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### Photoyellowing of Thermomechanical Pulp: Looking Beyond $\alpha$ -Carbonyl and Ethylenic Groups as the Initiating Structures

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**PHOTOYELLOWING OF THERMOMECHANICAL PULPS:  
LOOKING BEYOND  $\alpha$ -CARBONYL AND ETHYLENIC GROUPS AS  
THE INITIATING STRUCTURES**

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**ABSTRACT**

Photoyellowed and control unbleached, borohydride bleached, and bleached and diimide-reduced spruce thermomechanical pulps (TMPs) were studied using near-IR excited FT Raman, DRIFT, and diffuse reflectance UV-Vis. spectroscopies. In addition, extracts of yellowed pulps were analyzed spectroscopically. FT Raman spectroscopy was used for the first time in the study of the photoyellowing phenomenon. Post color number data of the yellowed TMP handsheets suggested that  $\alpha$ -carbonyl and ring-conjugated ethylenic groups did not play a significant role in the yellowing process. This suggestion was further supported by not only the similarity of the FT Raman and DRIFT spectra of the three yellowed pulps but by the similarity between the spectra of the pulps' yellow extracts. Raman spectra of the TMPs provided evidence for the following: (1) diimide-reduced TMP was indeed free of aromatic ring-conjugated ethylenic bonds; (2) photoexposure of unbleached TMP caused degradation of coniferaldehyde and coniferyl alcohol structures; and (3) photoexposure of bleached TMP caused the degradation of coniferyl alcohol structures. In addition, yellowing resulted in changes in the  $1600\text{ cm}^{-1}$  Raman band and a new broad feature appeared at  $1675\text{ cm}^{-1}$ . In the IR spectra of pulp extracts, the latter vibrational mode was detected at  $1673\text{ cm}^{-1}$ . IR spectra of the yellowed pulps and their extracts showed increased absorption at  $1727\text{ cm}^{-1}$ . Upon yellowing, contribution to this band was primarily from the

photoproducts of those lignin structures that did not contain a conjugated-ethylenic bond. These results suggest that there are yellowing initiating structures, other than  $\alpha$ -carbonyl and ethylenic groups, that are responsible for most of the yellowing in unbleached, borohydride bleached, and diimide-reduced TMPs.

## **INTRODUCTION**

Brightness loss of mechanical pulp-based papers during normal use is one main reason why such papers are not used in applications requiring permanence. One approach to solve this problem is to gain a fundamental understanding of the light-induced brightness reversion phenomenon (photoyellowing). Although lignin is known to be responsible for yellowing, characterization of its yellowing initiating structures is a challenging problem. This is an important issue because subsequent events leading up to yellowing can be better understood if the identities of the initiating structures are known.

A previously proposed photoyellowing mechanism, based on the existence of  $\alpha$ -carbonyl groups in pulp-lignin, could not be supported when it became clear that there are no significant differences between the photoyellowing behavior of unbleached and borohydride bleached mechanical pulps.<sup>[1,2]</sup> Similarly, the role of aromatic-ring conjugated ethylenic bonds in yellowing is not well established. Initial reports suggest that such structures were not involved.<sup>[3,4]</sup> However, research carried out in our laboratory indicated that this topic needed to be revisited<sup>[5]</sup>. This was largely so because previous conclusions<sup>[3]</sup> were based on studies that did not ensure that all C=C groups in pulps were reduced. Moreover, in some hydrogenation treatments (e.g., in diimide treated pulps), the pulp darkened.<sup>[3,6]</sup> This implied that additional chromophores were generated. What sensitivity these newly formed chromophores had towards light was not known. In the case of diimide-treated latex (diimide was one of the treatments that was used in the hydrogenation of TMP), for example, it was reported that the treated material darkened upon storage under ambient conditions.<sup>[7]</sup> Furthermore, studies of photoyellowed pulps indicated that lignin's coniferyl alcohol (CALC) and coniferaldehyde (CALD) structural units were involved in light-induced chemical changes.<sup>[8,9]</sup>

However, to what extent these structures in pulps were responsible for yellowing was not clear. Studies that investigated the photobehavior of CALC, CALD, and other ring-conjugated C=C models indicated that they yellowed when exposed to light.<sup>[10,11]</sup> But it was not clear if their yellowing photobehavior could be modified in a pulp environment where not only the neighboring structural units are different but also the molecular mobility is severely restricted.

In the present study, we evaluated the role of  $\alpha$ -carbonyls and ethylenic bonds in yellowing by using near-IR (infrared) excited FT (Fourier Transform) Raman, FT IR, and UV (ultraviolet)-Vis. spectroscopies. Three types of spruce thermomechanical pulps (TMPs)—unbleached, borohydride bleached, and borohydride bleached and diimide-reduced (diimide-reduced)—were chosen for this study. The FT Raman technique was applied for the first time in the investigation of the photoyellowing phenomenon. This recently developed technique in Raman spectroscopy has several advantages compared with conventional Raman techniques.<sup>[12]</sup> Spectra can be acquired rapidly, they are free of fluorescence (for most samples), and subtraction of spectra is more accurate.<sup>[13]</sup> These advantages along with the fact that Raman is more sensitive to covalent and conjugated structures than infrared spectroscopy make FT Raman an attractive analytical method.

## **EXPERIMENTAL**

### **Borohydride Bleaching**

Before bleaching, spruce TMP was acid treated (with 0.01N sulfuric acid) to remove most of the metal ions. Acid-treated pulp was washed, then treated with a 0.3M NaBH<sub>4</sub> solution at room temperature for 6 days. The solution was monitored for the presence of unreacted borohydride for the duration of the treatment. This was accomplished by using the iodine/iodide test. (In presence of borohydride, iodine is reduced to iodide, which is colorless.) If required, an additional amount of borohydride was added. After the sixth day, another acid treatment was performed. This was followed by washing the pulp and treating it again with 0.3 M sodium borohydride. To this new pulp suspension, sodium

hydroxide was added to increase the pH to 11. After 3 more days of treatment, the suspension was filtered and the pulp was washed thoroughly.

### **Diimide Hydrogenation**

Borohydride-treated pulp was prepared for treatment with diimide by first solvent exchanging to ethanol and then to n-octane. Except for the solvent used, the procedure used was similar to that reported previously.<sup>[3]</sup> Diimide is generated *in situ* when a solution containing hydrazine hydrate and copper sulfate is sparged with air. In our experiment, using a fritted glass device, the pulp suspension (1% solids in n-octane) was first sparged with air. This was followed by adding hydrazine hydrate and then copper sulfate. Quantities of reactants used per gram of TMP were as follows: 3.1 mmol of hydrazine and 0.0045 mmol of Cu. The reaction was conducted at room temperature for 17 h. At the end of the reaction period, octane solution was tested for the presence of unreacted hydrazine by using the iodine/iodide test. No reduction of iodine to iodide was observed. The pulp was filtered and washed with octane, then with absolute ethanol.

