

PRESENCE OF *p*-QUINONE STRUCTURES IN WOOD, MECHANICAL PULP, AND MWL – DIRECT RAMAN EVIDENCE

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ABSTRACT

Unbleached and bleached samples of wood (black spruce), mechanical pulp (spruce thermomechanical pulp), and MWL (black spruce) were studied using near-IR FT-Raman spectroscopy. When bleaching-related spectral changes were analyzed with the help of data from lignin and quinone models, it was found that the most important changes were due to coniferaldehyde and *p*-quinone structures. Whereas, in the past, Raman as well as other spectral evidence supporting presence of coniferaldehyde structures in the unbleached samples has been published, that is not the case for *p*-quinone structures. In the Raman spectra of wood, pulp, and lignin samples, contributions of *p*-quinones were detected in the region 1665 - 1690 cm^{-1} . An additional finding was that the thermomechanical pulp brightness increase was linearly correlated with the Raman intensity (area) decline in the *p*-quinone region indicating that the latter groups played an important role in determining the brightness of mechanical pulps. Finding of *p*-quinones in mechanical pulp lignin by FT Raman spectroscopy was further supported by ^{13}C NMR spectroscopy where a quinone signal at about 180 ppm was detected in softwood MWLs.

INTRODUCTION

To obtain information about the nature of chromophores in wood, mechanical pulps and lignin, one of the techniques that has been used extensively is UV/V is spectroscopy. For example, in the case of bleached and unbleached mechanical pulps diffuse reflectance UV/V is

studies indicated that bleaching resulted in not only removing chromophore contribution in the region where coniferaldehyde structures contributed but also absorption was removed at wavelengths where quinones absorbed [1]. However, because electronic bands due to *o*- and *p*-quinones are broad and overlap considerably [2], it is difficult to obtain specific information. As reported elsewhere [3], one of the techniques that are capable of distinguishing between *o*- and *p*-quinones is FT Raman spectroscopy. It has been reported that the Raman band frequencies of *o*- and *p*-quinones differ by more than 100 cm^{-1} and do not overlap with each other [4]. In addition to mechanical pulps, bleached wood and MWL were studied using Raman spectroscopy and the conclusions derived were similar. But due to space limitations, only results of mechanical pulp studies will be discussed

RESULTS AND DISCUSSION

Bleaching of thermomechanical Pulp

To understand what chromophores are affected when mechanical pulps are bleached using reductive or oxidative bleaching agents, a Raman study was undertaken. Spruce TMP was bleached in accordance with the sequence outlined in Fig. 1. After each bleaching step, the Raman spectrum of the bleached pulp was obtained. This spectrum was compared with the one obtained after the previous bleaching step in the sequence (Fig. 1). In addition, the spectrum of each bleached TMP was compared with that of unbleached TMP. Pulp brightness is listed in the flow diagram in Fig. 1.

The most prominent changes in the Raman spectrum occurred when the pulp was bleached for the first time with H_2O_2 (Fig. 2, plot c). The resultant changes showed peaks at 1135, 1595, 1622, and 1663 cm^{-1} . These band positions were similar to those reported for the borohydride bleached TMP [5]. This suggested that in both reductive and oxidative bleaching the nature of the changes was similar.

