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CONTRIBUTION OF CARBOHYDRATE-DERIVED CHROMOPHORES TO KRAFT PULPING LIQUOR COLOUR

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CONTRIBUTION OF CARBOHYDRATE- DERIVED CHROMOPHORES TO KRAFT PULPING LIQUOR COLOUR

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ABSTRACT

Pine wood, holocellulose, glucose and milled wood lignin were kraft cooked and the acid-insoluble materials isolated. Based on the amounts of precipitates isolated and their absorbances, most, or all, of the absorbance of the acid-insoluble material in kraft spent liquor (kraft lignin, KL) could be ascribed to lignin-derived chromophores. The absorption spectrum of kraft-cooked glucose (KG) differed significantly from that of KL and kraft-cooked milled wood lignin (KMWL), with a higher absorbance in the visible region of the spectrum. It also responded differently on treatment with a number of chemicals, strongly suggesting that carbohydrate-derived chromophores could only contribute slightly to the absorbance of KL. The effect of sequential treatment with oxygen, chlorine dioxide and alkali on the absorption spectra of KL, KG and KMWL was also determined. This produced no evidence to suggest that carbohydrate-derived chromophores contribute significantly to chromophore changes during these bleaching stages.

INTRODUCTION

Kraft cooking leads to formation of chromophores, or light-absorbing groups, in both the pulp and spent pulping liquor. The chromophores present in the pulp after cooking must be removed in subsequent bleaching stages. The nature of the chromophores responsible for kraft pulp colour is not well defined, mainly because analysis of the chromophores within the pulp matrix, or isolating this coloured material from the pulp in a pure and unmodified form, is very difficult. One frequently used model of the coloured material, and indeed the lignin, within kraft pulps is the precipitate formed on acidification of the spent pulping liquor. How closely the chromophores in this material, commonly called kraft lignin, mimic those in the fibre is, however, currently not well defined.

While the chromophores in kraft lignin are generally considered to be formed mainly by degradation of the lignin during pulping,¹⁻⁴ carbohydrate degradation products have also been suggested to contribute to the colour of kraft pulps and spent liquors. For example, Graef⁵ reported as early as 1939 that kraft cooking of cotton linters in the presence of glucose gave a brown fibre. This suggested that degradation products from alkaline digestion of sugars gave colours similar to those of unbleached kraft pulps, and that they may contribute to kraft pulp colour. Hartler and Norrström² compared the absorbance of kraft pulps at 457 nm to the absorbance of kraft-cooked holocelluloses, and concluded that at yields typical of those produced during kraft pulping, lignin contributed *ca.* 90% and carbohydrates *ca.* 10% to the absorbance of pulps. More recently, Ziobro⁶ and Tan and Reeve⁷ have reported that acidification of the liquor from kraft cooking of glucose gave dark precipitates which could potentially contribute to the colour of kraft lignin. Ziobro^{6,8} reported that this high molecular weight material (> 1,000 Daltons) had spectral properties similar to those of the material isolated from kraft cooking of wood, and suggested that keto-enols produced by kraft cooking of sugars were primarily responsible for the kraft colour. Kraft cooking of both holocellulose and fully bleached pulps leads to a drop in brightness, suggesting that carbohydrate-derived chromophores can also be produced in the fibre during alkaline cooking.^{2,9}

The objective of this study was to further examine the contribution carbohydrate-derived material makes to the absorbance of kraft pulping liquors, and more specifically, to determine whether degradation products produced by kraft cooking of carbohydrates could account for the liquor colour. To do this, wood and wood-derived components, including milled wood lignin (MWL), glucose and holocellulose, were kraft cooked and the material precipitated on acidification of the pulping liquors isolated. These materials were compared in terms of their absorption spectra, the amounts



produced and how their absorption spectra responded to a number of chemical treatments. Also, to determine whether any of the chromophore changes occurring during bleaching of pine kraft pulps could be ascribed to carbohydrate-derived chromophores, these precipitates were treated sequentially with oxygen, chlorine dioxide and alkali and the effect on the absorption spectra determined.