### **Analytical Methods**

FT Raman spectra were obtained using an RFS-100<sup>a</sup> instrument (Bruker Instruments, Inc., Billerica, MA<sup>1</sup>). Samples were excited using the 1064 nm line of the Nd:YAG diode laser. All spectra were obtained in the 180° scattering geometry. Pulp fibers were compressed into pellets, whereas handsheets were sampled directly. Spectra of handsheets were obtained by keeping a front surface mirror behind the samples. Solutions were sampled in shortened NMR-tubes. TMP extracted materials were sampled as solids using "aluminum wells," which were provided with the instrument as sampling accessories. Raman spectra of 1% CALD and 1% CALC were obtained by sampling them on bleached kraft pulp. Bleached kraft was preferred over

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<sup>1</sup> The use of trade or firm names is for information only and does not imply endorsement by the U.S. Department of Agriculture of any product or service.

cellulose because the former contains some hemicellulose; therefore, carbohydrate matrix interactions with lignin model compounds are expected to be similar to what lignin units experience in a TMP. Although spectra were obtained in the 250-3700  $\text{cm}^{-1}$  region, only the 850-1850  $\text{cm}^{-1}$  region is shown in the figures. Double-sided interferograms were obtained so that the data acquisition was rapid. On average, 600 scans were co-added before the interferogram was Fourier transformed to its corresponding power spectrum. Bruker's OPUS IR-2 (Bruker Instruments, Inc., Billerica, MA) software was used both to control instrument functions and process spectral data.

IR spectra were recorded on a Galaxy 5000 spectrometer (Mattson Instruments, Middleton, WI). Pulp fibers were studied in the form of pellets, and handsheets were sampled directly. DRIFT spectra were obtained from TMP samples. Extracted materials from yellowed pulps and o- and p-quinones were studied as KBr pellets, and their transmission spectra were obtained.

A PE lambda 6 spectrophotometer (Perkin-Elmer Corporation, Norfolk, CT), in conjunction with an integrating sphere (RSA-PE-60, Labsphere, Inc. North Sutton, NH), was used for recording diffuse reflectance UV-Vis. spectra. Absorbance spectra were obtained for the methanol solutions of the pulp extracts.

### **Other**

Using standard procedures, handsheets were made from unbleached, bleached, and diimide-reduced pulps. The basis weight of the sheets was approximately 300  $\text{g/m}^2$ . Diffuse brightness levels of thick handsheets were measured using Tappi method T 525 om-86<sup>[14]</sup> on a Technibrite TB-1 instrument (Technidyne Corporation, New Albany, NY).

The pulps were photoyellowed in fiber form and as handsheets for various durations (50% relative humidity) in a Rayonet RPR-100 (The Southern New England Ultraviolet Co., Hamden, CT) photoreactor. The irradiance of lamps ( $\lambda_{\text{max}} = 350 \text{ nm}$ ), measured in the center of the reactor, was 8  $\text{mW/cm}^2$ . To obtain extracts, photoexposed TMPs were immersed in excess methanol overnight and the solutions were filtered. Filtrates were concentrated using a rotary evaporator.

Coniferaldehyde and coniferyl alcohol were purchased from Aldrich Chemical Co. (Milwaukee, WI) and Fluka Chemical Corporation (Rokonkoma, NY), respectively. 2-Methoxy p-quinone was provided by the USDA Forest Service, Forest Products Laboratory, Madison, Wisconsin. 3-methoxy o-quinone was made using the method reported in the literature.<sup>[15]</sup> All model compounds were checked for purity using GC/MS, HPLC, and NMR. For Raman analyses, bleached kraft pulps containing 1% CALD (or 1% CALC) were pressed into pellets.

Raman intensity was calculated with reference to the 1098  $\text{cm}^{-1}$  band. In TMPs, the band at 1098  $\text{cm}^{-1}$  is primarily due to cellulose. On the other hand, the relative intensity in IR was calculated by using the 2900  $\text{cm}^{-1}$  band as an internal reference. This band was chosen because in this region diffuse-reflectance is less sensitive to sample surface-morphology. Full width at half maximum (FWHM) data were calculated for the Raman band at 1600  $\text{cm}^{-1}$ .

## **RESULTS AND DISCUSSION**

### **Borohydride Bleaching**

The effect of borohydride treatment on mechanical pulps was studied previously.<sup>[16,17]</sup> It is known that carbonyl groups are reduced. This conclusion is further supported by the Raman, IR, and UV-Vis. analyses presented here. FT Raman spectra of untreated and treated pulps and subtracted spectra are shown in Fig. 1a-e. The effect of borohydride bleaching on the mechanical pulp Raman spectrum (conventional) was also reported previously.<sup>[5,18]</sup> In near-IR excited FT Raman, the spectral features at 1122, 1600, 1622, and 1655  $\text{cm}^{-1}$  declined in intensity upon bleaching (Fig. 1a-b). Although it is possible that some intensity at one or more of these band positions was due to chromophores other than CALD, most intensity decline was attributed to CALD structures<sup>[8,19]</sup>. CALD has contributions at these wavenumbers (Fig. 2) and by using band intensity decline at 1122  $\text{cm}^{-1}$ , expected intensity reduction at other wavenumbers was calculated. Observed and calculated data were similar, indicating that most of the decline was due to CALD. The intensity reduction at these wavenumbers can be noted from Fig. 1d, where the subtraction result

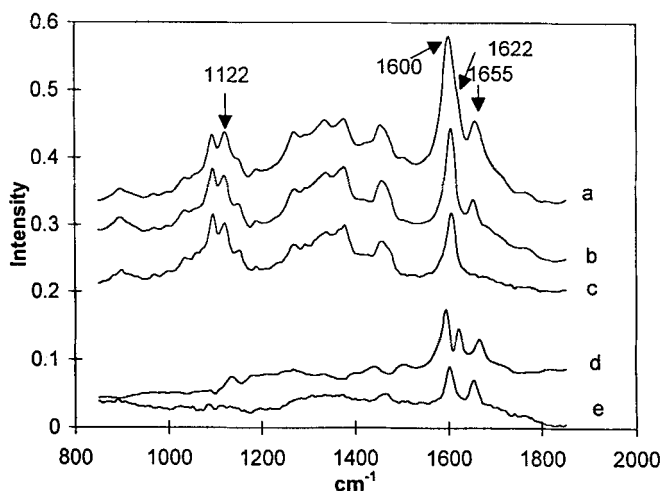


FIGURE 1. FT Raman spectra of TMPs: (a) unbleached, (b) borohydride bleached, (c) bleached and diimide-hydrogenated (diimide-reduced), (d) is (a-b), and (e) is (b-c). Changes in spectra upon borohydride bleaching can be noted through intensity decline at 1122, 1600, 1622, and 1655  $\text{cm}^{-1}$ . Diimide treatment resulted in the disappearance of the 1654  $\text{cm}^{-1}$  band and the decline of 1602  $\text{cm}^{-1}$  band.

of the unbleached and bleached TMP spectra is shown. In Fig. 1d, the positions where most intensity was removed were 1135, 1595, 1621, and 1663  $\text{cm}^{-1}$ . Except for the band at 1663  $\text{cm}^{-1}$ , the positions were located where contributions of CALD were expected<sup>[8]</sup> (Fig. 2a). In the Raman spectrum of CALD (in carbohydrate matrix), a band at 1657  $\text{cm}^{-1}$  was detected (Fig. 2a). Spectrum d in Fig. 1 indicates that from the Raman spectrum of unbleached TMP, more contribution was removed at 1663  $\text{cm}^{-1}$  than at 1657  $\text{cm}^{-1}$ . This observation suggests the presence of yet another chromophore (in addition to CALD) in unbleached TMP. Presently, its identity is unknown.