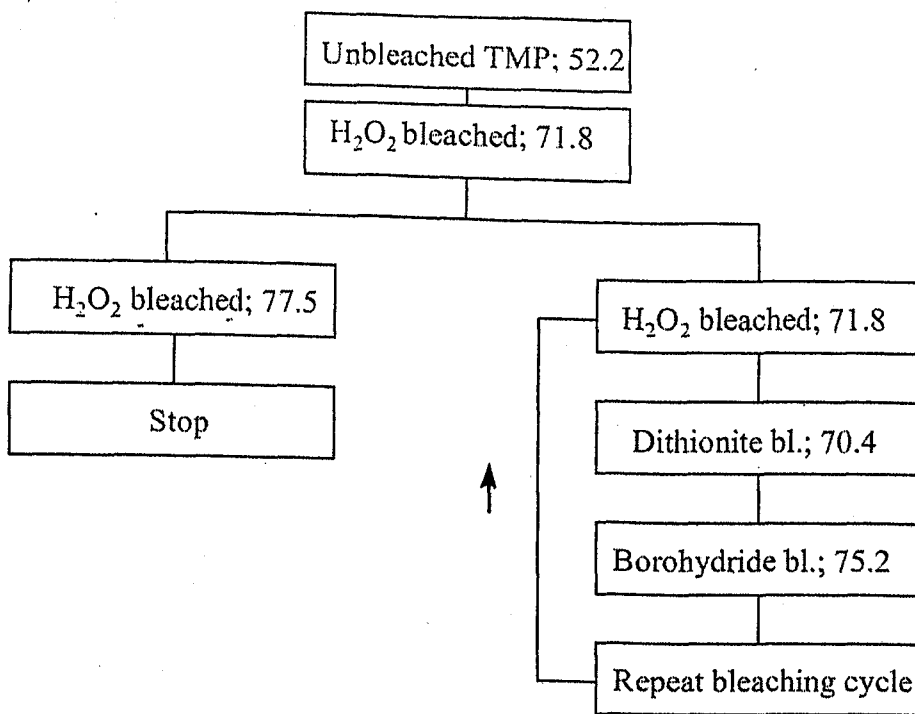


Figure 1. Flow diagram showing sequence of bleaching for thermomechanical pulp. Brightness values of bleached pulps are also given. Brightness data for pulps bleached the second time (using the repeat cycle) are not shown. These values were 78.8, 79.0, and 79.9, respectively, for H₂O₂, dithionite, and borohydride bleached TMPs.

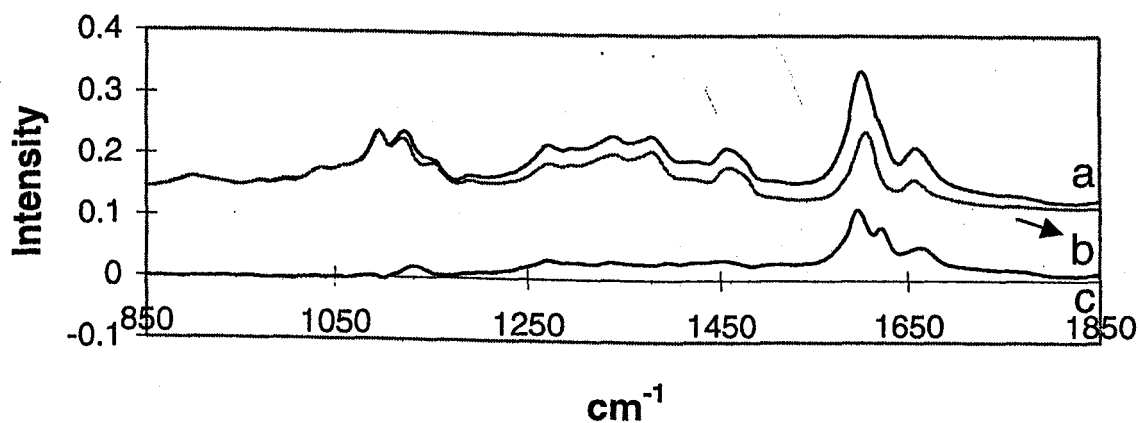


Figure 2. FT Raman spectra of unbleached (a, brightness 52.5) and H₂O₂ bleached (b, brightness 71.8) TMPs. Plot “c” is the difference of unbleached and bleached pulp spectra.

As pointed out previously [5], when TMP is bleached the decline in intensity at 1135, 1595, and 1622 cm⁻¹ can be explained by the fact that coniferaldehyde groups are being removed. Moreover, the presence of a peak at 1663 cm⁻¹ (in the difference spectrum) can be interpreted in terms of 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 whereas the *p*-quinones are expected to be in the 1665 - 1690 cm⁻¹ region. Some variation in the vibrational frequencies of coniferaldehyde and *p*-quinones, especially for the latter, is expected because of the dependence of the frequency on molecular structure and intermolecular interactions. This is supported by

plot "c" in Fig. 2 where instead of a narrow band a wider contribution in the 1665 - 1690 cm^{-1} region is detected. Because *p*-quinones entities in TMP are likely to have different molecular structures and different intermolecular interactions, the broadness of the Raman feature can be explained.

After the initial bleaching by peroxide, bleaching with either peroxide or dithionite resulted in only small changes in the spectrum (at 1600 cm^{-1} and in the 1665 - 1690 cm^{-1} region, Fig. 3 and 4). When spectra of pulps treated with any of the remaining bleaching steps (sequence in Fig. 1) were compared, either no changes or only small decline in band intensities were detected. This was interpreted in terms of *p*-quinones being oxidized and reduced depending upon the nature of the bleaching agent.