RESULTS

Proportion of Kraft Spent Liquor Colour Removed on Acidification

Before using acid-insoluble materials to examine the colour of spent kraft pulping liquor, the proportion of the absorption the liquor associated with the acid-insoluble material was determined. Figure 1 compares the absorption spectra of a sample of spent (black) liquor from kraft pulping of radiata pine (*Pinus radiata*) chips to kappa number 37.1 to that of the same liquor after acidification to pH 2 and removal of the precipitate. This showed that almost all the absorbance in the spent liquor was associated with the acid-insoluble material. For example, at 400 nm, more than 99% of the absorbance was removed from the liquor on acidification, along with 95% of the absorbance at 280 nm. The absorption spectrum of the KL was very similar to that of the spent pulping liquor when redissolved in the

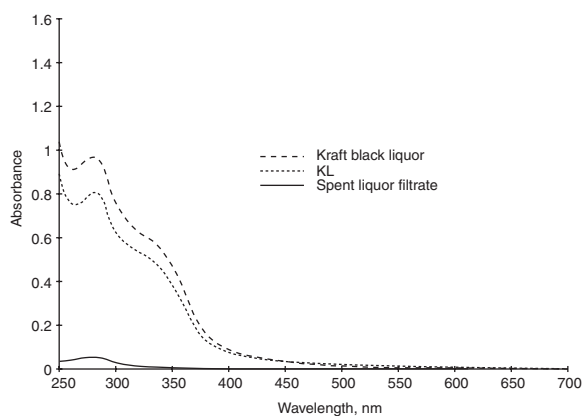


Figure 1. Comparison of absorption spectra of kraft black liquor, filtrate formed on acidification of this material to pH 2 and the resulting precipitated kraft lignin. Corrected for the volumes of acid and water added during acidification. Solvent: 1:1 methoxyethanol: pH 6.5 phosphate buffer.



solvent mixture at the same concentration as originally present in the spent liquor. This suggests that the chromophores present in KL and the spent liquor are very similar and have not been modified as a result of acidification during KL isolation. The discrepancy between the absorbance of the spent liquor and that of the KL plus the filtrate may well be associated with losses during the isolation of KL and/or impurities in KL.

Pulping of Wood Components

To compare the amount of acid-insoluble material from kraft cooking of the isolated wood components to that formed during pulping of wood, the amount of each component was set to be the same as that present when pulping the whole wood. Pulping of the radiata pine wood was carried out under typical conditions to give a pulp with a kappa number of 30.9 and a yield of 46.2%. The liquor: wood ratio was 4:1. As the wood used contained 28.9% Klason lignin, 100 g of wood was replaced by 28.9 g of milled wood lignin or 71.1 g of holocellulose for each 400 mLs of pulping liquor. To set a maximum possible level for the sugar degradation products, all the carbohydrates solubilised during pulping were assumed to be glucose. This corresponds to 30 g of glucose per 400 mL of liquor assuming a pulp yield of 46%, delignification of 90% and a typical initial wood Klason lignin content of 27%. It is also assumed that all monomeric carbohydrates behave similarly to glucose. Because wood contains small amounts of protein, and thermal reactions between monomeric carbohydrates and proteins can lead to colour formation,¹⁰ glucose was also kraft-cooked in the presence of 2% by weight of the amino acid, glycine.

Table 1 compares the amounts of acid-insoluble material obtained from liquors produced by kraft cooking of wood and isolated wood components. All results are expressed assuming pulping of 100 g of wood, although in reality the runs were performed on widely differing scales.

The results in Table 1 suggest that the acid-insoluble material in spent liquors from kraft pulping of wood is mainly lignin-derived, but that carbohydrates could contribute to a portion of the mass. However, it is not possible to draw any quantitative conclusion about the levels of carbohydrate-derived material in KL from this data. Comparing the response of isolated wood components and whole wood during pulping assumes that other components in the wood do not affect the degradation of the component of interest or the pulping conditions. This is clearly not correct. For example, because carbohydrates consume alkali during kraft cooking, the presence of carbohydrates in the wood will greatly change the alkali profile during cooking relative to that seen if lignin were cooked alone.



Table 1. Yields of Acid-Insoluble Materials from Kraft Cooking of Wood and Isolated Wood Components

	Starting weight, g	Acid-insoluble material	
		Weight, g ^a	Abbreviation
Wood	100.0	26.8	KL
MWL	28.9	17.6	KMWL
Glucose	30.0	1.3	KG
Glucose + glycine	30.0 + 0.6	1.1	KGGI
Holocellulose	71.1	5.9 ^b	KH
- ^c	-	0.06	

^aAssuming starting with hypothetical 100 g wood.