Similarly, the DRIFT spectrum of the borohydride bleached pulp provided support that this pulp was mostly free of carbonyl groups (Fig. 3). Upon bleaching, the peak at 1664  $\text{cm}^{-1}$  declined (Fig. 3b). In CALD, this band



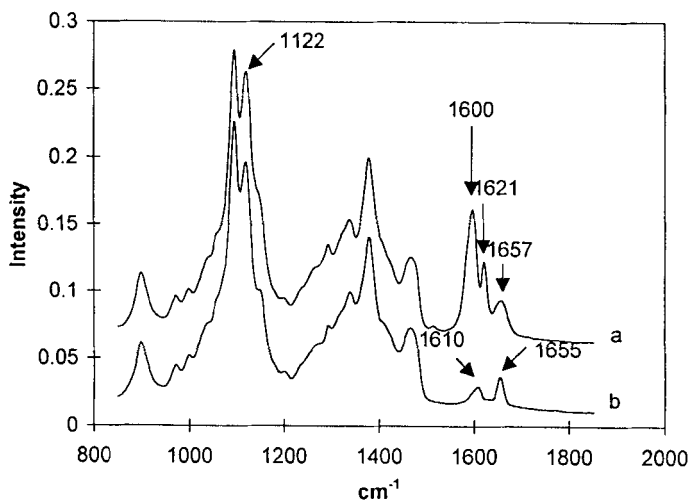


FIGURE 2. FT Raman spectra of 1% coniferaldehyde (a) and 1% coniferyl alcohol (b) in bleached kraft pulp. Important contributions of coniferaldehyde and coniferyl alcohol are annotated. At 1122  $\text{cm}^{-1}$  the major contribution is from cellulose and only a little from coniferaldehyde. Bleached pulp Raman spectrum (not shown) has no contribution beyond 1500  $\text{cm}^{-1}$ .

has been assigned to C=O stretch mode.<sup>[20]</sup> In addition, considering that in the IR spectrum of bleached pulp, no band was detected between 1660-1690  $\text{cm}^{-1}$ , where conjugated  $\alpha$ -carbonyl groups are expected to be detected<sup>[21]</sup>, it was concluded that in bleached TMP such groups were not present. Therefore, although some unknown chromophores remained in bleached TMP, the concentrations of CALD and  $\alpha$ -carbonyl (if present in unbleached TMP) groups were drastically reduced. Upon bleaching, the pulp brightened by 18 points (TABLE 1).

Difference diffuse reflectance ( $\Delta R$ ) UV-Vis. spectra of the handsheets made from nonyellowed TMPs are shown in Fig. 4.  $\Delta R$  spectra were obtained by subtracting the reflectance spectrum of a high brightness bleached kraft pulp sheet from the spectra of TMP handsheets. For bleached TMP, bleaching related changes can be better seen by subtracting curve b from curve a (Fig. 4).

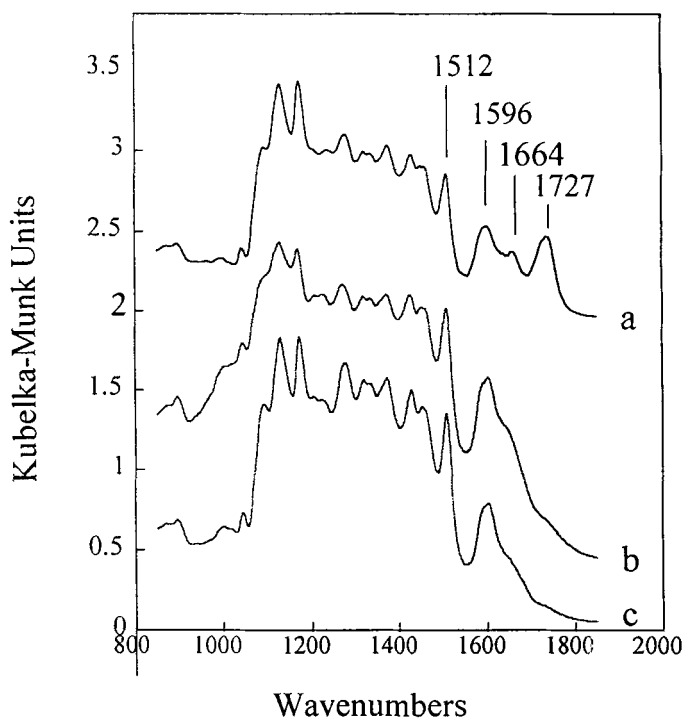


FIGURE 3. DRIFT spectra of TMPs: (a) unbleached, (b) borohydride bleached, and (c) diimide-reduced. Intensity reduction at 1664 and 1727  $\text{cm}^{-1}$  as a result of borohydride bleaching is shown. Also, spectra (b) and (c) are similar.

TABLE 1: Brightness Points and Post Color (PC) Numbers

TMP	Initial brightness	PC (4-h yellowed TMP)
Unbleached	52.2	10.75
Bleached	70.4	12.19
Diimide-reduced	73.9	11.48

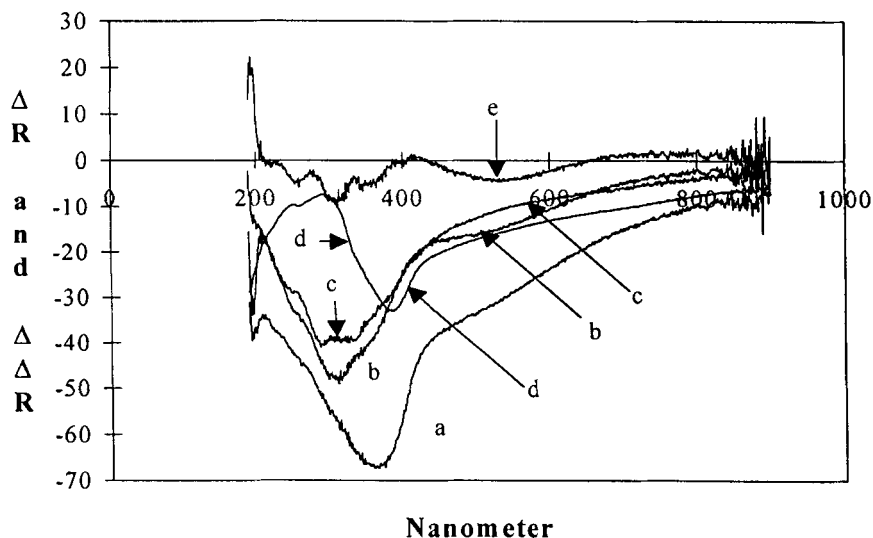


FIGURE 4. UV-Vis. diffuse reflectance difference ( $\Delta R$ ) and  $\Delta\Delta R$  spectra of the nonyellowed TMPs: (a) unbleached, (b) borohydride bleached, (c) diimide-reduced, (d) is (a-b), and (e) is (b-c). Absorption contribution of chromophores removed upon borohydride bleaching is shown in (d) and the effect of diimide treatment on bleached pulp can be noted from curve (e).

