UNDERSTANDING FUNGUS-INDUCED BRIGHTNESS LOSS OF BIOMECHANICAL PULPS

Umesh P. Agarwal
USDA - FS
Forest Products Laboratory
Madison, WI 53705

Masood Akhtar
Biopulping International Inc.
P.O. Box 5463
Madison, WI 53705

ABSTRACT

Benefits of energy savings and improved pulp properties are to be realized by substituting biomechanical pulps for normal pulps. However, because a biopulp is darker it requires additional bleaching to attain a specific brightness level. The cause of biopulp darkening remains not well understood. In the present study, UV/Vis, Raman, and IR spectroscopies were used to study the darkening phenomenon. The results indicated that quinones (both o- and p-) were produced when wood chips were treated with the fungus. This was also the case, when fungus-treated wood chips were refined at higher steaming pressures (up to 85 psi). For a given pressure, compared to control pulps, treated pulps were darker due to the fact that their quinone content was higher. Within the set of biopulps, produced at various steaming pressures, higher-pressure-pulps were darker and contained more quinones.

INTRODUCTION

The two important benefits of biomechanical pulping, wherein wood chips undergo fungal treatment prior to pulping, are energy savings (3040%) and improved paper strength properties [1]. Although the benefits of biomechanical pulping are significant, the process produces pulps that have lower brightness compared to normally produced pulps (2- 15 brightness points loss depending upon wood species) [1, 2]. To attain brightness level similar to that of an untreated bleached mechanical pulp, a biomechanical pulp requires additional bleaching which adds to the overall cost of pulp production. Much remains unknown about the cause of the brightness loss and about the chemical process that is responsible for it. Research is needed not only to better understand the problem but also to make progress towards finding a solution.

Darkening behavior of biomechanical pulps was investigated using UV/Vis, Raman, and IR spectroscopies. These techniques were selected because the methods lend themselves to *in situ* analysis of the samples. Additionally, it is known that UV/Vis and Raman techniques are quite sensitive in the study of chromophores [3].

EXPERIMENTAL

Spruce wood chips were treated for 2 weeks with *Ceriporiopsis subvermispora*. Treated chips were refined at various pressures (0, 50, 70, and 85). Control pulps were produced only at 50, 70, and 85 psi because it was expected that at 0 psi the brightness would be same as of other control pulps and untreated wood (about 56%).

ISO brightness was measured (Technibrite model TB-1) for all the pulps (made from white spruce) that were produced.
Diffuse reflectance UV/Vis spectra of biopulp handsheets were obtained using a Hitachi U3010 spectrophotometer. This instrument is equipped with a 150 mm $BaSO_4$ integrating sphere. Measurements were made with respect to the $BaSO_4$ as a reference. Loss of reflectance (D R) was obtained by simply subtracting one spectrum from another.

Near-IR FT-Raman spectra of the wood or pulp samples and their methanol extracts were obtained using a Bruker RFS 100 instrument. A 1000 mW 1064 nm Nd:YAG diode laser was used for sample excitation. While sampling pulps, a front surface mirror was used behind the samples to enhance the Raman signal. The methanol extracted materials were sampled in an ‘‘Aluminum Well” (a sampling device). Laser power used for sample excitation was between 330 and 660 mW, and, depending upon the signal-to-noise ratio, either 600, 1200, or 1800 scans were accumulated.

IR spectroscopy was also used to get further information on the nature of chemical changes that occurred upon fungal treatment and as a result of refining at different pressures (for both control and treated pulps). Samples that consisted of both wood or pulp and methanol extracted material were analyzed using Mattson's Galaxy 5000 spectrometer. Whereas wood and pulp samples were studied directly in the diffuse reflectance mode, extracted materials were sampled as a KBr pellet.

RESULTS AND DISCUSSION

Fungus Caused Changes in Wood

It is generally recognized that bright woods become darker upon fungal treatment. This was also the case with white spruce although no brightness data was obtained.

Raman spectra obtained from the treated and untreated white spruce are shown in Fig. 1.

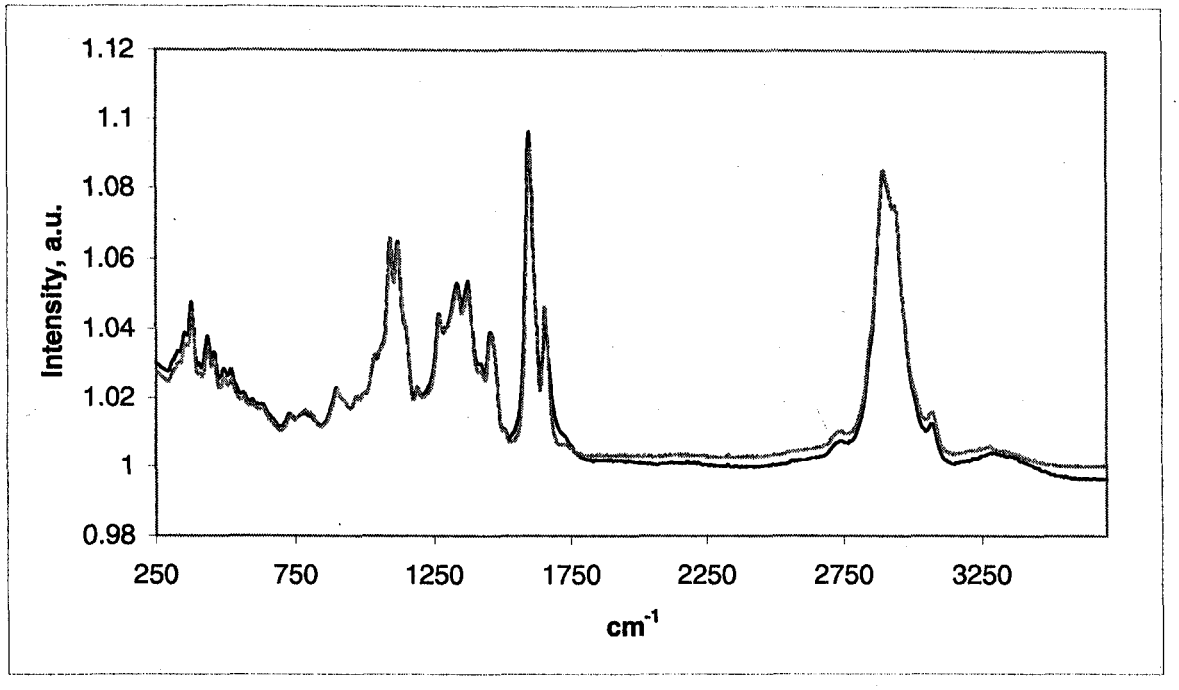

Fig. 1 FT-Raman spectra of untreated (less-dark dashed line) and fungus treated (dark continuous line) white spruce woods. Higher background and changes around the 1500-1800 cm^{-1} region were due to fungus treatment. a.u. means arbitrary units.