^bSee text.

^cPulping chemicals alone.

Also, physical factors, such as the penetration of the pulping chemicals into, and diffusion of the degraded material out of, the fibre are completely absent when cooking a homogeneous solution of a dissolved lignin or carbohydrate. In addition, MWL may not be representative of native wood lignin.

Absorption Spectra of Acid-Precipitated Materials

Figure 2 compares the absorption spectra of the acid-insoluble materials produced from kraft cooking of wood and isolated wood components at equal concentrations (0.05 mg/mL) in 1:1 methoxyethanol:water. This showed that KG absorbed more strongly in the visible region of the spectrum than either KL or KMWL. The similarity of the absorption spectrum of KL to that of KMWL and the higher absorbance of KG in the visible region of the spectrum suggests that the colour of KL is mainly lignin-derived. However, a small contribution from carbohydrate-derived materials cannot be ruled out on this basis.

Addition of glycine during kraft cooking of glucose had no significant effect on either the amount of the acid-insoluble material produced or its absorption spectrum (Table 1, Fig. 2). This suggests that Maillard-type chemistry does not contribute significantly to the colour of kraft spent liquors.

The acid-insoluble material from kraft cooking of the holocellulose (KH) was only partially soluble in methoxyethanol:water, and had a very



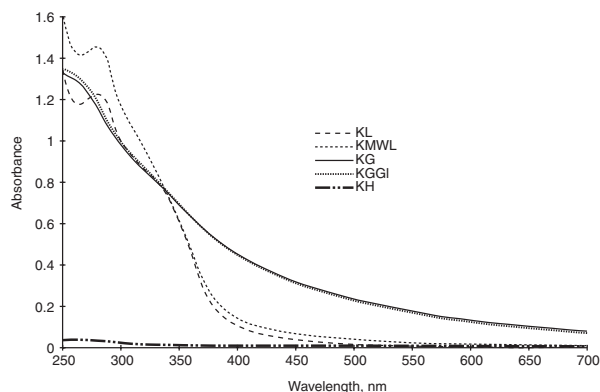


Figure 2. Absorption spectra of the acid-insoluble material from kraft cooking of wood and wood components.

low absorbance. It was observed that KH contained a significant portion of colourless material, perhaps polysaccharides, which precipitated when the pH of the cooking liquor was lowered. Only small amounts of KH were available, limiting further characterisation.

Characterisation of KG

While KG contained no appreciable methoxyl content, when analysed in the widely used Klason and acid-soluble lignin determinations, it analysed as >80% “lignin” (Table 2). Microanalysis showed that approximately half the weight of KG was composed of sulfur. Some elemental sulfur is frequently obtained in the precipitate on acidification of softwood kraft spent liquors,¹¹ and it is possible that acidification of liquors from kraft cooking of glucose leads to a higher proportion of elemental sulfur in the precipitate. KG was partially soluble in d_6 -DMSO and gave broad signals in the ^{13}C NMR spectrum suggesting that it contains carboxylic acid groups (signal centered around 170 ppm), a range of aromatic and/or olefinic carbons (signal envelope at 110–150 ppm) and aliphatic and hydroxylated carbons having signals between 10 and 80 ppm. Based on this spectrum, it would not be possible to use ^{13}C NMR spectroscopy to see whether KL contains a small amount of KG. A similar ^{13}C NMR spectrum was earlier reported for KG by Ziobro.⁸



Table 2. Analytical Data for the Precipitates from Kraft Cooking, % of Dry Material

	KL	KMWL	KG
Carbon	66.2	66.3	29.9
Hydrogen	4.3	4.6	2.5
Sulfur	7.1	5.2	52.6
Nitrogen	0.18	0.16	0.12
Oxygen ^a	22.3	23.7	14.9
Methoxyl	12.9	14.3	trace
Klason lignin	88.7	–	75.5
Acid-soluble lignin	3.5	–	5.5
Total Carbohydrates	5.0	–	0.5
Arabinose	0.70		n.d. ^b
Galactose	1.24		n.d.
Glucose	0.28		0.35
Xylose	2.74		0.16?
Mannose	n.d.		n.d.

^aBy difference.

^bNot detected.