The result is shown as a  $\Delta\Delta R$  reflectance spectrum ( $\Delta\Delta R$ , curve d) in Fig. 4. This curve indicated that chromophoric contributions were partially removed from the entire UV-Vis region. However, the removed contribution had a maximum at 380 nm, indicating that CALD structures were modified. (CALD's absorption maximum at 350 nm is known to undergo a bathochromic shift in the carbohydrate matrix.<sup>[22]</sup>) Other chromophores were also modified, but to a lesser degree.

### **Diimide Hydrogenation**

Diimide treatment was used to hydrogenate aromatic-ring conjugated ethylenic groups in pulp lignin. To evaluate the effectiveness of the hydrogenation treatment, a band at  $1654\text{ cm}^{-1}$  present in the Raman spectrum

of  $\text{BH}_4$  bleached TMP (Fig. 1b) was used. This Raman band was assigned to the C=C stretch mode in CALC structures in pulp.<sup>[5]</sup> Diimide treatment of the pulp resulted in the disappearance of the  $1654\text{ cm}^{-1}$  Raman peak (Fig. 1c). In addition, intensity declined at  $1602\text{ cm}^{-1}$  (Fig. 1e). These positions are approximately where the Raman contributions of CALC structures were detected (Fig. 2). Therefore, we concluded that the CALC structures in pulp were successfully hydrogenated. However, decline in relative intensity at  $1602$  and  $1654\text{ cm}^{-1}$  could not be interpreted solely in terms of coniferyl alcohol and/or *p*-methoxy coniferyl alcohol structures. (The latter was used as a model for non-free phenolic coniferyl alcohol units in lignin.) Therefore, we propose that other structures also contribute at these wavenumbers. Considering that Raman features were absent in the wavenumber region  $1620\text{-}1680\text{ cm}^{-1}$  (Fig. 1c), no ring-conjugated C=C structures (including stilbenes) were likely to be present in the hydrogenated TMP. (Stilbenes have an intense band due to C=C at  $1638\text{ cm}^{-1}$ .<sup>[5]</sup>) Treatment with diimide caused a small increase in the pulp's reflectance in the 400-600 nm region (TABLE 1, Fig. 4e).

The DRIFT spectra of diimide- and borohydride-treated TMPs were similar (Fig. 3) because no IR band due to C=C is expected.<sup>[5]</sup> The pulp brightness data (TABLE 1) indicated that the diimide reduction did not generate new chromophores. (The brightness of the diimide-reduced TMP was slightly greater than that of borohydride bleached TMP.) This is important because, in the past, diimide treatment caused darkening of the pulp.<sup>[3,6]</sup> We believe that the reactions that previously lowered pulp brightness were completely inhibited in octane. In addition to having higher reflectance in the region 400-600 nm, the diimide treatment resulted in reduced absorption in the 300-400 nm range (Fig. 4e). Higher reflectance in the latter region can be explained in terms of removal of CALC structures. (CALC's absorption, in the 300-400 nm region, depends on its concentration.) Considering the 400-600 nm range where higher reflectance was obtained, it is possible that some quinone contribution was removed. The diimide-reduced pulp showed significant absorption at wavelengths greater than 300 nm (Fig. 4c). A broad peak at 315 nm and a weak shoulder at approximately 375 nm could be detected. Which of the remaining lignin structures are responsible for such absorptions remains to be determined.

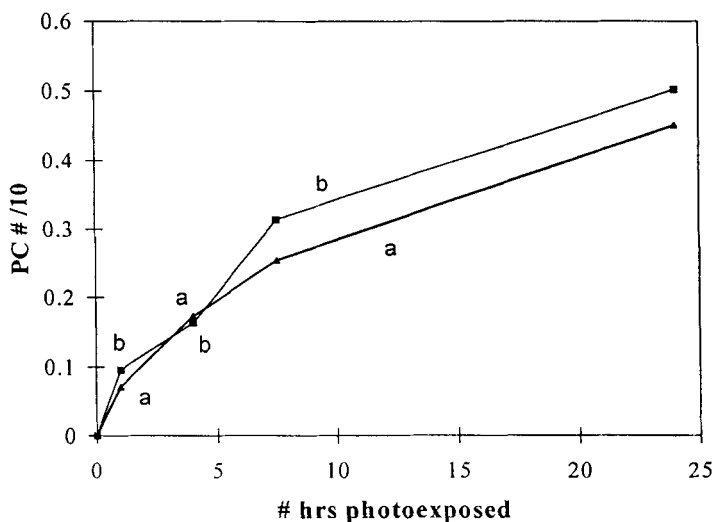


FIGURE 5. A comparison of the extent of photoyellowing for borohydride bleached (a) and diimide-reduced (b)TMPs. Within the experimental error, there are no significant differences.

## Photoyellowing

### *Pulps*

Accelerated photoyellowing of the three TMP handsheets resulted in rapid brightness loss as can be seen from the post color (PC) number data in TABLE 1. PC numbers indicate that the extent of yellowing for the three TMPs was similar. Yellowing behavior of bleached and diimide-reduced TMPs was compared by photoexposing them (under identical conditions) for various durations. PC data as a function of time of exposure is shown in Fig. 5. Within the experimental error, there seems to be no difference between their photoyellowing behavior. This observation is similar to the previously reported result, where no difference between the photoyellowing behavior of unbleached and borohydride bleached ground wood pulps was found.<sup>[1]</sup> Thus, the similarity of the yellowing behaviors between bleached and unbleached ground wood

