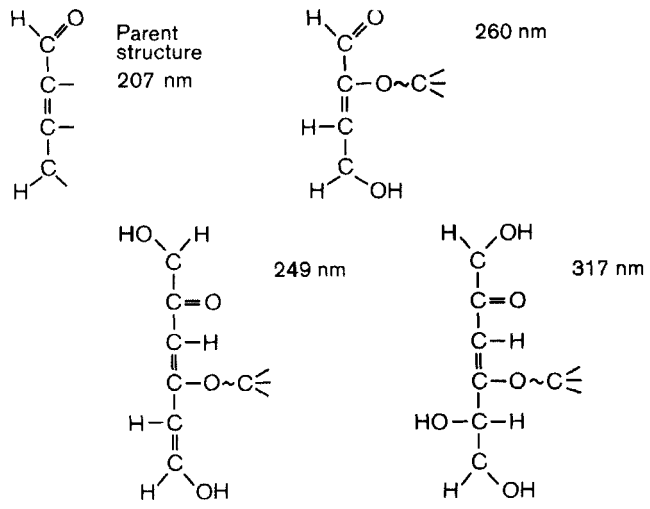


FIGURE 7. Some proposed chromophoric structures.

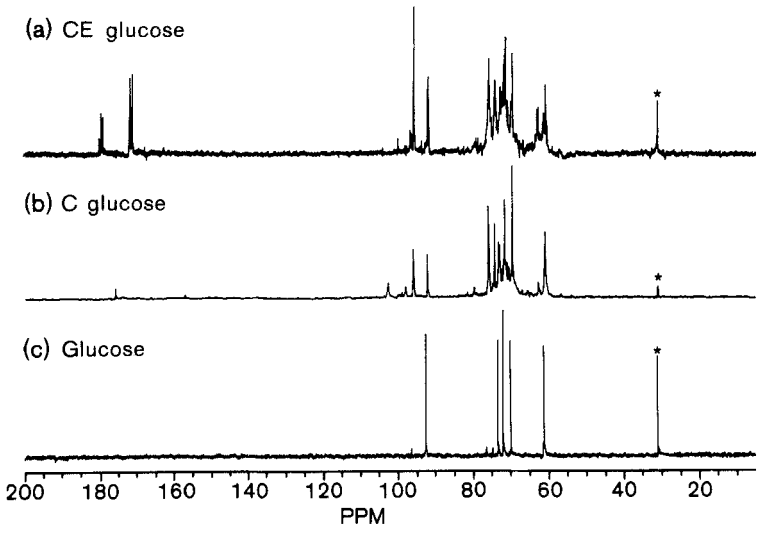


FIGURE 8. NMR spectra for the crude reaction products from the chlorination and extraction of glucose.

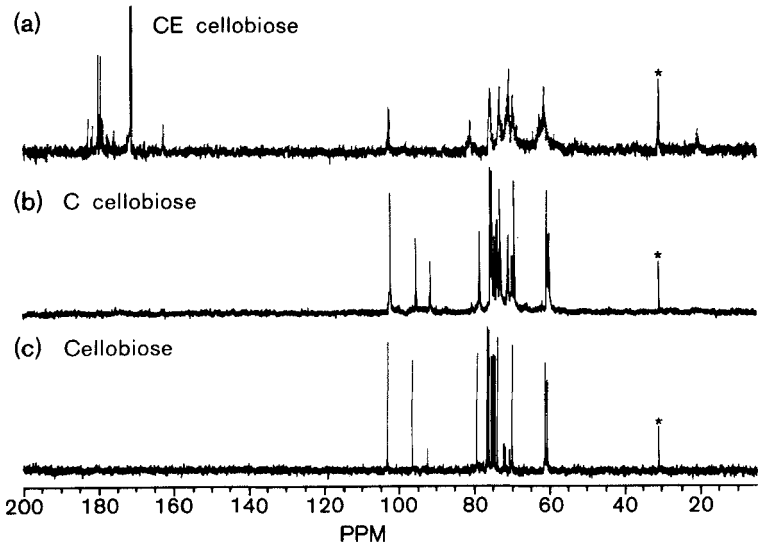


FIGURE 9. NMR spectra for the crude reaction products from the chlorination and extraction of cellobiose.

glucose (Fig. 8a), chlorinated glucose (Fig. 8b), and chlorinated and extracted glucose (Fig. 8a). A similar series is shown for cellobiose in Fig. 9. When glucose was chlorinated, a soluble black product was obtained upon freeze drying, while the chlorinated cellobiose product was white. After extraction, though, both had the typical kraft brown colour. Increasing the degree of polymerization led to an increase in the complexity of the spectra, seen by comparing Fig. 8a and 9a. Chlorination of the samples increases the band broadening, with the corresponding loss of fine structure. After extraction of cellobiose, the signals due to the free anomeric C (92 & 96 ppm) disappear and give rise to the carbonyl signals at 170 and 180 ppm. The signal for the bound anomeric carbons remains constant through the processing of the sample at 102 ppm.

CONCLUSIONS

This work has shown that chlorinated and extracted precipitated kraft lignin is identical to E stage effluent. Since E stage effluent is the product of the chlorination and extraction of residual lignin in pulp, then both kraft lignin and residual lignin are degraded by CE to a common high molecular weight polymer.

