FT–Raman Investigation of Bleaching of Spruce Thermomechanical Pulp

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Spruce thermomechanical pulp was bleached initially by alkaline hydrogen peroxide and then by sodium dithionite and sodium borohydride. Near-infrared Fourier-transform–Raman spectroscopy revealed that spectral differences were due primarily to coniferaldehyde and p*-quinone structures in lignin, new direct evidence that bleaching removes* p*-quinone structures. In unbleached pulp, the contribution of* p*-quinones was detected in the 1665–1690 cm^{-1} region. This contribution was removed to varying degrees in bleached pulps, depending on the extent to which the pulps were brightened. The relative change in the post-colour number of pulp was correlated linearly with the Raman intensity decline in the 1665–1690 cm^{-1} region, indicating that* p*-quinone structures were largely responsible for determining pulp brightness. The ^{13}C nuclear magnetic resonance spectra of milled softwood lignins, obtained to further support the Raman findings, exhibited a peak at ~180 ppm due to quinones. This peak was not detected in the spectra of milled hardwood lignins.*

De la pâte thermomécanique d'épinette a d'abord été blanchie avec du peroxyde d'hydrogène alcalin, puis avec du dithionite de sodium et du borohydrure de sodium. La spectroscopie à infrarouge Raman et transformées de Fourier a révélé que les différences spectrales étaient principalement attribuables aux structures aldéhydes des résineux et paraquinones dans la lignine, nouvelle preuve directe que le blanchiment élimine les structures paraquinones. Dans la pâte écrue, la contribution des paraquinones a été décelée dans la région 1665–1690 cm^{-1}. Cette contribution a été éliminée à divers degrés dans les pâtes blanchies, selon le degré de blanchiment de ces dernières. Le changement relatif de l'indice de jaunissement de la pâte était en corrélation linéaire avec le déclin de l'intensité Raman dans la région 1665–1690 cm^{-1}, ce qui indique que les structures paraquinones étaient en grande partie responsables du degré de blancheur imparti à la pâte. Le spectre ^{13}C résonance magnétique nucléaire des lignines de résineux moulus, déterminé afin de soutenir les résultats des essais avec la spectroscopie Raman, présentait une crête à ~180 ppm attribuable aux quinones. Cette crête n'a pas été décelée dans le spectre des lignines de résineux moulus.

INTRODUCTION

Bleached mechanical pulps are important furnish components in a number of paper grades. To further extend the use of these pulps, improvements are required in brightness and brightness stability. Progress in these and related issues, such as developing better bleaching agents and improving the efficiency of bleaching, can be made by understanding the nature of chromophores and their reactions with bleaching chemicals.

The intent of mechanical pulp bleaching is to achieve high pulp brightness by removing chromophores while retaining lignin and other pulp components. Pulp chromophores are present primarily in lignin and are responsible for low brightness. Most often, alkaline hydrogen peroxide is used for bleaching, although sodium dithionite and sodium borohydride have also been used when the targeted brightness is not high. The latter two compounds are classified as reductive bleaching agents, whereas peroxide is an oxidative agent. The effect of bleaching on hemicelluloses and extractives has been studied [1] but their removal seems to play no significant role in brightening.

To understand bleaching, bleached and unbleached pulps have been analyzed directly [2–10]. Additionally, reactions of bleaching agents with isolated lignins [11–13] and lignin models [11,14–18] have been carried out. Whereas direct analysis of spruce thermomechanical pulps (TMPs) has shown clearly that the chromophore coniferaldehyde is removed during both oxidative and reductive bleaching [5,8], such information is lacking for other pulp chromophores. The main reason for this lack of information is the low concentration of chromophores in pulp, which limits most techniques in characterizing them. For example, some information has been obtained by direct analysis of TMPs through ultraviolet/visible (UV/vis) [4,10,19], infrared (IR) [5,6], ^{13}C CP/MAS nuclear magnetic resonance (NMR) [9] and conventional Raman (sample excited by visible laser light) [7,8] spectroscopy. However, these methods are not able to detect quinones in pulps. In-situ detection of quinones is very important considering that quinones are likely to be the cause of low brightness of unbleached mechanical pulps [20–23]. Quinones are implicated because not only do they absorb at 457 nm, a wavelength where pulp brightness is measured, but they also have been found to be present in isolated lignins [22,23].