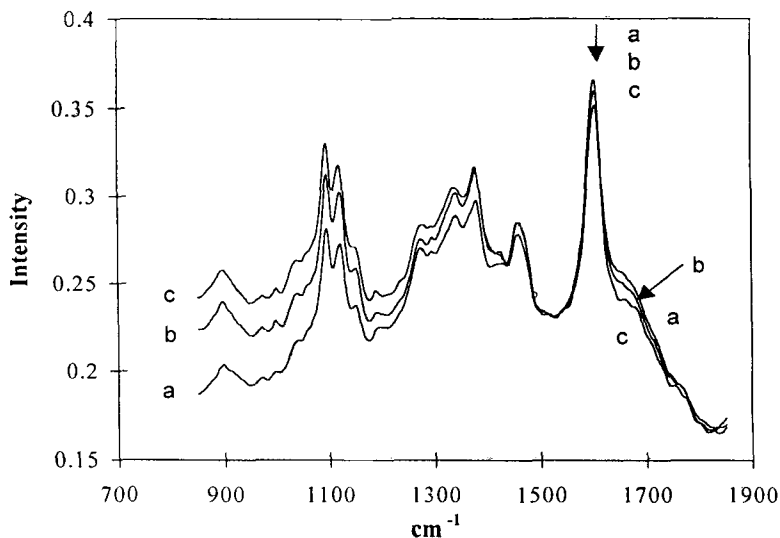


FIGURE 7. Similarity of DRIFT spectra of 24-h photoexposed pulps: (a) unbleached, (b) borohydride bleached, and (c) diimide-reduced. The  $1727\text{ cm}^{-1}$  band is present in all three spectra.

pulps and between bleached and diimide-reduced TMPs further imply that the yellowing mechanism is independent of the presence of  $\alpha$ -carbonyl and ethylenic groups.

When unbleached and treated TMPs were exposed to light (in fiber form) for 24 h, the chemical changes occurring in pulps were significant enough to be detected in both Raman and IR spectroscopy. Such changes occurred primarily in the spectral range of  $850\text{--}1850\text{ cm}^{-1}$  (Figs. 6, 7). This is not surprising considering that lignin's most intense vibrational bands are present in this region. Although the spectra of three nonyellowed TMPs differed (Figs. 1, 3) to some extent as a result of the presence (or absence) of certain structures, yellowed TMP spectra were very similar (Figs. 6, 7). When the Raman spectra of yellowed and nonyellowed pulps were compared, we found that the features associated with CALD/CALC groups declined (Figs. 1a, 6a) after yellowing.

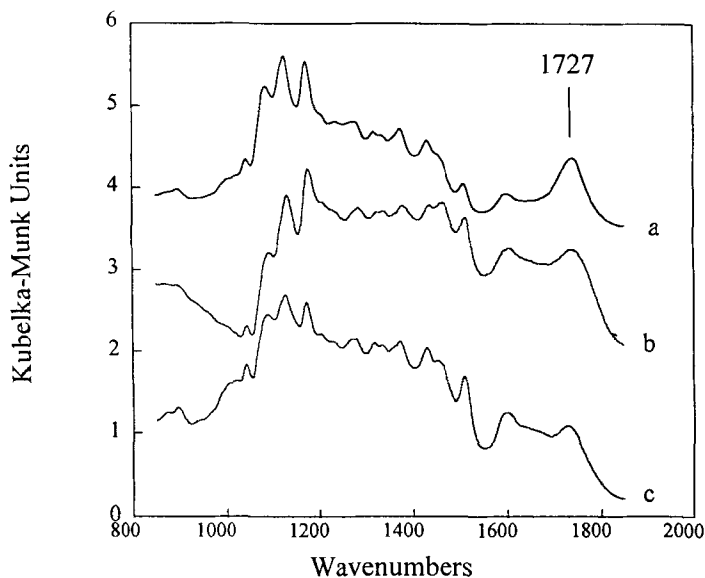


FIGURE 6. Similarity of FT Raman spectra of 24-h photoexposed pulps: (a) unbleached, (b) borohydride bleached, and (c) diimide-reduced. Particularly noticeable are the similarities of the 1600 and 1675  $\text{cm}^{-1}$  features.

Specifically, in unbleached TMP, intensity at 1135, 1600, 1621, and 1657  $\text{cm}^{-1}$  declined. At these wavenumbers, coniferaldehyde has FT Raman bands (Fig. 2a). Similarly, in bleached TMP, the decline occurred at 1654  $\text{cm}^{-1}$  (Figs. 1b, 6b)

— a band position that has been assigned to C=C stretch mode in coniferyl alcohol (Fig. 2b, [5]). These results supported previous findings that were obtained using conventional Raman spectroscopy.<sup>[8]</sup> The previously reported photobleaching of mechanical pulp<sup>[23]</sup> has been explained in terms of photodegradation of CALD groups.<sup>[24, 25]</sup> This provides further support to our Raman findings of CALD degradation in unbleached TMP. The decay of CALC groups in photoexposed mechanical pulps is also supported by thioacidolysis analyses of spruce mechanical pulp lignins.<sup>[9]</sup>

TABLE 2: Raman Features of the  $1600\text{ cm}^{-1}$  Band Before and After Photoyellowing

TMP	Intensity		FWHM, $\text{cm}^{-1}$	
	Before	After	Before	After
Unbleached	2.69	1.62	46	33
Bleached	1.71	1.32	31	33
Diimide reduced	1.15	1.25	31	33

A detailed analysis of the  $1600\text{ cm}^{-1}$  band indicated that changes occurred in both its intensity and its full-width-at-half-maximum value (FWHM, TABLE 2). A slightly higher intensity of the  $1600\text{ cm}^{-1}$  band in yellowed unbleached TMP, compared with that in the other two yellowed TMPs, might have resulted from incomplete decay of CALD structures. In addition, a new feature in the form of a shoulder appeared at  $1675\text{ cm}^{-1}$ . This was true for all three TMP spectra (Fig. 6). When the Raman spectra of 24-h yellowed TMPs were compared, it appeared that the characteristics of both the  $1600$  (TABLE 2) and  $1675\text{ cm}^{-1}$  features were similar among the three spectra. Moreover, the remaining regions in the spectra were also similar. This implied that the light-exposed pulps were similar to a significant degree.

DRIFT spectra of yellowed TMPs were also similar (Fig. 7). Moreover, when IR spectra of yellowed and nonyellowed bleached and diimide-reduced TMPs were compared, we noted that the  $1727\text{ cm}^{-1}$  was present in the yellowed pulps. This band was not detected in the IR spectra of nonyellowed pulps (Fig. 3b-c). Therefore, the band arose as a consequence of photoexposure. In addition, because the  $1727\text{ cm}^{-1}$  band was detected in both the ethylenic-bond containing and ethylenic-bond free TMPs that were photoexposed, it could not have been caused by the photo-oxidation of lignin's C=C conjugated structures. This is further supported by the results of the time-resolved photoyellowing study<sup>[26]</sup> (Fig. 8). In Fig. 8, for bleached TMP, intensity decline at  $1654\text{ cm}^{-1}$  and intensity enhancement at  $1727\text{ cm}^{-1}$  band positions are shown as a function of length of photoexposure. The  $1727\text{ cm}^{-1}$  band intensity continued to increase long after the  $1654\text{ cm}^{-1}$  band had declined completely. This indicated that