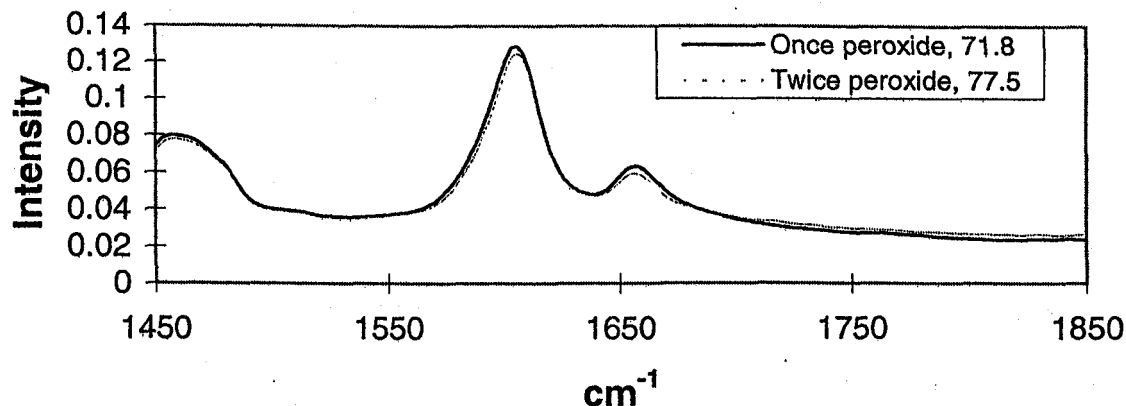


Figure 3. Spectra of once and twice H_2O_2 bleached TMPs. Upon second time bleaching (less dark line), intensity declined further in the region 1645 - 1690 cm^{-1} .

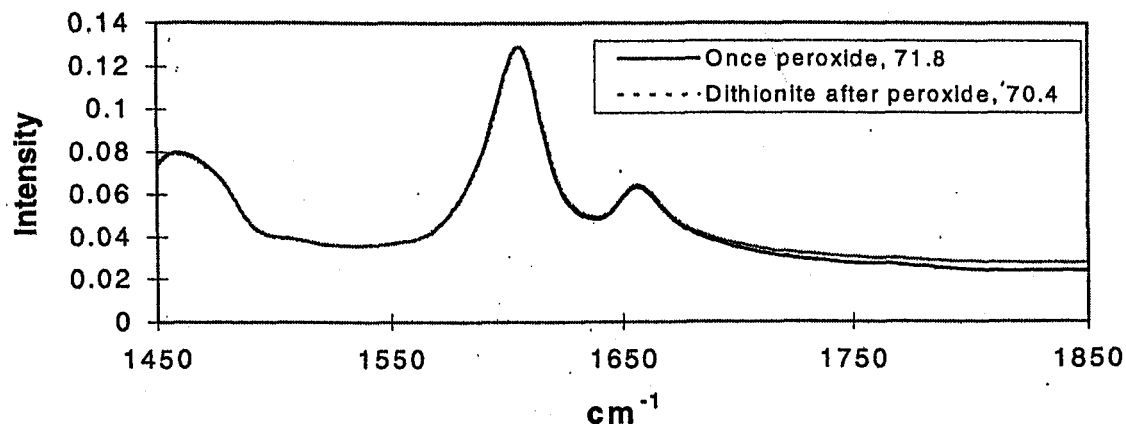


Figure 4. Spectra of once H_2O_2 bleached (dark line) and once dithionite bleached after-once- H_2O_2 -bleached (less dark line) TMPs. Upon dithionite bleaching no significant change occurred in the pulp's spectrum

If *p*-quinones are present, as suggested by the Raman analysis, they are likely to play a major role in determining pulp brightness. To test this, pulp brightness was correlated with the degree to which *p*-quinones structures are removed upon bleaching. Pulp brightness was plotted against decline in Raman intensity in the

1665 - 1690 cm^{-1} region. As shown in Fig. 5, pulp brightness was strongly correlated with the extent of *p*-quinones removed (linear regression correlation coefficient 0.89). This indicated that for the TMP brightness depended upon *p*-quinone concentration.