Previous work showed that near-IR (1064 nm excited) Fourier-transform (FT)–Raman is quite sensitive to detecting quinones and other chromophores [24]. In the present study, this technique was chosen to investigate the bleaching of spruce TMPs. Previously, FT–Raman

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spectroscopy was applied successfully in a number of areas in wood, pulp and paper research [13,25–34]. In particular, FT–Raman was found to be sensitive enough to detect quinones; in photoyellowed mechanical pulps, *p*-quinones were easily detected [29].

To obtain further supporting evidence for the existence of quinones in lignin, milled wood lignins (MWLs) from a number of softwoods and hardwoods were analyzed using ^{13}C NMR.

The goal of this study was to understand which chromophores are affected when spruce TMP is treated with oxidative and reductive bleaching agents in accordance with a bleaching sequence (Fig. 1). After each bleaching stage, the Raman spectrum of the bleached pulp was obtained and compared with the spectrum obtained after the previous bleaching stage in the sequence.

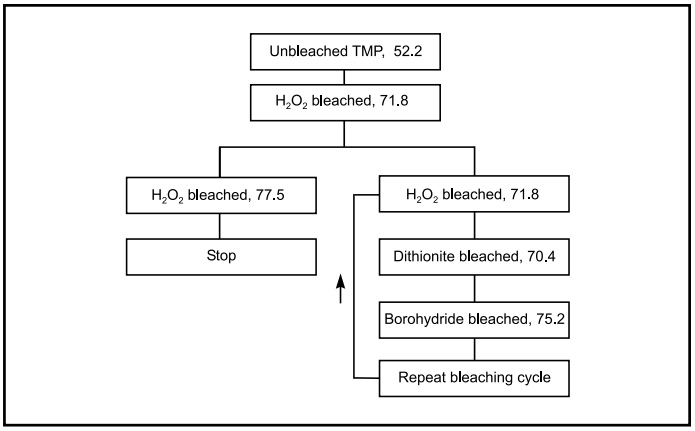

Fig. 1. Flow diagram showing sequence of bleaching for TMP. The number in each rectangle is the brightness of bleached pulp. Brightness values for pulps bleached the second time (using the repeat bleaching cycle) were 78.8, 79.0 and 79.9 for H_2O_2, dithionite and borohydride bleached TMPs, respectively.

EXPERIMENTAL

TMP Bleaching

Unbleached spruce TMP (*Picea glauca* and *Picea mariana*) was obtained from Stora Enso N.A. (Wisconsin Rapids, WI, USA, formerly Consolidated Papers). Unbleached pulp (12 g o.d. weight) was acid pretreated with sulphuric acid to remove metal ions. This pulp was washed by deionized water to neutrality and prepared for oxidative bleaching using alkaline hydrogen peroxide. Bleaching conditions for pulp on an o.d. weight basis were 5% H_2O_2, 5.3% total alkali, 0.1% Mg and 4% Na_2SiO_3. Initial pH just after mixing the chemicals with the pulp was 11.7 and bleaching was performed at 11% consistency. The TMP and bleaching solution were put in a zip-lock bag and mixed by kneading. The bag was kept in a 70ºC water bath for 2.5 h. Pulp was remixed periodically by kneading to ensure uniform distribution of bleaching chemicals. After 2.5 h, the pulp was filtered and washed first with deionized water and then with dilute sodium bisulphite solution. The residual peroxide concentration was 13.5%.

A small portion (1 g) of this pulp was stored in a freezer for making handsheets and for Raman analysis. Another portion (0.8 g) was bleached again with alkaline peroxide and saved for further analysis. The remainder of the bleached TMP was treated with 2% (o.d. basis) sodium dithionite at 4% consistency at 70ºC for 1 h (pH 7.8). A portion of the dithionite-bleached pulp was saved and the remainder was treated with sodium borohydride. The conditions of the reductive borohydride treatment were 0.5 mol/L $NaBH_4$ at 1% pulp consistency for 24 h at room temperature. As in prior steps, a small amount of pulp was saved for analysis and the remainder was subjected to further bleaching. The entire bleaching cycle, from peroxide to borohydride, was repeated one more time; after each bleaching stage, a small amount of pulp was saved for analysis. Bleaching stages and pulp brightness data are summarized in Fig. 1.