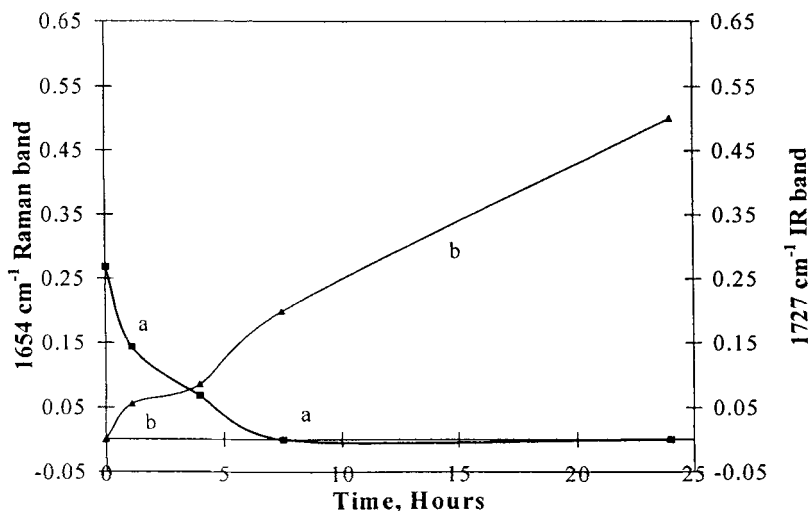


FIGURE 8. Changes in band intensity with time of photoexposure for the borohydride-bleached TMP: (a)  $1654\text{ cm}^{-1}$  (Raman), (b)  $1727\text{ cm}^{-1}$  (IR). Decline at  $1654\text{ cm}^{-1}$  is mostly due to degradation of coniferyl alcohol units. Increment of  $1727\text{ cm}^{-1}$  band is related to formation of photoproducts.

intensity enhancement at  $1727\text{ cm}^{-1}$  was not related to the band decline at  $1654\text{ cm}^{-1}$ . Furthermore, we found evidence that the intensity of the IR band at  $1727\text{ cm}^{-1}$  was linearly related ( $R^2 = 0.95$ ) to the PC number (Fig. 9). This was true for both bleached and diimide-reduced pulps. This observation suggested that the band at  $1727\text{ cm}^{-1}$  is related to the yellowing photoreactions in some way. The photo-product responsible for this band may or may not be colored. Previously, in lignocellulosics, this IR band has been assigned to C=O of acid and/or ester functional group<sup>[16]</sup>. When such IR spectra of yellowed and nonyellowed unbleached TMP (in the latter,  $1727\text{ cm}^{-1}$  is present originally) were compared, we found that the yellowing enhanced the intensity of the  $1727\text{ cm}^{-1}$  band.

Again, similarity in the chemical nature of the photoexposed pulps can be noted from Fig. 10 where diffuse reflectance UV-Vis. spectra of yellowed handsheets of bleached and diimide-reduced TMPs are shown. These spectra

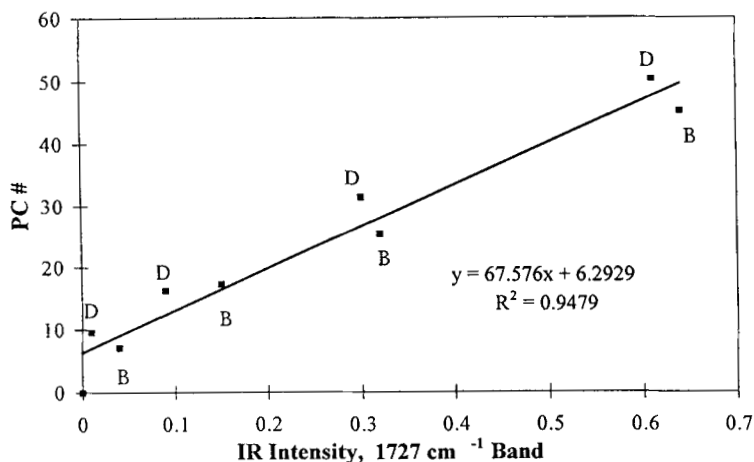


FIGURE 9. Linear correlation between PC number and IR intensity (1727 cm<sup>-1</sup> band) for handsheets made from borohydride bleached and diimide-reduced pulps. Data were obtained from handsheets that were photoexposed to 0, 1, 4, 7.5, and 24 h. B is borohydride bleached, and D is diimide reduced pulp.

were obtained using a bleached kraft pulp handsheet as a reference. Diffuse reflectance values greater than 100 (Fig. 10) are seen because the spectra were not normalized.

### Extracts

Methanol extracts (yellow) of photoexposed pulps were analyzed using all three spectroscopic techniques. Raman spectra (Fig. 11) indicated that extracted materials from all three pulps had similar spectral features. The spectrum in Fig. 11d, shown only in the 850-1850 cm<sup>-1</sup> region, is the subtraction result of the Raman spectra obtained before and after methanol extraction of the yellowed borohydride-treated TMP. All four spectra showed the 1675 cm<sup>-1</sup> band. The changes in the 1600 cm<sup>-1</sup> Raman band are difficult to analyze because extracts could not be obtained from nonyellowed pulps. The other spectral features were similar to those present in the FT Raman spectrum of black spruce milled-wood lignin.<sup>[27]</sup>

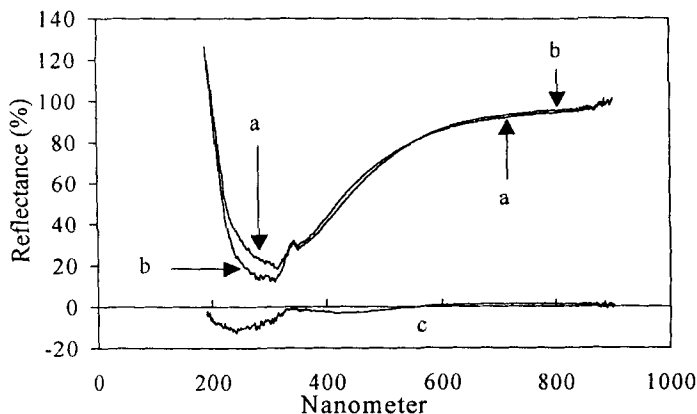


FIGURE 10. Similarity of the diffuse reflectance spectra (with reference to a fully bleached kraft pulp sheet) of 24-h yellowed TMPs: (a) borohydride bleached, (b) diimide-reduced, and (c) is (b-a). Small differences in their spectra are shown in (c).