The fluorescence background underlying the spectrum of the fungus treated sample was higher indicating that the sample had a higher concentration of chromophores. When spectra were normalized using the 1098 cm^{-1} band (used as an internal reference) and compared, the most prominent differences were detected in the 1500–1800cm^{-1} region (Fig. 2). Specifically, the differences consisted of a slight shift to lower wavenumber of the 1600 cm^{-1} band, an increase in intensity around 1550 cm^{-1}, decline of the 1654 cm^{-1} band, and Raman intensity enhancement in the 1665–1690cm^{-1} region. Although the reason for the 1600 cm^{-1} band shift is not clear, the intensity enhancements in the 1550 and 1665–1690cm^{-1} regions of the spectrum can be assigned to, respectively, o- and p-quinones. Previous research [4] has identified the regions where quinone structures contribute in the FT-Raman spectra of lignocellulosics. Lastly, the decline at 1654 cm^{-1} is likely to be associated with the destruction/modification of coniferyl alcohol structures in wood-lignin. Previously, 1654 cm^{-1} band intensity has been shown to be mostly due to aromatic ring conjugated C=C bonds in coniferyl alcohol structures [5].

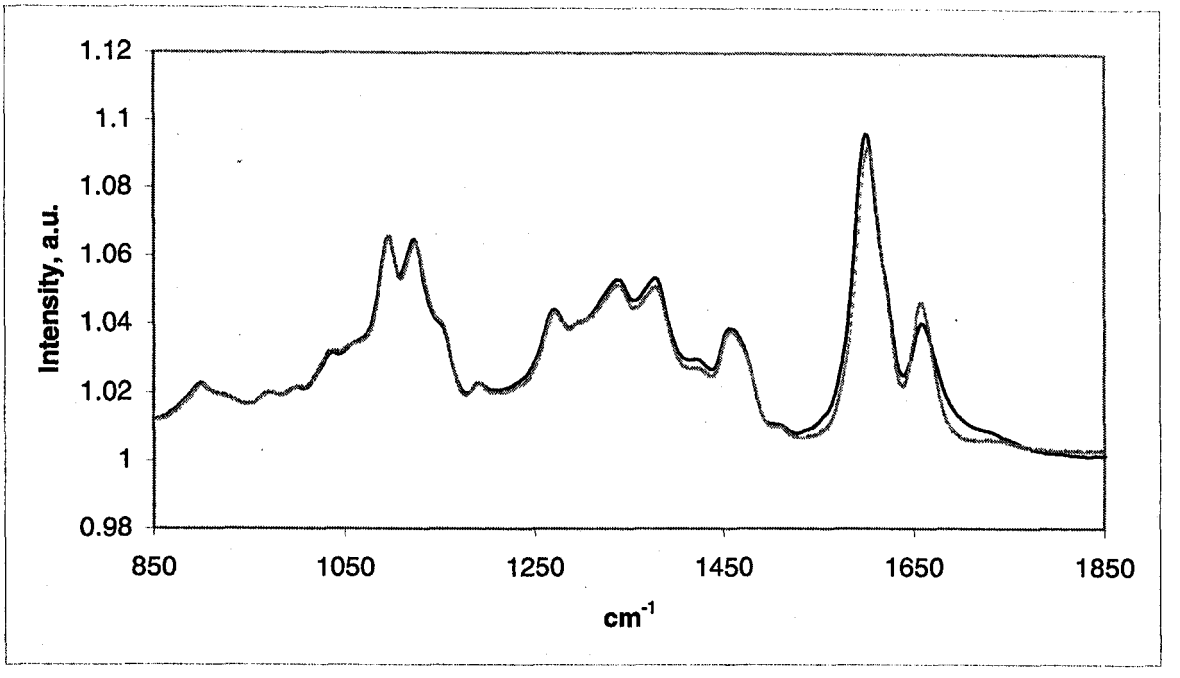

Fig. 2 The spectra of Fig. 1 plotted in the 850-1850 cm^{-1} region to better visualize the changes that occurred upon fungal treatment. The spectra are normalized on 1098 cm^{-1} band. Legend same as in Fig, 1

The above indication that quinones are produced in white spruce upon fungal treatment is further supported by the Raman spectrum of the material that was extracted (using methanol) from the treated wood (Fig. 3). Although some material could be extracted from the untreated spruce, the amount was much greater for the fungus treated wood. The latter seems to be due to the likelihood that fungus degraded lignin was solubilized by methanol. Because the wood was not pre-extracted, the untreated-wood-extracted-material is expected to be composed of extractives that were soluble in methanol. Therefore, Raman spectrum of this material would represent the extractives that were present in wood. Compared to the Raman spectrum of untreated-wood-material, spectrum of the fungus-treated-wood-material had weak broadening around 1550 cm^{-1} and a strong shoulder at 1670 cm^{-1} (Fig. 3). These aspects of the spectrum are likely to represent changes in lignin upon fungus treatment. As pointed out above, 1550 and 1670 cm^{-1} are the spectral regions where Raman contributions of quinones are detected.

From the diffuse reflectance IR spectra of woods (spectra not shown), fungus induced changes could not be discerned and therefore, the methanol extracted materials were analyzed (Fig. 4). From the spectrum of the treated wood material it can be observed that it has an additional band at 1637 cm^{-1}. This feature is likely to be due to p-quinone structures. An IR band about 1640 cm^{-1} has previously been seen due to p-quinines [6], Rest of the spectrum had features that were similar between the two extracted materials. Although extracted material from the treated wood is expected to contain lignin in addition to extractives, the spectra resemble each other very well. That's not unusual given the fact that the substructures of lignin have components that resemble molecular structure of extractives.