Raman Spectra

FT–Raman spectra were obtained using an RFS-100 instrument (Bruker Instrument, Inc., Billerica, MA, USA). A 1064 nm Nd:YAG diode laser was used to excite the samples, which were analyzed in the back-scattering mode. The TMP was compressed into pellets using an IR press, but less than 2812 t/m^2 pressure was used. Spectra were obtained in the 250–3700 cm^{-1} region using a liquid nitrogen- cooled germanium detector. Data were obtained using the double-sided interferogram option; 1024 scans were co-added before the interferogram was Fourier transformed to its corresponding power spectrum. OPUS IR-3 (Bruker Instrument, Inc.) software was used both to control both the instrument function and to process Raman spectra.

To compare spectral features and calculate bleaching-related changes in the region of 1665–1690 cm^{-1}, TMP spectra were normalized using the 1098 cm^{-1} band as an internal reference. The *p*-quinone contribution removed as a result of bleaching was calculated by first subtracting the spectrum of bleached TMP from the spectrum of unbleached TMP. Next, using the subtracted spectrum, an integration method from the OPUS software was used to draw a sloping background between 1645 and 1690 cm^{-1}; within this interval, the *p*-quinone region between 1665 and 1690 cm^{-1} was selected for band integration.

Brightness Measurement

Thick handsheets (296 g/m^2) were made from all pulps. Using TAPPI test method T 525 [35], diffuse brightness data were obtained on a Technidyne Technibrite TB–1 instrument (Technidyne Corporation, New Albany, NY, USA).

Preparation of MWL

MWLs from black spruce (*Picea mariana*), loblolly pine (*Pinus taeda*), radiata pine (*Pinus radiata*), ginko (*Ginko biloba*), paper birch (*Betula papyrifera*), American elm (*Ulmus americana*), European beech (*Fagus sylvatica*) and red oak (*Quercus rubra*) were prepared. Softwood and hardwood MWLs were isolated using the method described previously [30].

Preparation of Dehydrogenation Polymer Containing Quinone Functionalities

Solutions of coniferyl alcohol (162 mg, 0.90 mmol) and 2-methoxyhydroquinone (14 mg, 0.10 mmol) in pyridine (10 mL) and manganese (III) triacetate dihydrate (483 mg, 1.75 mmol) in pyridine (20 mL) were added in separate streams to a reaction flask containing pyridine (10 mL) and a trace of water (50 μL) at 50°C while stirring with a slow stream of nitrogen. After the addition was complete (24 h), acetic anhydride (3 mL) was added, heat was removed and stirring with nitrogen gas was continued for 3 h. The dark solution was then added to water (100 mL) with stirring and the resulting cream-coloured suspension was acidified with concentrated HCl (~9 mL) to a pH of 1. Extraction of the mixture with ethyl acetate (5 × 25 mL) produced a bright orange organic layer.

The organic layer was dried with brine and anhydrous magnesium sulphate and the solvent evaporated. This was followed by several dilutions/evaporations with toluene and finally acetone to azeotrope off excess pyridine. The acetylated product, a red–orange oil (224 mg), was obtained and chromatographed on a Bio-Bead S-X3 column (96 × 5.1 cm) (Biorad Laboratories, Richmond, CA, USA) with methylene chloride as eluant. The UV absorption (280 μm) of the eluant was monitored with an ISCO UA-6 UV/vis detector (Instrumentation Specialties Company, Lincoln, NE, USA) and 18 mL fractions were collected. The first eight fractions following the exclusion (highest molecular weight portion, fractions 7–14) were separated and the solvent was removed, leaving an amber oil (80 mg, 40% of total weight applied to column).