As previously found by Erickson and Dence[6] and Lindström and Österberg[2] the high molecular weight solids in Eo effluent are very low in aromatic content with the remaining aromatic structures derived primarily from the phenol residues. Therefore it is extremely doubtful that any of Gierer's[4] proposed leucochromophoric groups would survive a CE bleaching sequence. This work has also shown that Eo effluent colour is independent of guiacyl content.

It is proposed that the termination of kraft "peeling" reactions could result in terminal keto-enols, and that these enols are responsible for the kraft colour. There is no one chromophore but a "family" of compounds depending on the extent of conjugation and/or substituents attached to the enol. It has been possible to generate crude mixtures of the proposed chromophores by the chlorination and extraction of glucose or cellobiose.

EXPERIMENTAL

Sources of Materials

E stage effluent was collected from a commercial kraft paper mill operating predominantly on *Pinus radiata*, and was stored at 4°C until used. The

bleaching sequence of the mill is (C+D)EoDED. Precipitated kraft lignin (KL) was prepared from a kraft cook of *Pinus radiata* chips. The cook had a sulphidity of 27.1, 17% AA, 1900 H factor and the pulp had a kappa number of 27.1. The kraft lignin was precipitated from black liquor by adjusting the pH to 3 with 3M sulphuric acid. The abbreviations for the various samples tested are listed in Table 2.

Kraft Cooked Sugars

Kraft cooked glucose samples were prepared by dissolving 10 g glucose (Sigma G-5000), in 3.5 g NaOH and 3.1 g $Na_2S \cdot 9H_2O$/100 ml distilled water in a teflon-lined bomb. The reaction bombs were purged with nitrogen before being sealed. The samples were then submerged in a preheated oil bath at 80°C. The temperature was raised to 170°C over 70 minutes and maintained at 170°C for 95 minutes. During cooking the vessels were agitated every half hour. The reaction was stopped by rapidly chilling the vessels in cold water.

Precipitated kraft sugars (sugar degradation products) were isolated by adjusting the pH of the black liquor to 3 with 3 M sulphuric acid, yielding 0.7 g precipitated kraft cooked sugars. The precipitated kraft sugars were then dissolved and extracted three times with chloroform. The aqueous phase was then ultrafiltered (see below) against MilliQ water until the conductivity of the permeate was less than 3.0 µs/cm.

Ultrafiltration

Ultrafiltration was carried out according to the method of Alen *et al.*[20], using either an Amicon model 52 stirred well (working volume of 75 ml) with a YM2 membrane, or an Amicon DC2A hollow fibre system with an H1P3 cartridge. The retentate from the ultrafiltration was freeze dried and stored as a freeze dried powder at room temperature.

Bleaching Procedures

Samples (0.3–1.5 g) were bleached with an aqueous solution of 5–6% chlorine. The KG and KL were first dissolved in a minimum of 10% NaOH (less than 1 ml). Chlorine was added at the level of 1–1.5 mg chlorine per mg sample, to ensure complete chlorination. The pH was adjusted to less than 2.0 and the flasks were stoppered and stirred for half an hour at room temperature. Initial and final chlorine levels were measured according to the method of Seymour and

Lavigne[21]. After the determination of residual chlorine, the excess was vented by bubbling nitrogen through the liquor until no chlorine could be detected. The chlorinated sample was divided into two fractions. In one fraction the pH was then adjusted to 10.5-11.5 with NaOH, and the sample was heated at 65°C for 1 hour, to mimic the extraction stage.

The CEKL and CEKG samples were ultrafiltered to remove low molecular weight products and salts. All samples were freeze dried and stored as freeze dried powders at room temperature.

Hydrogen Peroxide Bleaching

To 900 ml of E stage effluent, was added 100 ml of 30% hydrogen peroxide. The solution was stirred at room temperature for up to 2 weeks. The bleached E effluent (PE) was ultra-filtered and freeze dried. The pH was 10.5.

Permanganate/Periodate Oxidation

Oxidation and subsequent gas chromatographic analysis were performed as previously described by Ziobro[22].

Nuclear Magnetic Resonance

The NMR spectra were run on a Bruker AC-200 NMR spectrometer using a 10 mm broadband probe operating at 50.33 MHz for ^{13}C. All spectra were recorded relative to external acetone (30.4 ppm). Sample temperatures were maintained at 25°C. A WALTZ-16 power gated ^{1}H-decoupling sequence was used with a spectral width of 12 kHz and 16K data points. A 60°C pulse angle was used with a repetition delay of 1 second, and an acquisition time of 0.7 seconds. An exponential line broadening of 2 Hz was applied to improve the S/N ratio. On average 100,000 transients were recorded.

Spectral Analysis

Known amounts of freeze-dried samples were dissolved in 0.05 M phosphate buffer at pH 7.6 and UV-visible absorption curves obtained using a Perkin-Elmer 402 UV-visible spectrophotometer, using phosphate buffer as the reference.

Absorbances at selected wavelengths were obtained with a Pye Unicam SP6-550 UV-visible spectrophotometer.

ACKNOWLEDGEMENTS

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