Response of KL, KMWL and KG to Chemical Treatment

If carbohydrate-derived chromophores are responsible for the colour of kraft lignin, we must also be able to show that the absorption spectra of products from kraft cooking of carbohydrates respond to chemical treatments in the same way as does that of kraft lignin. To test this, the effects of sodium borohydride, sodium dithionite and alkaline hydrogen peroxide on the absorption spectra of KL, KMWL and KG were determined. The results are shown in Figures 3–5 as difference spectra where Δ absorbance = $A_{\text{original}} - A_{\text{treated}}$. The effects of these treatments on KL were similar to those we have observed previously.¹²

Figure 3 shows that KMWL responded similarly to KL on reduction with borohydride, whereas KG behaved significantly differently, consistent with KL being mainly lignin-derived. KMWL also responded much more similarly to KL than to KG on peroxide treatment, particularly in the visible region of the spectrum (Fig. 4). The lower response of KMWL to peroxide around 335 nm may be associated with a lower content of phenolic stilbenes (λ_{max} 340 nm) in this material. Ionisation difference spectra¹³ (data not shown) indicated that KL contained more phenolic stilbenes than KMWL,



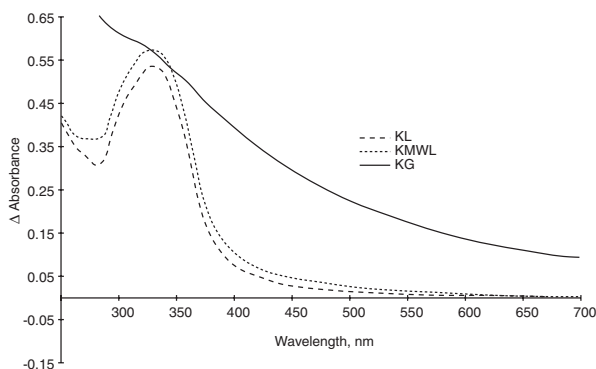


Figure 3. Effect of reduction with sodium borohydride on the absorption spectra. Conditions: excess NaBH_4 ; 1:1 methoxyethanol: water; room temperature; 8 days.

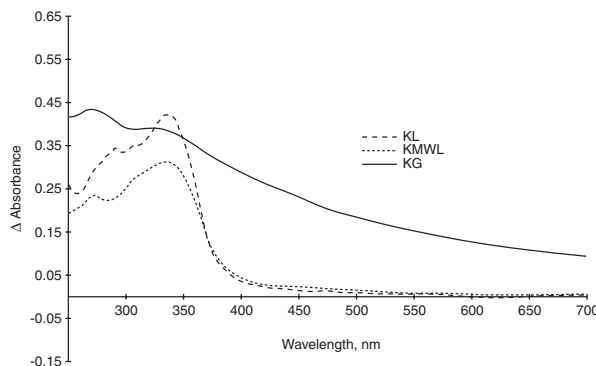


Figure 4. Effect of treatment with alkaline hydrogen peroxide. Conditions: excess H_2O_2 ; pH 11 buffer; 70°C ; 4 h; N_2 atmosphere.

and that these groups were largely or totally removed from both materials on peroxide treatment. While hydrogen peroxide does not degrade stilbenes directly, they are readily degraded by traces of oxygen which are likely to be present in the alkaline treatment as a result of peroxide decomposition or because they were incompletely removed when purging the reaction mixture with nitrogen.¹⁴ The results in Figure 5 suggest that the broad absorbance around 360 nm eliminated on reduction of KL with sodium dithionite, could, in part, be due to carbohydrate-derived chromophores. Alternatively, the differing responses of KL and KMWL to dithionite could be associated with differences in the structures of the two lignins.



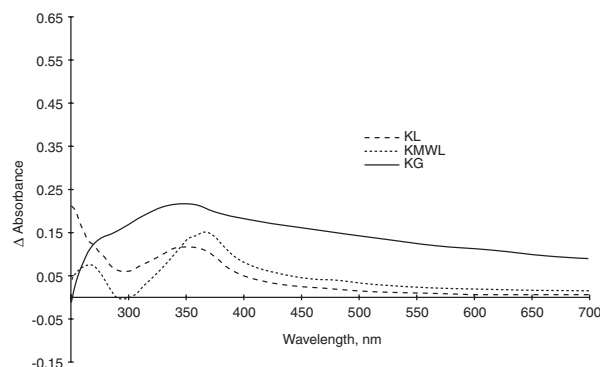


Figure 5. Effect of reduction with alkaline sodium dithionite. Conditions: excess $\text{Na}_2\text{S}_2\text{O}_4$; 1 M NaOH; reflux; 1 h; N_2 atmosphere.