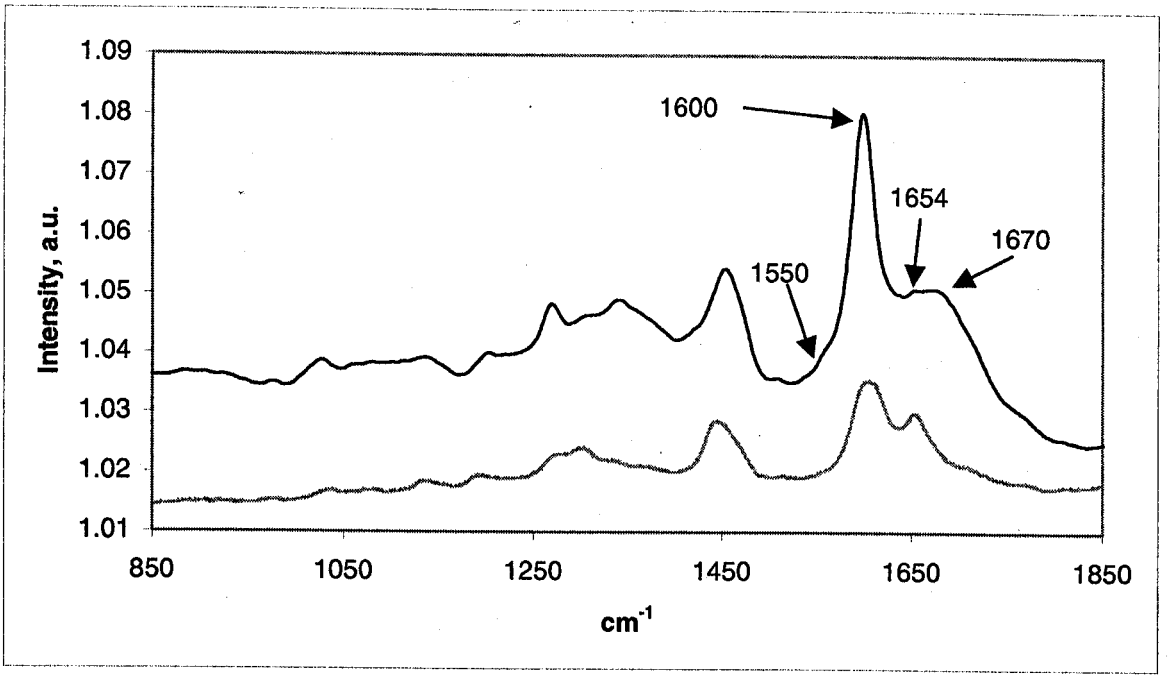

Fig. 3 Raman spectra of methanol-extracted materials from wood; top – fungus treated, bottom – untreated. In the top spectrum, o-quinones contribution at 1550 cm^{-1} and p-quinones contribution at 1670 cm^{-1} were detected.

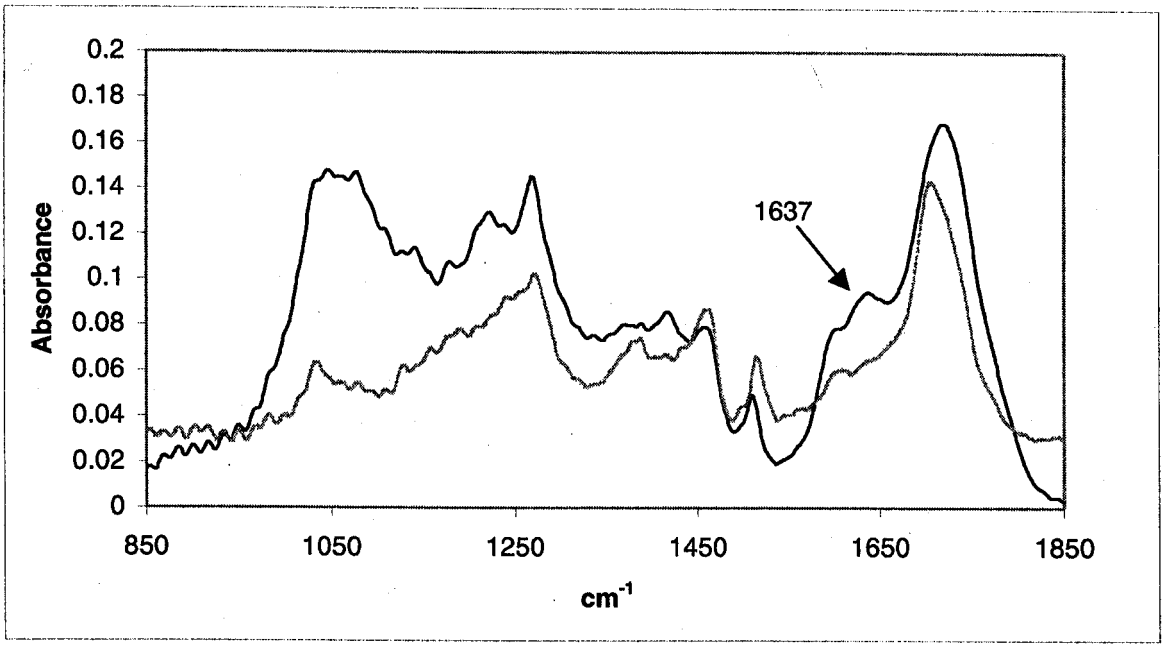

Fig. 4 IR spectra of methanol-extracted-materials from wood; top (solid dark line) – fungus treated, bottom – untreated. The extra band in the treated case is likely to be due to p-quinones.

Steaming Pressure Induced Changes – Control Pulps

The ISO brightness of control pulps and biopulps are shown in Table I. It is obvious that for control pulps no significant darkening occurred as a result of higher pressure (50, 70 and 85 psi pulps had similar brightness).

Table I: ISO Brightness of Pulps

Pressure, psi	**Fungus treated, %**	**Control, %**
0	39.9	Not done (about 56)
50	32.2	56.0
70	31.3	57.0
85	27.8	56.0

Diffuse reflectance UV/Vis spectrum was obtained on the handsheets made from these pulps. The difference in reflectance (A reflectance) plots are shown in Fig. 5. It can be noted that only small differences existed between the reflectance spectra of the control pulps. Moreover, at 457 nm, where ISO brightness is measured, the reflectance differences were close to zero. The latter observation supported the brightness data in Table I.