^{13}C NMR Spectroscopy

The NMR data were obtained at ambient temperature with a Bruker DPX-250 spectrometer (62.9 MHz C-13) in acetone–d6 solutions. All chemical shifts are given in δ ppm and are referenced to the centreline of the solvent at 29.83 ppm, which is based on tetramethylsilane (δ = 0.0 ppm). Quantitative spectra were obtained and processed using techniques described previously [36].

RESULTS AND DISCUSSION

Previously, FT–Raman bands of spruce wood have been assigned in terms of both individual components [30] and specific structures within cellulose [37] and lignin [38]. (See [30,

37,38] for information on band assignments.)

Bleaching, Stage by Stage

To understand which chromophores are affected when mechanical pulps are bleached, spruce TMP was treated with oxidative and reductive bleaching agents in accordance with the sequence outlined in Fig. 1. After each bleaching stage, the Raman spectrum of the bleached pulp was obtained and compared with the spectrum obtained after the previous bleaching stage in the sequence. Pulp brightness values for the first bleaching cycle are shown in Fig. 1 and for the second bleaching cycle in the figure caption.

Table I shows the FT–Raman contributions of various chromophores either known to be present in lignin or expected to be useful in pulp spectra analysis. Note that Table I does not list all Raman bands of a chromophore; only those that are useful in distinguishing chromophores.

The most prominent changes in the Raman spectrum of TMP occurred when the pulp was bleached for the first time with alkaline H_2O_2 (Fig. 2, spectrum (c) and Table II, ID 2). In Fig. 2, spectrum (c) was obtained when the bleached TMP spectrum was subtracted from the unbleached pulp spectrum. This difference spectrum (c) showed peaks at 1133, 1274, 1340, 1393, 1435, 1452, 1509, 1596, 1621 and 1663 cm^{-1} and arose as a result of the removal of chromophore contributions from the spectrum of unbleached TMP. These band positions were similar to those obtained previously [19] after a sodium borohydride-

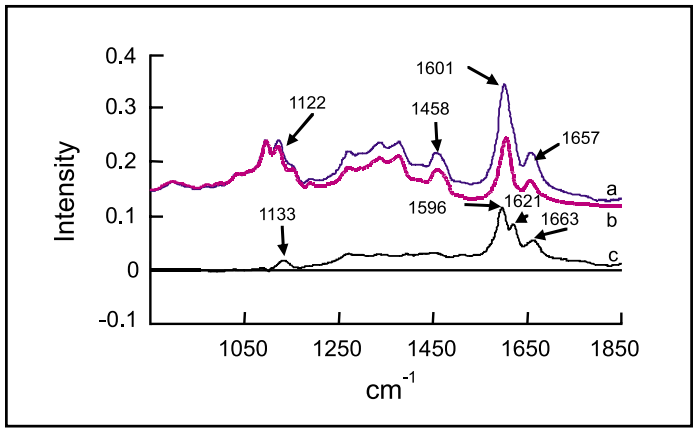

Fig. 2. FT–Raman spectra of (a) unbleached TMP, brightness 52.5 and (b) H_2O_2 bleached TMP, brightness 71.8. Spectrum (c) is the difference between the unbleached and bleached pulp spectra.

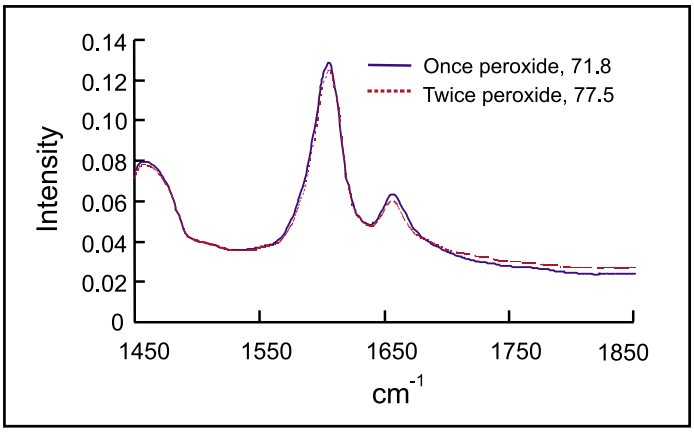

Fig. 3. Spectra of TMPs bleached once or twice with peroxide. The second bleaching caused a further decline in intensity in the 1645–1690 cm^{-1} region.

