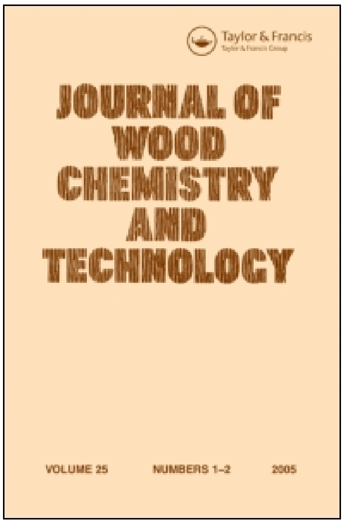

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BRIGHTNESS REVERSION OF MECHANICAL PULPS PART XIII: PHOTOINDUCED DEGRADATION OF LIGNIN ON CELLULOSE MATRIX

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ABSTRACT

An acidic dioxane extraction procedure was employed to isolate lignin from softwood bleached chemithermomechanical pulp (BCTMP). The isolated lignin was characterized spectroscopically and applied on cellulose test sheets. The treated cellulose test sheets were shown to exhibit photoyellowing properties comparable to those of BCTMP. The photolyzed lignin was re-isolated and characterized using spectroscopic techniques. UV-VIS and FT-IR studies implied elimination of the guaiacyl structure of lignin and the formation of carboxyl and/or unconjugated carbonyl groups during the photoyellowing process. The steady-state emission intensity of the excited states of guaiacyl structures decreased with increasing photolysis time, suggesting the formation of quinones during photolysis. NMR spectroscopic analysis of the photolyzed lignin indicated that the formyl, methoxyl, and uncondensed phenolics decreased in concentration as the irradiation proceeds. In contrast, condensed lignin and carboxylic acids increased as photolysis time was increased. These results are explained within the mechanism of lignin photodegradation.

INTRODUCTION

High-yield mechanical pulping is an attractive technology for addressing many of the challenges of modern papermaking operations. The production of high-yield pulps provides a valuable furnish having little adverse environmental impact, improved wood utilization practice, and simplified manufacturing techniques. Unfortunately, the well-known photoyellowing properties of mechanical pulp have hindered additional usage of this valuable furnish.[1]

The photoyellowing of mechanical pulp is generally attributed to the lignin component of the fiber. Although the exact mechanism of photoyellowing is not fully understood, substantial advancements have been made in this field of wood chemistry over the last two decades.[1-3] It is generally believed that several subunits of lignin, including stilbenes, conjugated phenolics, coniferyl aldehyde, α-carbonyl-β-O-aryl structures, and catechols, can absorb near ultraviolet light (λ: 300-400 nm) eventually resulting in the photoformation of chromophores in the visible spectrum.[2] *Para-* and *ortho*-quinones have been detected in irradiated pulp and are believed to contribute to the discoloration of mechanical pulp along with other color bodies. Inasmuch as these photoproducts are formed in small amounts and are difficult to isolate from irradiated mechanical pulp, a variety of model systems have been employed to study the photodegradation of lignin. This report examines the photodegradation properties of lignin extracted from BCTMP pulp and photolyzed with near-UV light.

EXPERIMENTAL

Materials

All reagents and solvents were commercially purchased and used as received. A commercial softwood BCTMP, impregnated and bleached with hydrogen peroxide, was employed for all studies in this report. Whatman No. 3 filter paper was used as cellulose test sheets. All water used in this investigation was initially deionized and then purified by passage through an Ultrapure Water System.

Instrumentation

All NMR spectra were recorded on a 400 MHz Bruker DMX spectrometer at 25°C. A Perkin-Elmer 320 UV-VIS spectrophotometer was used to measure the absorption spectra. FT-IR spectroscopy was carried out with a Nicolet 550 spectrometer at room temperature. Emission spectrum measurements were performed with a Perkin-Elmer LS-5B luminescent spectrometer (λ_{ex}= 280 nm). The photoaging experiments were performed using a Rayonet Photochemical Reactor (RPR-100) equipped with 16 black lamps (λ_{max}: 350 nm). A fan located at the bottom of the photochemical reactor was employed to maintain a photolysis temperature of <30°C. A Technidyne Brightimeter Micro S-5 was used to measure the TAPPI brightness of each test sheet according to TAPPI procedure T452 om-92.[5]

Procedures

Isolation of lignin from BCTMP.[6] Before isolation of the lignin, the softwood BCTMP was Soxhlet-extracted with acetone for 24 h. The dry pulp (150 g) was then refluxed in a 0.01 N HCl dioxane-water (3 L, 8.5:1.5) solution under argon for 1 h. The pulp was filtered and washed with fresh dioxane (200 mL × 3). The combined aliquots were neutralized with powdered $NaHCO_3$, filtered, and concentrated under reduced pressure at ~ 45°C. The concentrated solution was added to 700 mL of a 0.006 N aqueous HCl and the precipitated lignin was twice washed with acidified water (pH 2-3) and then freeze-dried. The lyophilized lignin was subsequently dried under high vacuum (~ 0.006 Torr) at 50°C for at least 24 h. The lignin yield was calculated to be 0.7% based on the mass of pulp initially used (% lignin yield = mass of lignin isolated/mass of lignin in pulp).