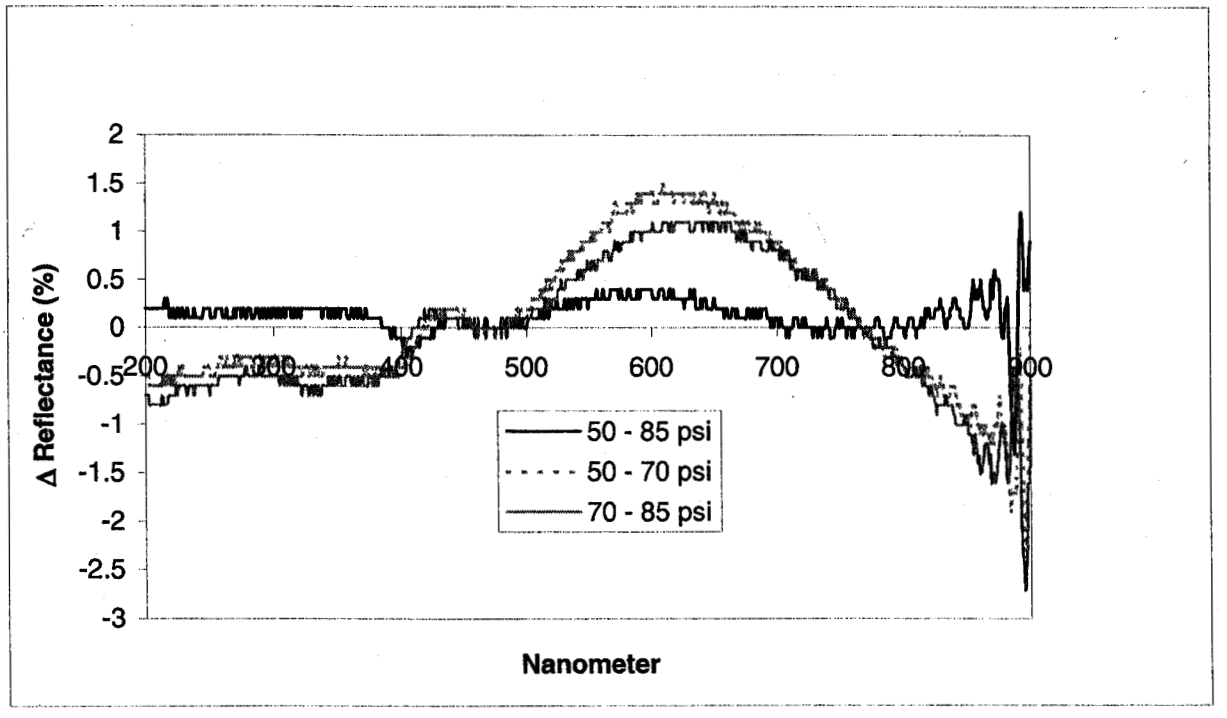

Fig. 5 Difference in the reflectance of the control pulps; the differences are small, and at 457 nm where brightness was measured (Table I), the differences are close to zero.

Raman spectra were obtained to detect chemical changes that were related to steaming pressure differences. Although spectra are not shown here, for the 3 control pulps, no significant differences were detected. This was also the case for the underlying backgrounds. This clearly indicated that the control pulps were chemically very similar and the any existing differences among pulp properties are likely to be physical.

Because more informative IR spectra were obtained from the extracted-material than by direct sampling the wood, for control pulps, only the extracted materials were analyzed. The spectra of the materials extracted from the 50 and 70 psi control pulps were similar whereas the spectrum of the 85 psi pulp material was somewhat different (Fig. 6). Specially, in the latter, the bands at 1604 and 1734 cm^{-1} had different shapes and widths. The reasons for this are presently not known.

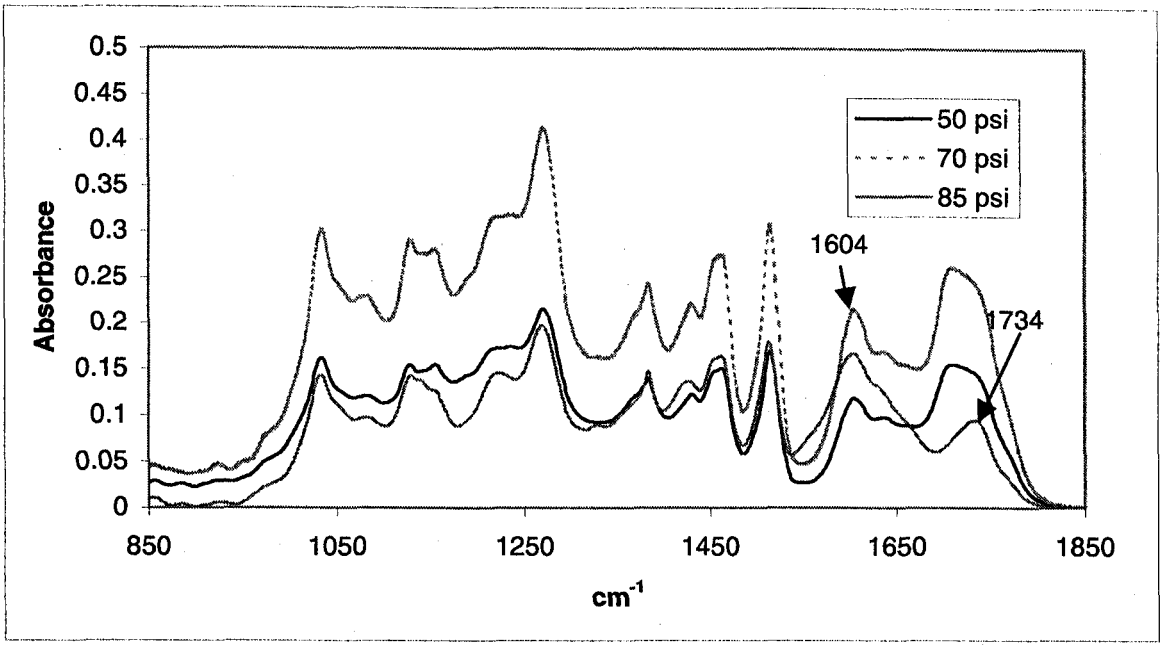

Fig. 6 IR spectra of methanol-extracted-materials from control pulps; only spectrum for the 85 psi pulp material (less dark continuous line) was somewhat different.

Steaming Pressure Induced Changes – Biopulps

From Table I, it can be seen that in the pulping of fungus-treated-woods-chips steaming pressure is an important consideration because higher pressure resulted in significantly darker pulps. This observation is further supported by the UV/Vis spectra of these pulps where, compared to 0 psi pulp, 50, 70, and 85 psi refined biopulps showed significant absorption between 400 and 800 nm (Fig. 7). Although absorption changed non-uniformly in this region as steaming pressure increased, most absorption was in the region where quinones (both o- and p-) are known to absorb [7]. It can therefore be argued that the absorption changes detected as function of pressure are due to decrease or increase in the concentration of various quinones.

Raman spectra of biopulps produced at 0, 50, 70, and 85 psi steaming pressure indicated that spectral fluorescence background increased with the pressure (Fig. 8). The latter is an indication of the increase in concentration of chromophore. Moreover, Raman region around 1670 cm^{-1} indicated that the pressure increase resulted in additional contribution of p-quinones.