TABLE I
USEFUL RAMAN CONTRIBUTIONS OF CHROMOPHORES[1]

Chromophore	Band position, cm^{-1}	References
o-Quinone	1559	[19,24,29]
Coniferaldehyde	1654, 1620, 1135	[8,24,34]
Stilbene	1635	[24,34]
Coniferyl alcohol	1654	[24,34]
p-Quinone	1665–1690[2]	[24,29]

1. Except for the 1135 cm^{-1} band of coniferaldehyde, bands of chromophores are due to C=C and/or C=O groups.
2. In *p*-quinone, the exact band position depends on the molecular structure, but most bands have been detected in this region.

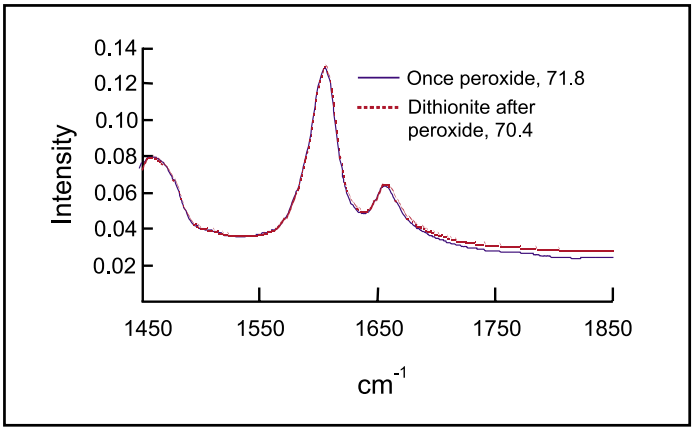

Fig. 4. Spectra of TMPs bleached once with peroxide or with peroxide and then dithionite. Dithionite bleaching caused no significant change in the spectrum.

TABLE II
SPECTRAL CHANGES AFTER EACH STAGE OF BLEACHING

Sample ID	TMP	Brightness	Visually detected changes in spectrum by band position, cm^{-1}									
			898	1096	1122	1151	1272	1338	1378	1458	1601	1657
1	Unbleached	52.2	—	—	—	—	—	—	—	—	—	—
2	H_2O_2	71.8	No	No	↓	↓	↓	↓	↓	↓	↓	↓
3	2 + H_2O_2	77.5	No	No	No	No	No	No	No	No	↓	↓
4	2 + $Na_2S_2O_4$	70.4	No	No	No	No	No	No	No	No	No	No
5	4 + $NaBH_4$	75.2	No	No	No	No	No	No	No	No	↓	↓
6	5 + H_2O_2	78.8	No	No	No	No	No	No	No	No	↓	↓
7	6 + $Na_2S_2O_4$	79.0	No	No	No	No	No	No	No	No	No	No
8	7 + $NaBH_4$	79.9	No	No	No	No	No	No	No	No	No	No

For example, for ID 4 pulp, there are no significant differences between H_2O_2 and $Na_2S_2O_4$-after-H_2O_2 bleached pulps. Band positions are those of unbleached TMP. On bleaching, some positions changed slightly as a result of removal of contributions from chromophores. "No" designates no significant change. Downward arrow (↓) designates a decrease in band intensity.

bleached TMP spectrum was subtracted from the spectrum of control TMP, which suggests that the changes in Raman spectra were similar in alkaline hydrogen peroxide and sodium borohydride bleaching.