Response of KL, KMWL and KG to Bleaching

It is possible that while carbohydrate-derived chromophores contribute only slightly to the colour of the kraft lignin, they could make an important contribution to the chromophore changes in one or more of the bleaching stages. To investigate this, the effects of sequential treatment with oxygen, chlorine dioxide and alkali on the absorption spectra of KL, KMWL and KG were examined. The necessary pH adjustments and chemical additions could be made without isolating the lignin after each treatment. Ethanol was added during the D stage to ensure the materials remained soluble under the mildly acidic conditions, and was consequently also present during the subsequent E stage. After each treatment, aliquots were removed, neutralised and diluted to a constant concentration (0.05 mg/mL as original substrate) before recording their absorption spectra. Trials using blank chemicals showed no interferences in the absorption spectra. Table 3 gives the absorbances at 400 and 465 nm of the three materials after each of the stages.

Oxygen delignification: Figure 6, which plots the change in the absorption spectrum on oxygen treatment of the three materials, shows that KL and KG responded very differently to oxygen, particularly in the visible region of the spectrum. While both KL and KMWL showed very slight chromophore formation on oxygen delignification around 400 nm, oxygen treatment of KG led to substantial chromophore elimination. This result suggests that kraft-cooked glucose contributes little, if anything to the colour of KL around 400 nm. The greater reduction in the absorption of



Table 3. Absorbances of KL, KMWL and KG After Sequential Treatment with Oxygen, Chlorine Dioxide and Alkali

	Original	O	OD	ODE
400 nm				
KL	0.086	0.091	0.031	0.067
KMWL	0.112	0.115	0.033	0.064
KG	0.347	0.135	0.033	0.064
465 nm				
KL	0.028	0.031	0.009	0.024
KMWL	0.045	0.041	0.009	0.022
KG	0.210	0.057	0.013	0.028

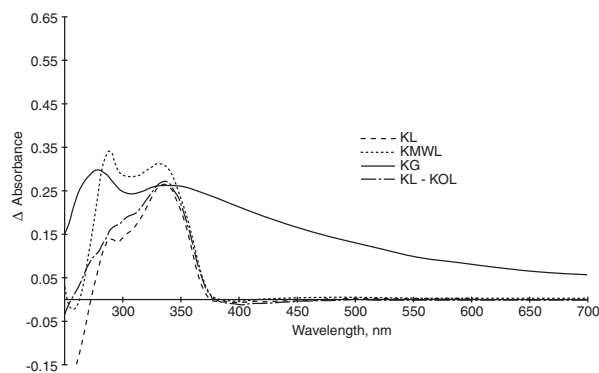


Figure 6. Effect of oxygen treatment on the absorption spectra of KL, KMWL and KG at equal concentrations. Conditions: pH 11 buffer; 100°C; 1.1 MPa oxygen; 4 h.

KMWL around 280 nm on oxygen treatment may be associated with a greater removal of phenolic guaiacyl units. Ionisation difference spectra (data not shown) indicated that, compared to KL, KMWL contained a higher proportion of phenolic guaiacyl units, and that a greater proportion of these groups were removed on oxygen delignification.

Figure 6 also shows that the change in the absorption spectrum of KL on oxygen treatment was in reasonable agreement with the difference in the absorption spectrum of untreated KL and KOL, where KOL is the acid-insoluble material isolated from the spent liquor following oxygen delignification of the kraft pulp to kappa number 18.3. This suggests that KL models reasonably well the behaviour of the lignin remaining within the kraft pulp, at least in terms of its response to oxygen.



Chlorine dioxide: Figure 7 compares the effect of chlorine dioxide on the absorption spectra of oxygen-treated KL, KMWL and KG. Commercial chlorine dioxide, containing 12% of the total active chlorine as Cl_2 , was used for these treatments. Excess chlorine dioxide remaining at the completion of all the reactions was removed by thorough purging with nitrogen. These results indicated that, while there were some differences in the extent of the treatment, the changes in KL were much more similar to those of KMWL than to KG. This is again consistent with the chromophore changes in the D stage being largely those of lignin-derived material. The differences