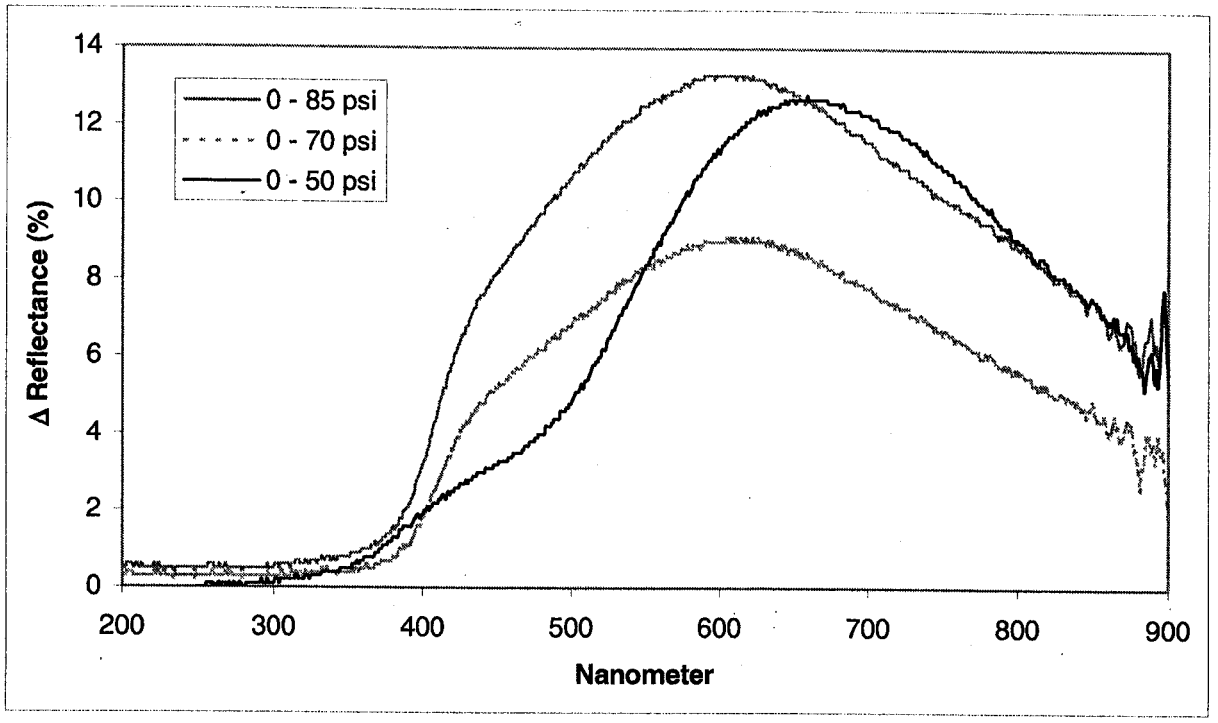

Fig. 7 Refining pressure induced changes in the reflectance spectrum of biopulp; data is platted after subtracting the reflectance of the 0 psi biopulp. The results suggest that changes in both the o- and p-quinones absorptions were taking place.

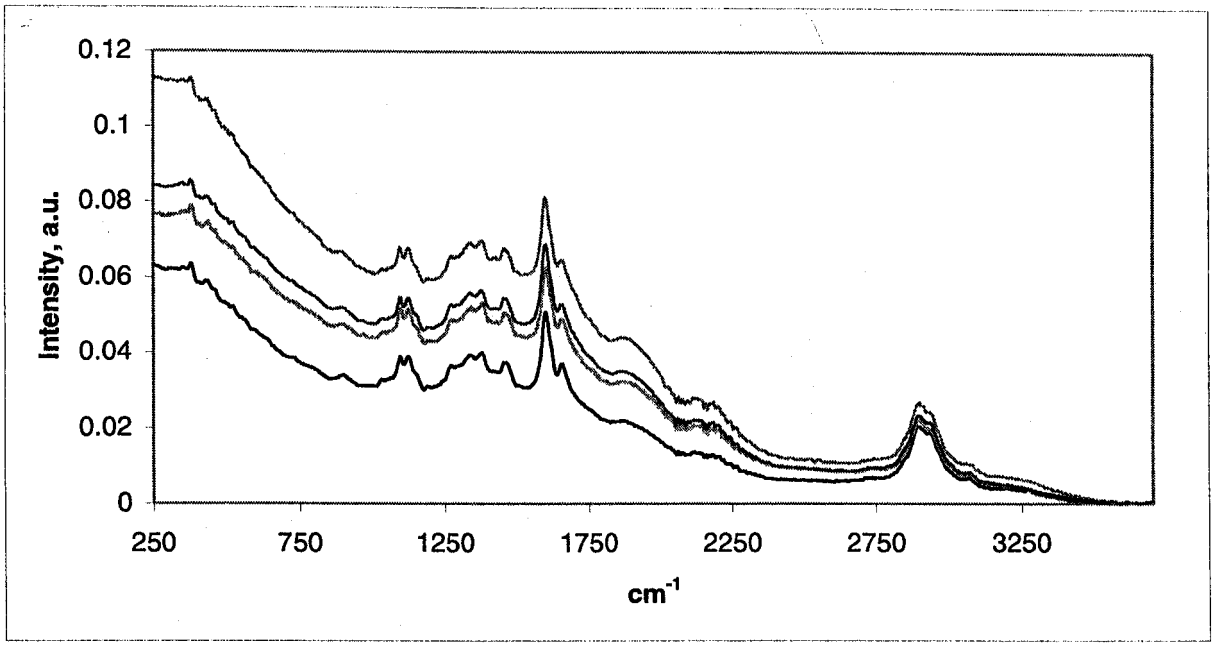

Fig. 8 FT-Raman spectra of biopulps; top to bottom – 85, 70, 50 and 0 psi. Fluorescence background, underlying the spectra (low wavenumber side), increased with the increase in steaming pressure.

Methanol extracts of the 4 biopulps were obtained and the extracted-materials were studied using Raman spectroscopy (Fig. 9). The most noticeable difference was detected in the p-quinone region where it was found that the 0 psi biopulp-material had the strongest contribution. This contribution-order was followed by the 70 and 85 psi pulp-materials. Within this set of 4 pulp-materials, the least amount of p-quinones were present in the 50 psi pulp-material. There did not seem to be much difference in the o-quinone region.