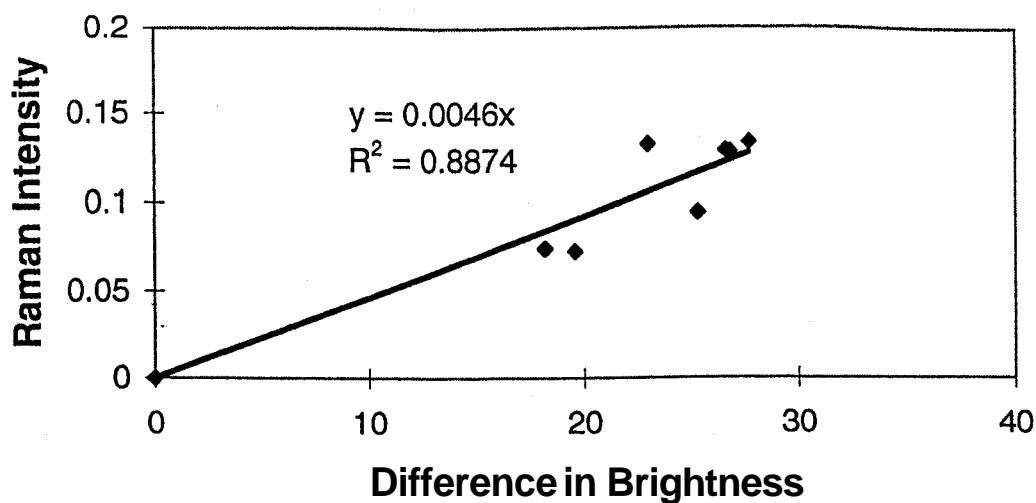


Figure 5. Linear regression between increase in brightness (upon bleaching) and decline in the 1665 - 1690 cm^{-1} region Raman intensity. The contribution in the 1665 - 1690 cm^{-1} region is primarily due to *p*-quinones.

^{13}C NMR of MWLs

Although FT Raman studies of bleached and unbleached black spruce MWL (not reported here) produced results that were similar to those obtained in the case of spruce TMP indicating that *p*-quinones were present in the MWL, ^{13}C NMR method was selected to determine if indeed a signal due to the carbon of the quinonoid carbonyl group could be detected. In addition to the loblolly pine MWL the samples

included conventional G-DHP and biomimetic G-DHP (with and without the *p*-quinone unit; Fig. 6). Because the relaxation times of the carbonyl groups are long, inverse gated experiments were performed and the obtained NMR spectra are shown in Fig. 6. A signal at ~ 180 ppm was present in the spectrum of the loblolly pine MWL indicating that quinones were present.

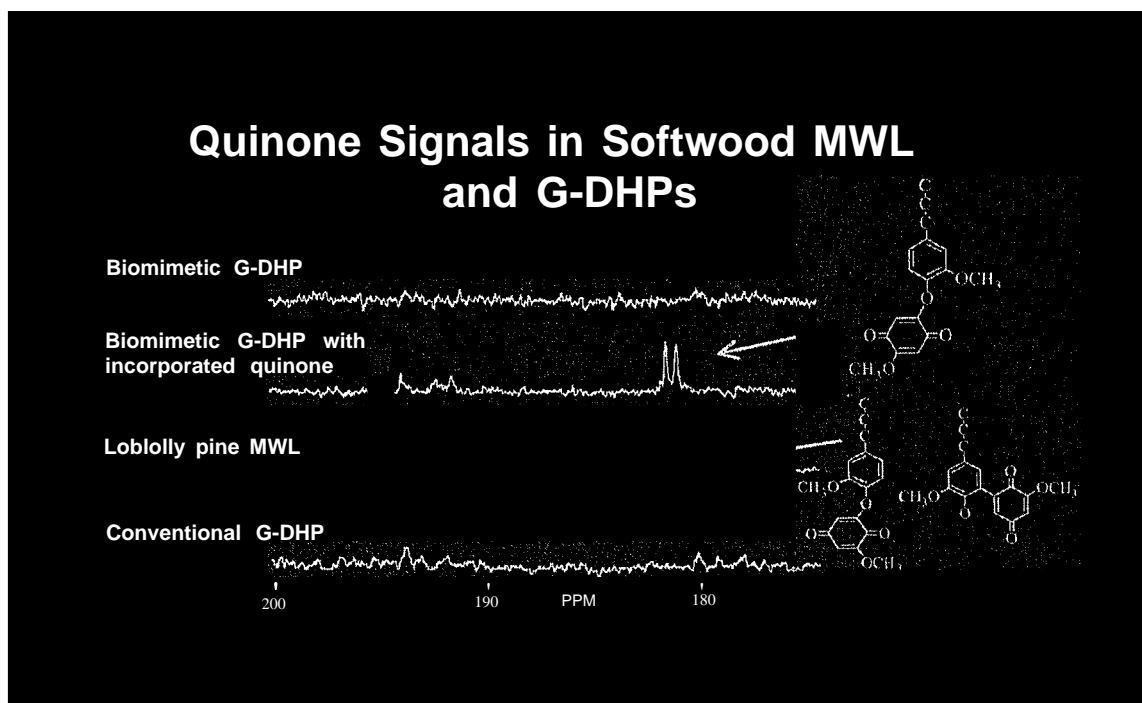


Figure 6. ^{13}C NMR spectra of conventional G-DHP, loblolly pine MWL, biomimetic G-DHP with incorporated *p*-quinone, and biomimetic G-DHP. The signal at ~ 180 ppm is due to quinone units.