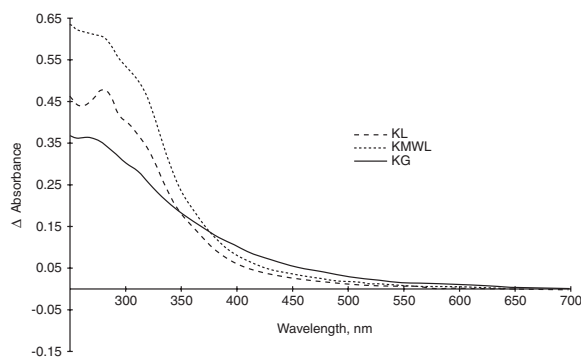


Figure 7. Effect of chlorine dioxide treatment on oxygen-treated KL, KMWL and KG. Conditions: excess ClO_2 ; 1:1 ethanol:pH 4 buffer; 50°C ; 1 h; N_2 atmosphere.

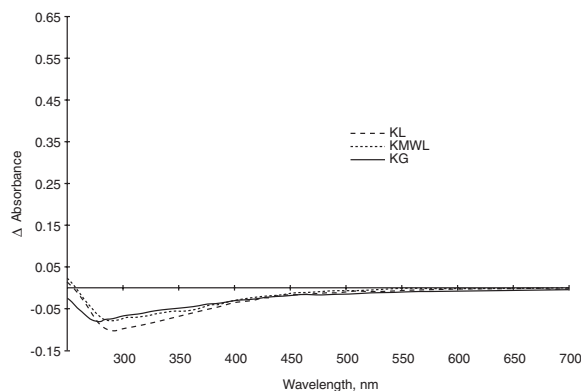


Figure 8. Effect of alkali treatment on the absorption spectra of oxygen and chlorine dioxide-treated KL, KMWL and KG. Conditions: 1:1 ethanol:pH 11 buffer; 50°C ; 1 h; N_2 atmosphere.

between the response of KL and KMWL may again be associated with differences in the structure of the two lignins.

Extraction: Figure 8 shows that alkali treatment led to chromophore formation (darkening) and that all three materials responded similarly. Chromophore formation in the E stage was recently suggested by Boman and Annergren¹⁵ on the basis of the absorption coefficient of the pulp plus spent liquor after (C + D)E treatment. Note that such colour formation is distinct from the effect of an E stage on the pulp, where higher pulp brightness after extraction is associated with removal of the degraded lignin from the pulp.

DISCUSSION

In this study, the contribution that carbohydrate-derived materials make to the colour of kraft lignin was assessed in terms of three criteria:

- The amount of colour produced by kraft cooking of carbohydrates and then precipitated on acidification of the liquor, relative to that produced during kraft cooking of wood and isolated lignin.
- The similarity between the absorption spectra of the kraft-cooked carbohydrates and that of the kraft lignin.
- The similarity between the response of the absorption spectra of the kraft-cooked carbohydrates and KL to further bleaching or chemical treatment.

Figure 9 compares the amount of colour produced at 400 nm during

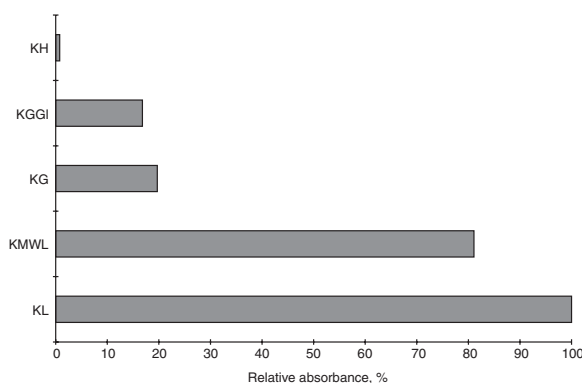


Figure 9. Relative amount of colour produced at 400 nm during kraft pulping of radiata pine wood and isolated wood components.

kraft cooking of the isolated wood components to that produced during kraft cooking of wood. These values were determined from the product of the mass proportions of precipitate produced during the various pulping runs (Table 1) and the absorbances of the corresponding precipitates at 400 nm. This suggests that degraded carbohydrates could potentially contribute a small extent to the colour of KL at 400 nm, but that most of the colour is lignin-derived. As discussed above, more quantitative conclusions are not possible, because of the limitations inherent in comparing kraft cooking of isolated wood components and whole wood. The amount of colour produced on kraft cooking of holocellulose probably gives a better indication as to the levels of carbohydrate-derived colour produced than kraft cooking of glucose, as holocellulose is much more similar to the carbohydrates actually present in the pulp. Even then, the holocellulose cook may overestimate the carbohydrate-derived colour, as the holocellulose still contained a small amount of lignin, and the colour observed could originate from this material.