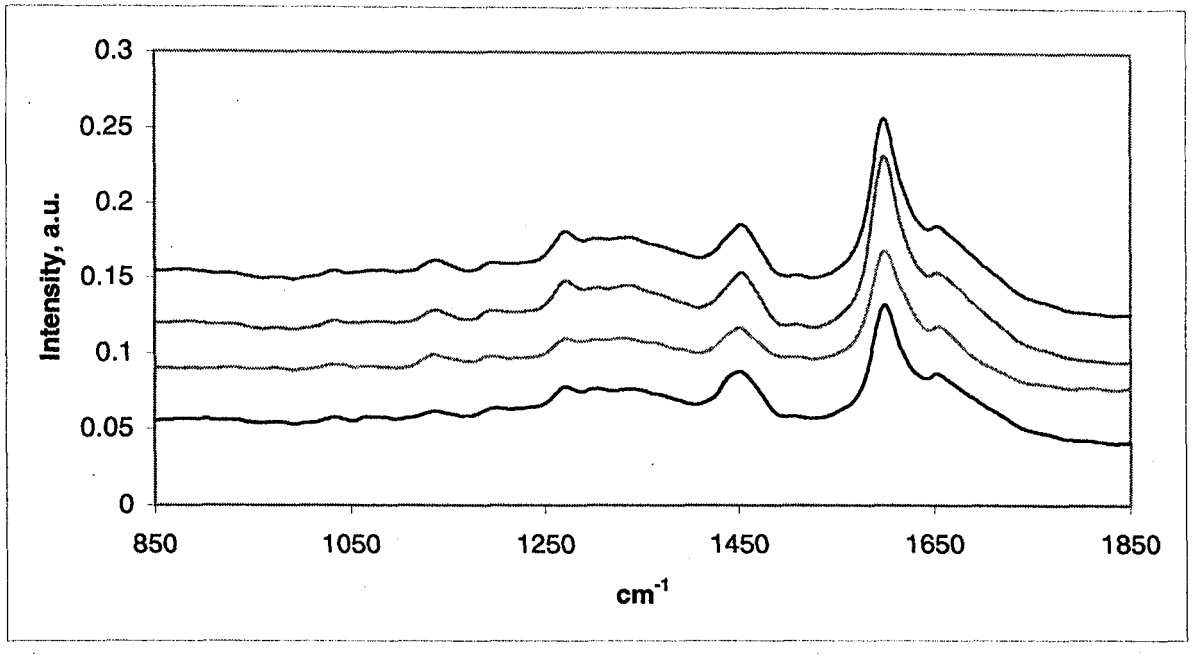

Fig. 9 Raman spectra of materials extracted from different pressure biopulps; top to bottom – 85, 70, 50, and 0 psi. The 1665-1690 cm^{-1} spectral region indicated that different steaming pressure produced different amount of p-quinones in pulps.

Of the 4 IR absorbance spectra of biopulp-extracted-materials, the 50 psi pulp-material gave a spectrum that was somewhat different (Fig. 10). In the latter, the 1740 cm^{-1} band was not as strong. Also, 1610 and/or 1640 cm^{-1} band was considerably stronger than its intensity in the spectra of 0, 70, and 85 psi biopulp-extracted-materials.

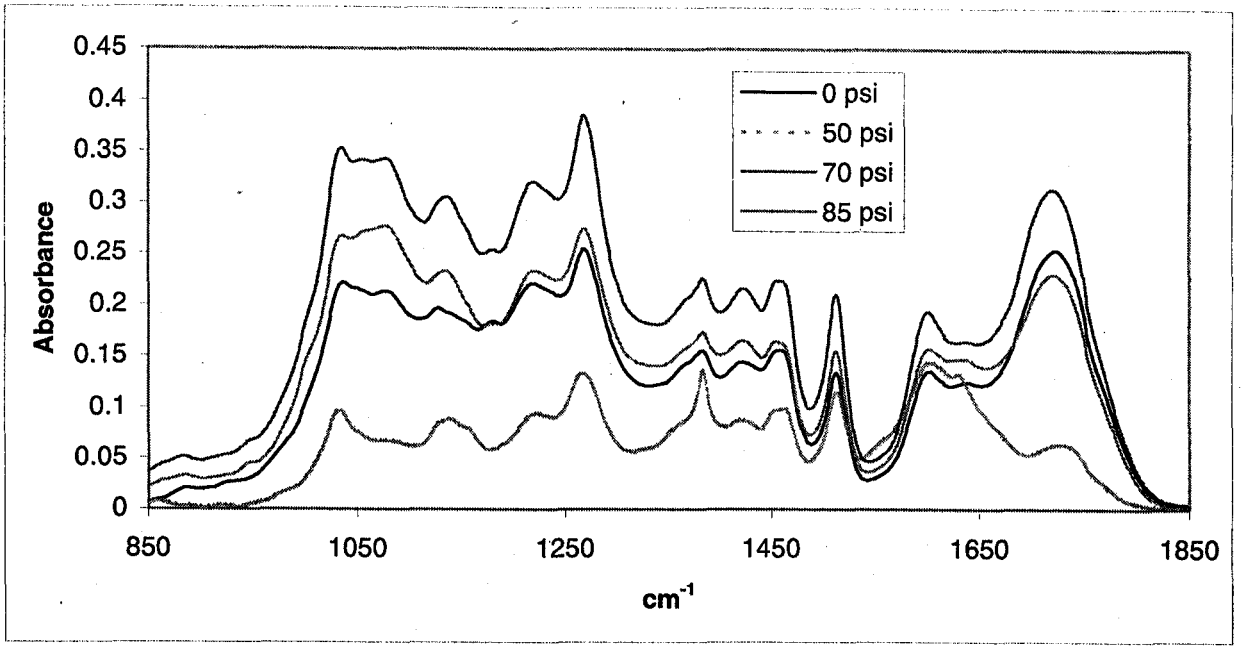

Fig. 10 IR spectra of biopulp extracted materials; except for the 50 psi case (dashed line) where 1740 cm^{-1} band was significantly weaker other spectra resembled each other very well.

Control Pulps vs. Biopulps

From the brightness data of treated pulps, it is clear that at all steaming pressures, biopulps were darker than the same pressure control pulps. Indeed, as discussed above, the pressure was detrimental only to the brightness of biopulps – control pulps had the same brightness irrespective of the steaming pressure (Table I). From Table I, treated pulps refined at 0, 50, 70, and 85 psi steaming pressure had brightness, respectively, of 39.9%, 32.2%, 31.3%, and 27.8%. All these values are lower compared to the control pulp brightness of about 56% (for all steaming pressures). This indicated that in addition to having lower brightness (compared to control) at 0 psi, the treated wood lost additional brightness during refining at higher steaming pressure.