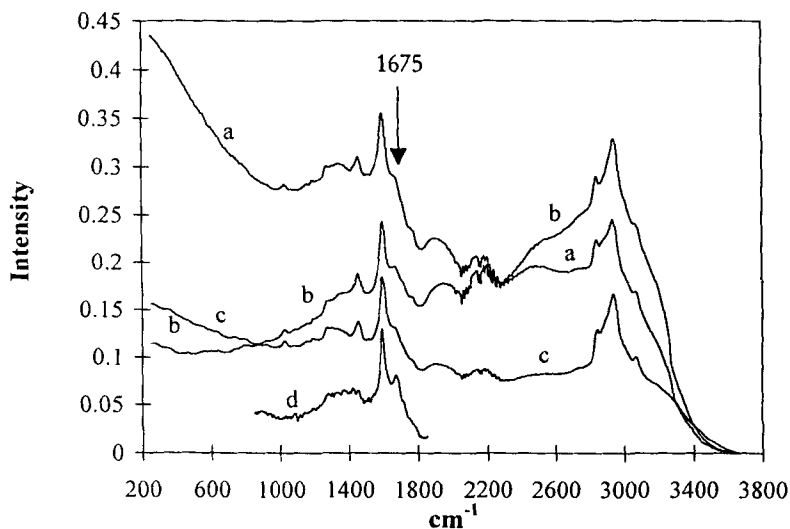


FIGURE 11. FT Raman spectra of materials extracted from 24-h yellowed pulps: (a) unbleached, (b) borohydride bleached, (c) diimide-reduced, and (d) difference between spectra obtained before and after methanol extraction of a 24-h yellowed borohydride-bleached pulp sample. All spectra contain a shoulder at  $1675\text{ cm}^{-1}$  which is related to yellowing.

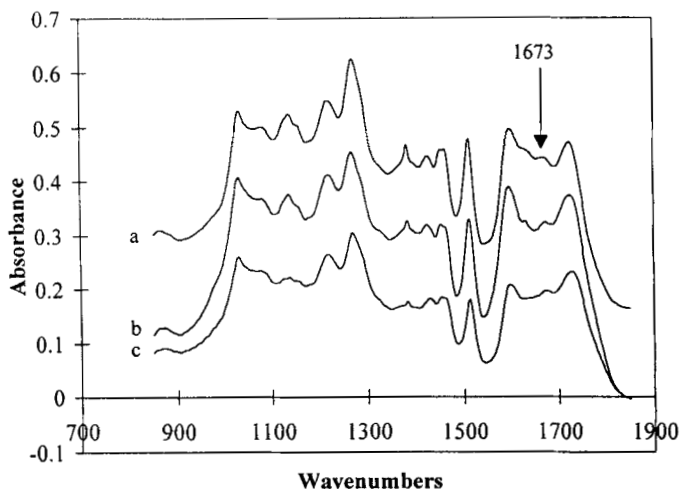


FIGURE 12. IR absorbance spectra showing a band at  $1673\text{ cm}^{-1}$  in the case of extracted materials obtained from 24-h yellowed pulps: (a) unbleached, (b) borohydride bleached, and (c) diimide-reduced. Remaining IR features are also very similar.

In contrast to the DRIFT spectra of yellowed TMPs, IR absorbance spectra of all three extracts showed an additional peak at  $1673\text{ cm}^{-1}$  (Fig. 12). This finding further supported Raman observations and suggested that the Raman and IR bands, respectively at  $1675$  and  $1673\text{ cm}^{-1}$ , were most likely due to the same group. (The small difference of  $2\text{ cm}^{-1}$  in the vibrational mode frequency between IR and Raman spectra is not significant.) The  $1727\text{ cm}^{-1}$  IR band, detected initially in the DRIFT spectra of yellowed pulps (Fig. 7), appeared as a strong band in the spectra of extracts as well (Fig. 12). Overall, the three spectra were similar, which provided further support to the suggestion that the extracts were quite similar.

UV-Vis absorption spectra of the extracts were almost identical (Figs. 13-14). In Fig. 14, spectra were obtained after diluting the extract-solutions so that the absorption in the 250-350 nm region could be better detected. As shown, a strong shoulder at 280 nm was present in all three spectra. Because this band is generally associated with the guaicyl moiety of lignin<sup>[28]</sup> and upon

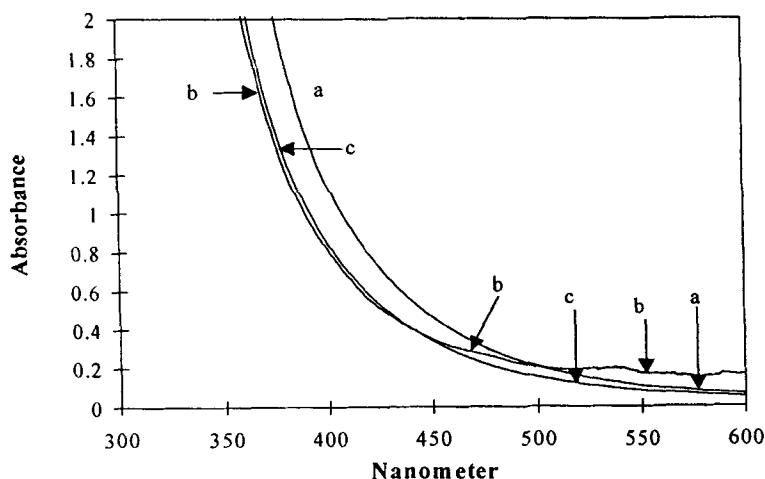


FIGURE 13. Similarity of the electronic spectra, in the visible region, of the methanol extracts of 24-h yellowed pulps: (a) unbleached, (b) borohydride bleached, and (c) diimide-reduced. Absorbance axis was expanded for comparison purposes. Spectra are not quantitative but are overlaid for comparison purposes.

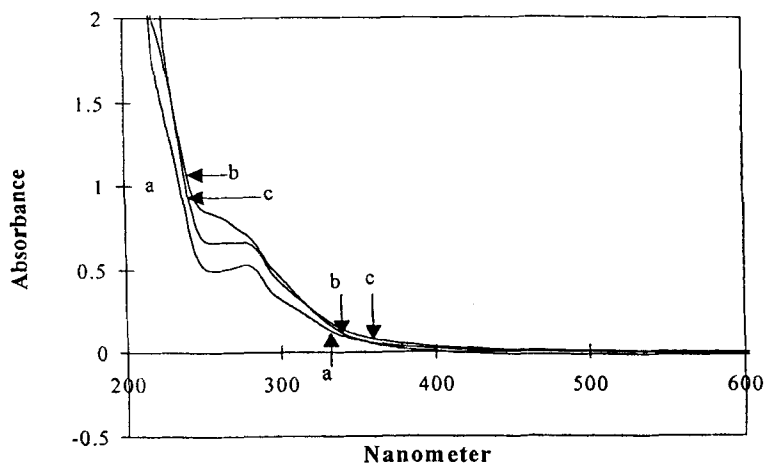


FIGURE 14. UV spectra of methanol extracts (diluted) of 24-h yellowed pulps: (a) unbleached, (b) borohydride bleached, and (c) diimide-reduced. The UV absorbance is mostly similar. Visible region is better shown in Fig. 13.

photoexposure only a small portion of lignin structure is modified<sup>[29]</sup>, it is likely that this shoulder is due to the unmodified part of lignin structure. On the other hand, featureless absorption in the 350-600 nm region is due to light-produced yellow chromophores. In both these regions, similarity among the spectra of extracts implied that not only the natures of the photomodified groups but that of the remaining lignin units were largely similar.