As discussed previously [8,19], when TMP is bleached, the decline in intensity at 1133, 1596 and 1621 cm^{-1} is explained by the removal of coniferaldehyde groups. These are some of the most prominent peaks in the Raman spectrum of coniferaldehyde [24]. Moreover, the presence of a peak at 1663 cm^{-1} (in the difference spectrum (c), Fig. 2) can be interpreted in terms of the removal of the contributions of both coniferaldehyde and *p*-quinone groups. The C=O stretch in coniferaldehyde has a Raman band at or near 1654 cm^{-1} [8,24], whereas the *p*-quinones are known to contribute in the 1665–1690 cm^{-1} region [29]. Some variation in the vibrational frequencies of the C=O group of coniferaldehyde and *p*-quinones, especially for the latter, is expected because of the dependence of the frequency on molecular structure (heterogeneity of *p*-quinone structures in TMP) and intermolecular interactions (local environment). This is observed in spectrum (c) in Fig. 2 where, for *p*-quinonoid C=O, a wide contribution is detected in the 1665–1690 cm^{-1} region instead of a narrow band.

After the initial bleaching by peroxide, bleaching again with alkaline peroxide resulted in only small changes in the spectrum at 1601 and 1657 cm^{-1} (Table II, ID 3; Fig. 3). While some decline in intensity occurred at these wavenumbers, the rest of the spectrum (not shown) did not change.

Results of further bleaching stages are summarized in Table II. Some treatments showed no change, as was the case for sodium dithionite-treated pulp (Table II, ID 4; Fig. 4), whereas others produced a small decline in the band centred at 1601 cm^{-1} and in the 1665–1690 cm^{-1} region (Table II, ID 5 and 6; Fig. 5). The latter was interpreted in terms of reduction or oxidation of *p*-quinones depending on the nature of the bleaching agent. Bleaching-induced changes in the 1665–1690 cm^{-1} region were accompanied by a parallel decline in the intensity of the 1601 cm^{-1} band. However, it is not clear whether the two changes are related. When thrice-H_2O_2-bleached TMP (Table II, ID 6, brightness 78.8) was further brightened (Table II, ID 7 and 8, brightness 79.0 and 79.9), the

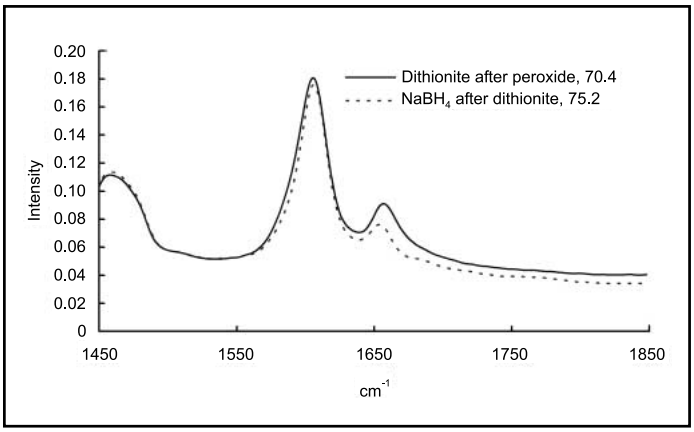

Fig. 5. Spectra of TMPs treated with dithionite after bleaching with peroxide (H_2O_2) or treated with borohydride ($NaBH_4$) after bleaching with dithionite. Bleaching caused a significant change in the *p*-quinone region.

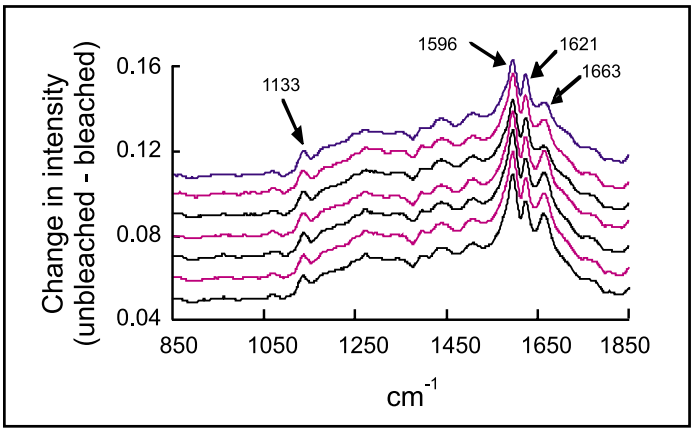

Fig. 6. Difference spectra (unbleached–bleached) in the 850–1850 cm^{-1} region for bleached TMPs in Table II; from top to bottom, TMP ID 2–8. The spectra were not corrected for underlying fluorescence and were offset by 0.01 units on the y axis for display purposes.