Difference diffise-reflectance UV/Vis spectra obtained after subtraction of corresponding control-pulp spectrum (Fig. 11) indicated that, compared to controls, biopulps absorbed strongly between 400 and 800 nm. In addition, such difference spectra were quite similar to each other for the 70 and 85 psi biopulps and differed significantly from the spectrum of the 50 psi biopulp. This characteristic of the 50 psi biopulp is similar to the situation above where its IR spectrum was found to have important differences as well (Fig. 10).

When Raman spectra were compared, the underlying background was found to be very significantly enhanced for biopulps. This was taken as evidence of more colored species being present in biopulps. Beyond that, 4 key observations that were noted from the spectra of fungus-treated and untreated woods (above section, Fungus Caused Changes in Wood) were also made. The Raman spectra of 85 psi control pulp and biopulp are compared in Fig. 12. In addition, spectra of the materials that were obtained from these two pulps are compared (Fig. 13).

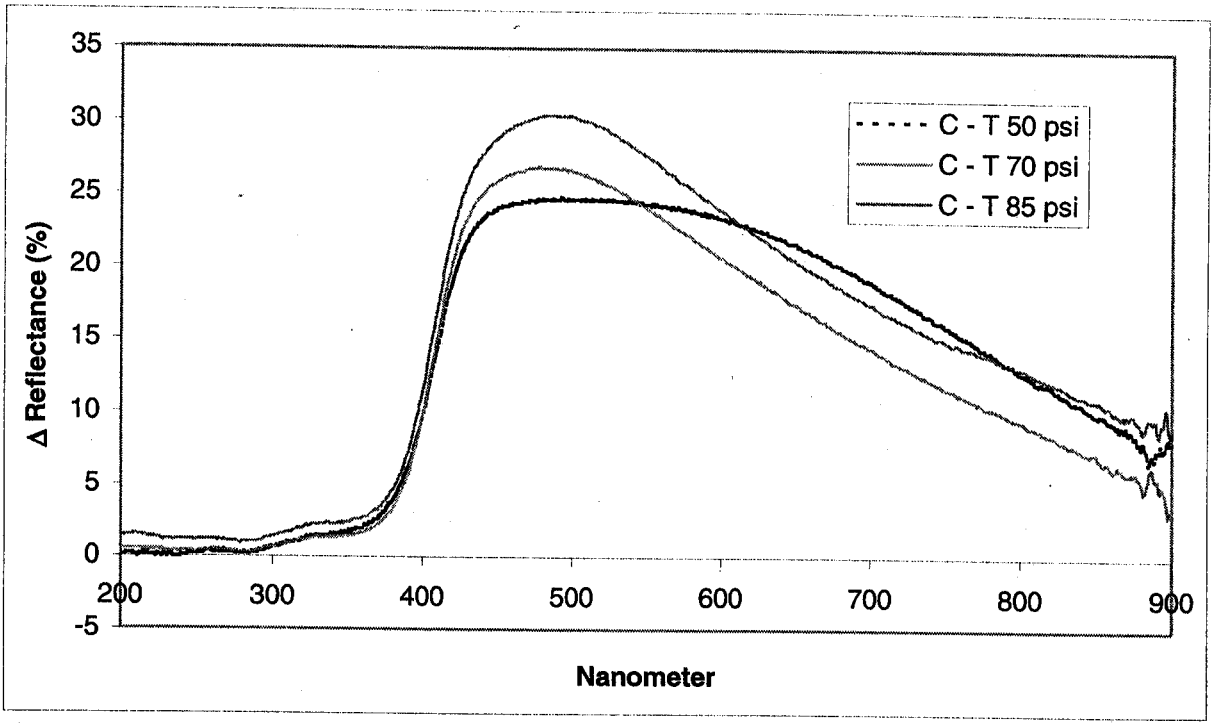

Fig. 11 Difference in the reflectance of the control pulps and biopulps (at the same steaming pressure); For the most part, higher pressure meant more reflectance loss or lower biopulp reflectance. The loss curve for the 50 psi pulp (most dark dashed line) showed differences in the 600-800 nm region that were not as prominent in the 70 and 85 psi pulps.

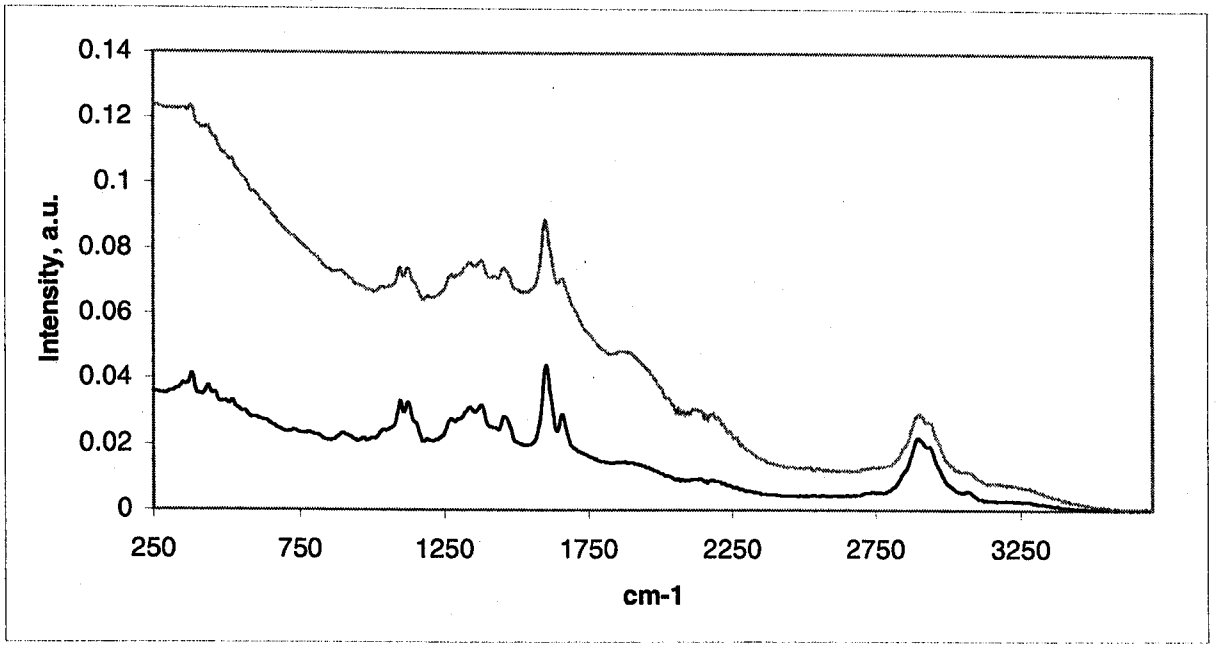

Fig. 12 FT-Raman spectra of 85 psi biopulp (top) and 85 psi control pulp (bottom). The biopulp spectrum has significantly higher background implying that higher amount of chromophores were present.