The comparisons between the absorption spectra of the kraft lignin and precipitates derived from kraft cooking the wood components, plus the results of the various chemical treatments on these materials, were all consistent with chromophores in the kraft lignin being mainly, or totally, lignin-derived. The results from oxygen delignification of the various precipitates (Fig. 6), are of particular interest. Oxygen delignification of KG led to significant chromophore elimination around 400 nm, whereas with both KL and KMWL there was slight chromophore formation. This result strongly suggests that chromophores such as those derived from kraft cooking of glucose do not contribute significantly to the colour of the kraft lignin, at least at this wavelength. The dithionite treatments were the only experiments to suggest that carbohydrate degradation products may contribute to the absorbance of the kraft lignin. However, it is possible that the difference in response between KL and KMWL to this treatment may be associated with differences in the structures of kraft-cooked wood lignin and MWL.

Overall, the study showed that while dark coloured material can be produced on kraft cooking of sugars, there was no evidence to indicate that such material contributed significantly to the colour of kraft spent pulping liquor, or to the chromophore changes occurring during bleaching of kraft pulps. The study also suggests that kraft pulp colour is largely lignin-derived, as it seems likely that the colour of the fibres and corresponding liquors will be of similar origin. Consistent with this suggestion, we showed in Figure 6 that the difference between the absorption spectra of KL and the corresponding material isolated from filtrates following oxygen delignification of kraft pulp was similar to the change in the absorption spectra of oxygen-treated KMWL or KL, but dissimilar to that of oxygen-treated KG.



Further work is clearly required to determine what role, if any, carbohydrate-derived chromophores play in determining kraft pulp colour.

Ziobro^{6,8} earlier proposed that 'kraft colour' was primarily due to degradation products produced by kraft cooking of wood sugars. His main reason for suggesting that the colour was not lignin-derived was that the high molecular weight material in E stage effluents following CE bleaching of pine kraft pulp had a much lower aromatic content than KL, but that this was not paralleled by the corresponding decrease in colour which would be expected if the colour is associated with aromatic residues, *i.e.* lignin-derived. The validity of the key assumption inherent in this line of reasoning – that the chromophores responsible for kraft colour are the same for both KL and material isolated from extraction effluents⁶ remains to be established. He showed, as confirmed here, that kraft cooking of sugars such as glucose and cellobiose produced a dark liquor, which afforded a dark precipitate on acidification. He then proposed such material was responsible for kraft colour, but did not test his proposal in the more detailed manner undertaken in this study.

EXPERIMENTAL

Pulping

Kraft pulping of *Pinus radiata* chips (300 g od) was carried out in 2 L stainless steel reactors at a liquor:wood ratio of 4:1, an effective alkali charge of 16% as Na₂O and a sulfidity of 31.3%. The pulping liquor for these experiments was prepared in distilled water from analytical-grade reagents. The temperature was ramped from ambient to 170°C over 90 minutes and held at this temperature for 60 minutes. The pulp yield was 46.2% and kappa number 30.9.

The isolated wood components were treated under the same conditions with the same pulping liquor. Thus, *P. radiata* milled wood lignin¹⁶ (0.957 g) was treated with 13.8 mL of liquor, *P. radiata* holocellulose¹⁷ (1.0 g od, 0.6% Klason lignin) with 5.6 mL of liquor, glucose (90 g) with 1200 mL of liquor and a mixture of glucose (90 g) plus glycine (1.8 g) with 1200 mL of liquor.

Oxygen Delignification

Oxygen delignification of a sample of the above pulp was performed at 10% consistency using an oxygen pressure of 1.1 MPa O₂ in the presence of 1.5% sodium hydroxide and 0.1% magnesium sulfate for 60 minutes at 100°C. Samples of the resulting liquor were collected for lignin isolation



prior to pulp washing. The kappa number of the oxygen-delignified pulp was 18.3.

Isolation of Acid-Precipitated Materials

The kraft lignin and other precipitable materials were isolated from all, or a portion of the spent pulping liquors by adjustment to pH 2 with 20% H₂SO₄. The precipitates were separated with the aid of a centrifuge and washed three times with water adjusted to pH 2. The washed precipitates were then dried under reduced pressure and further under high vacuum.