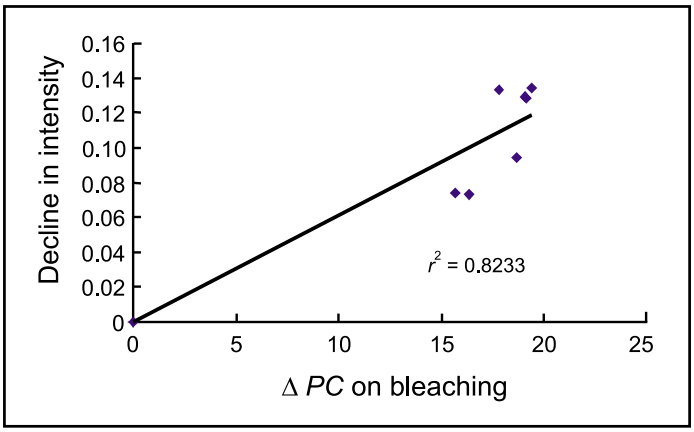

Fig. 7. Linear regression between ΔPC and the decline in Raman intensity of the 1665–1690 cm^{-1} region (contribution primarily due to *p*-quinones).

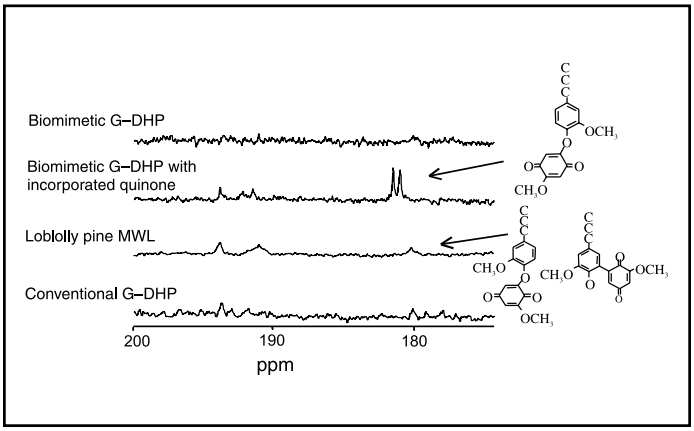

Fig. 8. ^{13}C NMR spectra of conventional G–DHP, loblolly pine MWL, biomimetic G–DHP incorporated with *p*-quinone and biomimetic G–DHP. The signal at ~180 ppm was due to quinone units.

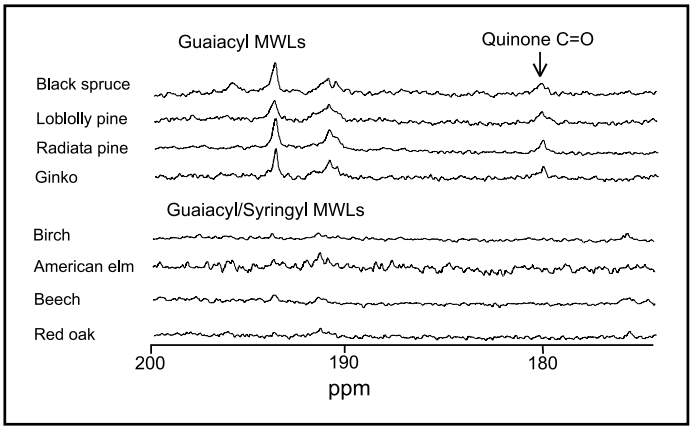

Fig. 9. ^{13}C NMR spectra of softwood and hardwood MWLs. Quinones were detected only in softwood lignins, as noted by the signal at 180 ppm.

Raman spectra were almost identical and showed no change.

Bleaching, Total Change

In addition to the above-described spectral subtractions, a spectrum of each bleached TMP was subtracted from the spectrum of unbleached TMP (Fig. 6). These difference spectra showed that subtraction of brighter pulp spectra produced higher intensity in the 1665–1690 cm^{-1} region. This, in turn, meant that efficient bleaching resulted in a lower 1665–1690 cm^{-1} contribution in the spectra of the bleached pulps. Brighter TMP underwent more extensive removal of *p*-quinones. Additionally, small differences were also detected in non-*p*-quinone regions.