### ~1675 cm<sup>-1</sup> Band

Of the two distinct features, 1727 and ~1675 cm<sup>-1</sup>, that were found in the vibrational spectra of yellowed-pulps/extracts, the former has been assigned to carboxyl, carbonyl, and/or ester functional groups.<sup>[16]</sup> On the other hand, the 1675 cm<sup>-1</sup> band had not been detected previously, not even in the study that used conventional Raman spectroscopy.<sup>[8]</sup> The contribution at 1675 cm<sup>-1</sup> could be due to quinone type structures, because such groups have bands at or near 1675 cm<sup>-1</sup> (Figs. 15 and 16 where Raman and IR spectra of 2-methoxy p-quinone (a) and 3-methoxy o-quinone (b) are shown.) and absorb in the 400-600 nm region.<sup>[30]</sup> However, based on the IR and Raman data of 2-methoxy-p-quinone, if p-quinone groups are present then additional vibrational bands are expected to be detected around 1645 cm<sup>-1</sup> (both IR and Raman). No such bands were detected in the spectra of either pulps or their extracts. Similarly, o-quinones expected contributions at 1620 (IR) and 1560 cm<sup>-1</sup> (Raman) were not found. Although o-quinones have been detected<sup>[31]</sup> and p-quinones are thought to be present<sup>[32]</sup> in photoyellowed pulps, it is not clear why these additional intense bands associated with them were not detected.

### Proposed Scheme

Based on the results of this study, Scheme 1 proposes to show a better understanding of the photochemical behavior of various structural units in lignin. In this scheme, CALD and CALC structures are classified as nonyellowing structures. Although in solution both of these compounds produce yellow chromophores when exposed to light, in pulps either this does not happen or their concentration is such that their yellowing contribution is

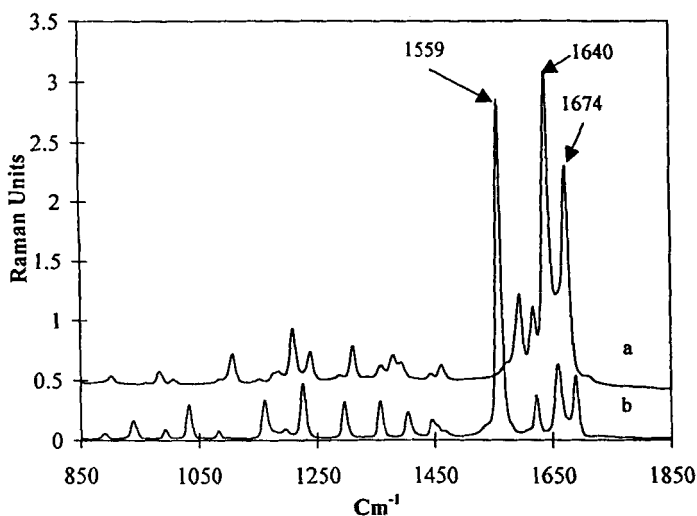


FIGURE 15. Raman spectra of quinones: (a) 2-methoxy p-quinone and (b) 3-methoxy o-quinone. Important band positions of the quinone groups are annotated.

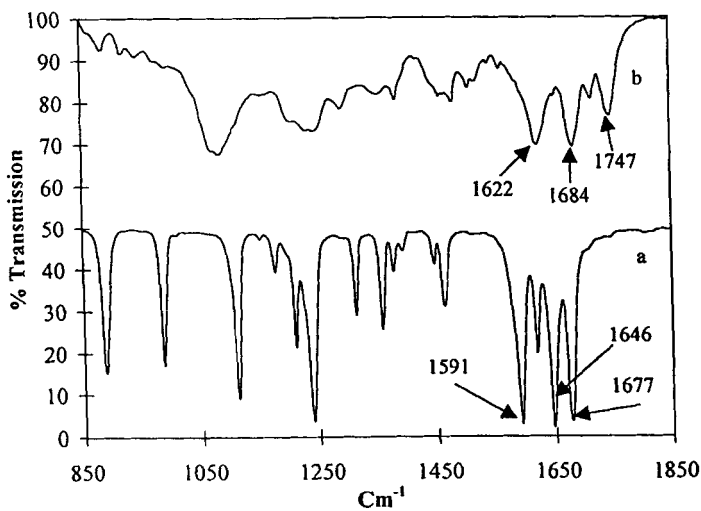
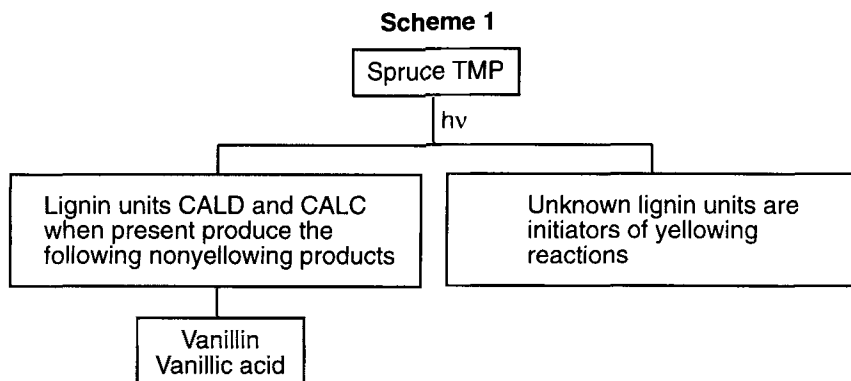


FIGURE 16. IR spectra of quinones: (a) 2-methoxy p-quinone and (b) 3-methoxy o-quinone. Spectrum (a) was divided by 2 to avoid its overlapping with spectrum (b).



negligible. Moreover, it is known that upon photoexposure, these structures yield both vanillin and vanillic acid among other products.<sup>[19,33,34]</sup> At present, Scheme 1 does not contain any structural units in lignin that can be held responsible for initiating yellowing reactions. Although it has been suggested that phenolic units in lignin<sup>[35]</sup> and  $\beta$ -O-4 models containing  $\alpha$ -carbonyl group<sup>[36,37]</sup> may be responsible for initiating yellowing, these are unlikely possibilities because without an  $\alpha$ -carbonyl, an ethylenic, or an additional aromatic OH group the model compounds do not absorb in the 300-400 nm region.<sup>[38-39]</sup> In this context, it's noteworthy that our as well as others research work has failed to find evidence for the existence of  $\alpha$ -carbonyl groups in wood pulps. Therefore, it remains undetermined what structures in lignin are responsible for initiating photoyellowing in pulps. Hopefully, as further information becomes available, such units will be identified.

## CONCLUSIONS

Results of this study indicate that no significant differences existed in the photoyellowing behaviors of unbleached, borohydride bleached, and diimide-reduced TMPs. Lignin structural units containing either  $\alpha$ -carbonyl or ring conjugated ethylenic groups were not the initiators of yellowing reactions. CALD and CALC groups when present in pulps were degraded upon



photoexposure. It is likely that the Raman bands at 1600 and 1675  $\text{cm}^{-1}$  and IR bands at 1673 and 1727  $\text{cm}^{-1}$  are due to products that are formed as a result of yellowing photoreactions.

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