Treatments with Sodium Borohydride

Sodium borohydride (200 mg) was added to a stirred 100 mL aliquot of a solution of the precipitates (15 mg) dissolved in 1:1 v/v 2-methoxyethanol:water (250 mL). Additional sodium borohydride was added on day 6 (100 mg) and day 7 (50 mg). A 15 mL aliquot was removed after 8 days, neutralised with 20% H₂SO₄ and centrifuged to remove boric acid salts.

Sodium Dithionite Treatment

The precipitates (15 mg) were added to a stirred deoxygenated solution of aqueous NaOH (50 mL, 1 mole/L) at room temperature. After an aliquot (5 mL) was removed for the reference, sodium dithionite (43.5 mg, 3 equivalents assuming a C₉ unit molecular weight of 180 g/mole) was added. The solution was heated at reflux for 1 hour under nitrogen, cooled and another aliquot (5 mL) removed. The aliquots were added to a deoxygenated mixture of 0.5 mol/L H₂SO₄ (5 mL) and 2-methoxyethanol (10 mL), and the resulting solution made up to 25 mL with deoxygenated 1:1 v/v 2-methoxyethanol:water.

Hydrogen Peroxide Treatments

The precipitates (15 mg) were added to a stirred deoxygenated solution of pH 11.0 carbonate buffer and hydrogen peroxide (8.65 mL, 0.048 mol/L, 5 equivalents/C₉ unit) and heated at 70°C. After 4 hours, a 5 mL aliquot was removed and added to a deoxygenated mixture of aqueous H₂SO₄ (5 mL,



0.02 mol/L) and 2-methoxyethanol (10 mL) and made up to 25 mL with deoxygenated 1:1 v/v 2-methoxyethanol: water.

Reaction with Oxygen

Oxygen was bubbled through a solution of the precipitate (150 mg) in pH 11.0 buffer (100 mL) in a 2 L stainless steel reactor for 5 minutes. The reactor was sealed and heated at 100°C for 4 hours under oxygen at a pressure of 1.1 MPa. An aliquot (2 mL) was removed from the cooled reaction vessel and neutralised with dilute H₂SO₄ (2 mL, 0.02 mol/L). Ethanol (4 mL) was added and the solution made up to 50 mL with 1:1 v/v ethanol: water.

Reaction with Chlorine Dioxide

Commercial chlorine dioxide water (23 mL, containing 6.2 g/L ClO₂ and 2.26 g/L Cl₂) was added to a 50 mL aliquot of the solution after oxygen treatment which had been adjusted to pH 7.2 with aqueous 20% H₂SO₄. The resulting mixture was diluted to 100 mL with pH 4.0 phosphate buffer. Ethanol (100 mL) was added, the volume adjusted to 200 mL with 1:1 v/v ethanol: pH 4.0 buffer, and the resulting solution stirred under nitrogen at 50°C for 1 hour. Nitrogen was then bubbled through the cooled reaction mixture to remove excess ClO₂. A 4 mL aliquot was diluted to 25 mL with 1:1 v/v ethanol: water for analysis.

Reaction with Alkali

A 100 mL aliquot of the solution after chlorine dioxide treatment was neutralised with a solution of NaOH in 1:1 ethanol: water and then diluted to 250 mL with 1:1 v/v ethanol: pH 11 buffer. The resulting solution was stirred under nitrogen at 50°C for 1 hour, cooled and an 8 mL aliquot removed. This was neutralised with 0.5 mol/L H₂SO₄ and diluted to 20 mL with 1:1 v/v ethanol: water ready for analysis.

Analyses

Absorption spectra were recorded from 200 to 700 nm using a path length of 1 cm, a bandwidth of 1.0 nm and a scan speed of 250 nm/min.



Spectra were determined at a constant concentration of 0.05 mg/mL by adding an aliquot (5 mL) of the lignin solution or neutralised reaction mixture (0.06 mg/mL in 1:1 v/v 2-methoxyethanol or ethanol : water) to 1 mL of pH 6.5 phosphate buffer.

Klason lignin was measured according to TAPPI Std T222 OM-83 and carbohydrate content by a method based on that of Pettersen and Schwandt.¹⁸ Microanalyses and methoxyl analyses were performed by the Campbell Microanalytical laboratory, Otago University.

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