Considering that pulp reflectance measurements are only indirect measurements of the concentration of absorbing species, it is better to calculate changes in pulp absorption so that the 1665–1690 cm^{-1} Raman intensity and pulp absorption data can be correlated. This can be accomplished if reflectance change is interpreted in terms of the change in *K/S* value, which is based on sound principles of the Kubelka–Munk theory of absorption and scattering [39]. Using *K/S* data, where *K* is a specific absorption coefficient and *S* is a scattering coefficient, the relative post-colour number (ΔPC) for each pulp was calculated using the formula

$$\Delta PC = 100[(K/S)_{\text{unbleached}} - (K/S)_{\text{bleached}}] \quad (1)$$

K/S was obtained from the Kubelka–Munk relationship

$$K/S = (1 - 0.01R_\infty)^2/0.02R_\infty \quad (2)$$

where R_∞ is the reflectance of the infinitely thick pulp sheet.

If *p*-quinones are present, as suggested by the Raman analysis (Fig. 6), they are likely to play a major role in determining pulp brightness. Although coniferaldehyde structures were present in unbleached pulp, they do not play an important role in brightness determination at 457 nm [21]. To investigate the role of *p*-quinones, ΔPC was correlated with the degree to which *p*-quinone structures are removed on bleaching. The decline in Raman intensity in the 1665–1690 cm^{-1} region was plotted against ΔPC. As shown in Fig. 7, pulp ΔPC was correlated with the extent of *p*-quinones removed (linear regression correlation coefficient 0.82). This indicates that TMP absorption and therefore TMP brightness depend on *p*-quinone concentration.

^{13}C NMR

Although FT–Raman studies of unbleached and bleached black spruce MWL [13] produced results that were similar to those obtained here for spruce TMP, indicating that *p*-quinones were present in MWL, the ^{13}C NMR method was selected as an additional independent method to determine whether indeed a signal due to the carbon of the quinonoid carbonyl group could be detected. In addition to loblolly pine MWL, samples included conventional guaiacyl dehydrogenation polymer (G–DHP), a model for softwood lignin, and biomimetic G–DHP (with and without the *p*-quinone unit; Fig. 8). Because the relaxation times of the carbonyl groups are long, inverse gated experiments [40] were performed. The NMR spectra of the acetylated samples are shown in Fig. 8. A signal due to *p*-quinone carbonyl groups at ~180 ppm was present in the spectrum of loblolly pine MWL, indicating that quinones were present. Quinoid signals were only observed in quantitative spectra as a result of the relaxation properties of quinoid functionality. This, along with the low abundance, is consistent with the lack of reports in the literature regarding this signal. However, a few recently reported results also support the assignment of this NMR signal to quinones [41,42].

To investigate whether other softwood and hardwood MWLs contained quinones, isolated lignins from softwoods (black spruce, radiata pine and gingko) and hardwoods (paper birch, American elm, European beech and red oak) were analyzed (Fig. 9). The NMR data indicated that the quinone signal was present only in the softwood MWLs; none of the hardwood MWL spectra showed a 180 ppm signal. Compared to softwood lignins, hardwood MWLs are likely to contain lower amounts of quinones and are therefore harder to detect.

CONCLUSIONS

FT–Raman spectra of bleached and unbleached spruce TMPs indicated that *p*-quinones were present in unbleached and less than fully bleached pulps. A linear correlation was found between a bleaching-related decline in PC number and a decrease in *p*-quinone Raman intensity. Although the regression was not very good ($r^2 = 0.82$), this nevertheless suggested that *p*-quinone structures play an important role in determining the brightness of spruce TMP. As evidence of further support, ^{13}C NMR of softwood and hardwood MWLs showed that quinones could be detected in softwood MWLs. On the contrary, quinones were not detected in hardwood MWLs, most likely because of the lower concentration of quinones in hardwood lignins.

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