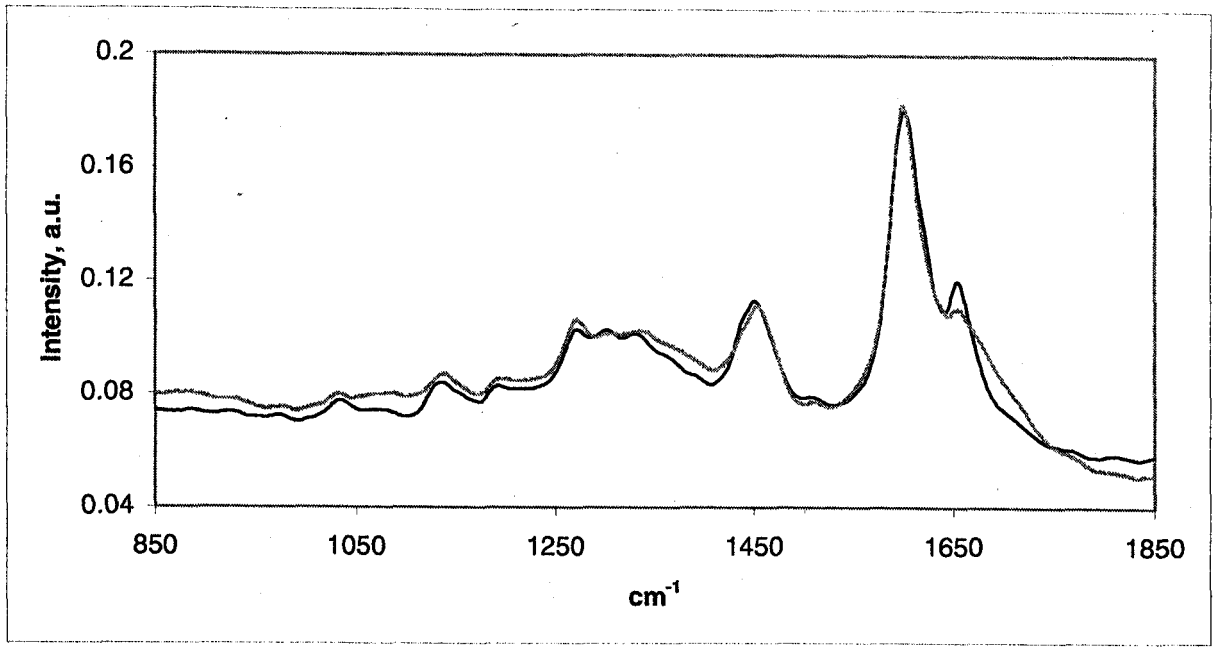

Fig. 13 FT-Raman spectra of extracted materials; 85 psi biopulp (less dark dashed line) and 85 psi control pulp (dark line). The contribution of p-quinones in the spectrum of biopulp extracted material can be easily seen in the region 1665-1690 cm^{-1}.

IR spectra were obtained of the materials that were extracted from the control pulps and biopulps. Except for the 50 psi pulp materials spectra (Fig. 6), there does not seem to be any great difference between the two sets (Fig. 6 and 10). This may be because, between the control pulps and biopulps, most chemical difference is due to chromophoric content for which IR spectroscopy is not very sensitive.

CONCLUSIONS

Findings of the present work are that fungus treated wood and biopulps loose brightness (become darker) because, compared to controls, such wood and pulps have more quinones (both o- and p-). Although, among biopulps produced at different steaming pressures, some difference in the amounts of quinones seems to be present, in general, higher pressure meant more quinones. For the biopulps investigated, it was found that compared to 0 psi biopulp, 50, 70, and 85 psi biopulps had significantly more quinones.

ACKNOWLEDGEMENTS

Authors are grateful to Kolby Hirth (Analytical Chemistry and Microscopy Laboratory, FPL) and Anita Cannon (Chemistry and Pulping, FPL) for recording, respectively, IR and UV/Vis spectra of the samples that were used in this research.

REFERENCES

1. Akhtar, M., Blanchette, R.A., Myers, G., and Kirk, T.K., "An Overview of Biomechanical Pulping Research" in Environmentally Friendly Technologies for Pulp and Paper Industry, Eds. R.A. Young and M. Akhtar, John Wiley & Sons, 1998, New York, Chapter 10.
2. Sykes, M, "Bleaching and Brightness Stability of Aspen Biochemical Pulps", Tappi J., 76, 121(1993).
3. Agarwal, U.P. and Atalla, R.H., "Using Raman Spectroscopy to Identify Chromophores in Lignin-lignocellulosics", in Lignin: Historical, Biological, and Materials Perspectives, Eds. W.G. Glasser, R.A. Northey, and T.P. Schultz; ACS Symp. Series # 742; ACS Washington DC; 1999; Chapter 11.

4. Agarwal, U.P., "Assignment of the Photoyellowing-related 1675 cm^{-1} Raman/IR Band to p-Quinones and Its Implications to the Mechanism of the Color Reversion of Mechanical Pulps". J. Wood Chem. Tech. 18, 381(1998).
5. Agarwal, U.P. and Atalla, R.H., "Raman Spectroscopic Evidence for Coniferyl Alcohol Structures in Bleached and Mechanical Pulps", in Photochemistry of Lignocellulosic Materials, Eds. C. Heitner and J.C. Scaiano, ACS Symp. Series 531, ACS Washington DC, 1993, Chapter 2.
6. Agarwal, U.P. and McSweeny, J.D., "Photoyellowing of Thermomechanical Pulps: Looking Beyond the a-Carbonyl and Ethylenic Groups as the Initiating Structures," J. Wood Chem. Tech. 17, 1(1997).
7. Forsskahl, I., Tylli, H., and Olkkonen, C., "Influence of Quinoid and Aromatic Chromophores on the Light-induced Yellowing of High-Yield Pulps", Proc. 7th International Symp. Wood and Pulping Chemistry, Beijing, May 25-28, 1993, Vol. 2, pp 750.

2000 TAPPI Pulping/Process & Product Quality Conference

Sheraton Boston
Boston, MA USA
November 5-8, 2000

© 2000 TAPPI All rights reserved, www.tappi.org
Order number: PULP/PPQCD-00
ISBN 0-89852-974-3

Copyright©2000 Adobe Systems Inc. All rights reserved. Adobe, Acrobat, and Acrobat Exchange are trademarks of Adobe Systems Incorporated.