To investigate if other softwood and hardwood MWLs contained quinones, isolated lignins from softwoods (black spruce, radiata pine, and ginkgo) and hardwoods (birch, american elm, beech, and red oak) were analyzed (Fig. 7). NMR data indicated that the quinone

signal was present only in the softwood MWLs, none of the hardwood MWL spectra showed 180 ppm signal. It is likely that compared to softwood lignins hardwood MWLs contain lower amounts of quinones and are harder to detect.

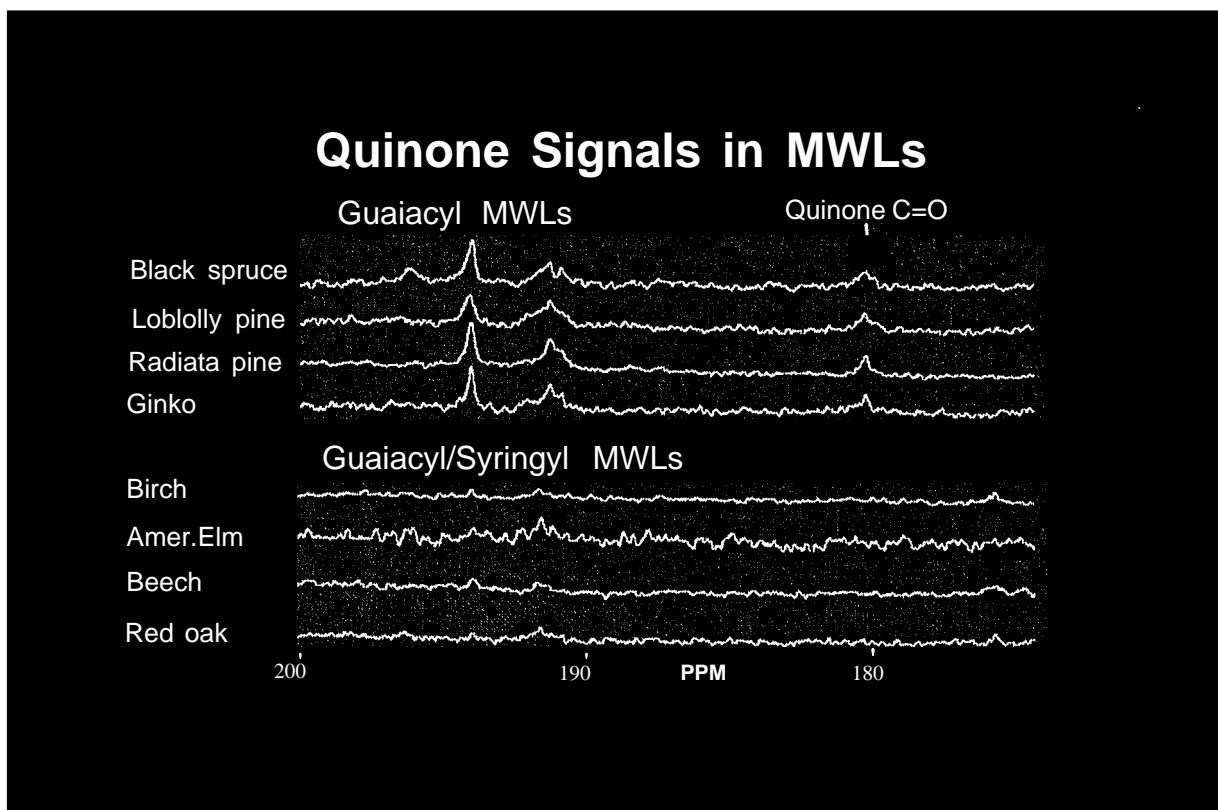


Figure 7. ^{13}C NMR spectra of softwood and hardwood MWLs. Quinones were only detected in softwood lignins as noted by the signal at 180 ppm

CONCLUSION

FT Raman spectra of bleached and unbleached spruce thermomechanical pulps indicated that *p*-quinones are present in unbleached and not fully bleached pulps. A good linear correlation existed between the bleaching related brightness increase and the decrease in *p*-quinone Raman intensity. This suggested that mechanical pulp brightness is determined by the *p*-quinone content of pulp. ^{13}C NMR MWLs showed that quinones could only be detected in softwood MWLs.

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Publications
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