Filter papers treated with lignin. Cellulose test sheets (~ 150 g/m^2) were sprayed with a 9:1 dioxane-water solution (5 mL) containing BCTMP lignin

(0.0870 g). The treated handsheets were dried overnight in the absence of light prior to undergoing irradiation.

UV photolysis of the treated filter papers. Four lignin-impregnated cellulose test sheets were attached to a merry-go-round and photolyzed in a Rayonet RPR-100 photochemical reactor at ~30°C. Each side of the paper was photolyzed for half the photolysis period. At selected time periods, the irradiated test sheets were removed from the reactor and equilibrated to a constant temperature of 22°C (± 2.0°) and a relative humidity of 50% (± 2.0%) for 4 h prior to measuring TAPPI brightness values.[5]

Extraction of the photolyzed lignin. The photolyzed filter papers were extracted with 9:1 dioxane-water mixture (100 mL × 3). The combined extracts were filtered and concentrated under reduced pressure at 45°C. The photolyzed lignin was freeze-dried and then further dried with a high vacuum pump at 50°C for 24 h. This procedure typically yielded 83-99% lignin recovery (see Table 1).

Quantitative ^{1}H NMR spectroscopy. Functional group analysis of the residual lignin samples was accomplished, in general, following Lundquist's procedure for analyzing lignin (0.0150 g) in dry DMSO-d_6 (0.50 mL).[7] As a slight modification to this procedure, we employed sodium-3-trimethylsilyl propionate-2,2,3,3-d_4 (0.0480 g) as an internal standard to quantify functional groups.[8]

FT-IR spectroscopy. Lignin samples (0.1 mg) were mixed with KBr powder (0.20 g) and immediately analyzed. Typical spectral data were recorded with 128 scans/sample at room temperature. Background spectra were collected using a pure KBr pellet.

TABLE 1: Recovery of Lignin from Cellulose Test sheets.

Irradiation Period, min	Mass Recovery,[a] %
0.0	99
1.0	99
2.0	97
4.0	93
8.0	91
30.0	88
60.0	83

[a] Calculated by determining initial mass of lignin applied onto testsheet and mass of lignin recovered after *p*-dioxane extraction.

UV-VIS spectroscopy. Lignin samples (0.18 mg) were dissolved in 9:1 dioxane-water mixture (100 mL) and the spectra (λ: 200-800 nm) were recorded immediately thereafter at room temperature; absorption at 280 nm was also measured.

Emission spectroscopy. The BCTMP lignin solutions used in the UV-VIS absorption spectrum measurements were then used to determine the emission spectra by steady-state excitation at 280 nm.

RESULTS AND DISCUSSION

The fundamental photoyellowing chemistry of mechanical pulp has been frequently studied with lignin model compounds.[1,9] These investigations have established many of the key reactions believed to be involved in the photoyellowing process. To further broaden our knowledge of the mechanisms of brightness reversion, several researchers have begun to examine the photochemistry of isolated lignin. The most common source of lignin studied to date is milled wood lignin (MWL). Destiné *et al.*[10] have demonstrated that the photodegradation of MWL is influenced by the presence of oxygen and Argyrolpoulos *et al.*[11] have noted that changes in functional groups of MWL depend upon the length of the irradiation period.

Isolation of lignin from BCTMP. Gellerstedt *et al.*[12] employed a mildly acidic aqueous dioxane solution (pH 4) to liberate the end-groups of mechanical pulp lignin and thereafter examined their photochemistry. To facilitate the release of additional lignin, we examined the use of a more acidic aqueous dioxane solution (pH 2) to extract lignin from BCTMP.

The extraction of lignin from a softwood BCTMP was accomplished using a modification of the acidic dioxane extraction procedure that has been commonly employed to recover lignin from kraft pulps. One of our primary considerations for the lignin isolation procedure was to extract lignin from BCTMP without significantly introducing new chromophores absorbing in the visible range. A series of preliminary studies in our lab indicated that these concerns were best addressed by refluxing BCTMP pulp in a 0.01 N HCl 9:1 dioxane-water solution for 1 h under an argon atmosphere. Under these conditions the isolated lignin had minimal absorption in the visible light range.

Photoreversion properties of isolated lignin. To determine if the lignin isolated from the BCTMP fibers exhibited brightness reversion properties, the extracted lignin was redissolved in an aqueous dioxane solution and applied onto cellulose test sheets. Initially, we examined several levels of lignin applications (0.5–5% by weight). The treated test sheets were irradiated with a 300–400 nm light source and TAPPI brightness measurements were periodically taken. The photoreversion properties of these test sheets are summarized in Figure 1. These plots demonstrate that the lignin-impregnated sheets exhibit brightness reversion properties, and also suggest that the photoreversion properties of these sheets approach an asymptotic reversion limit near a 3% lignin application.

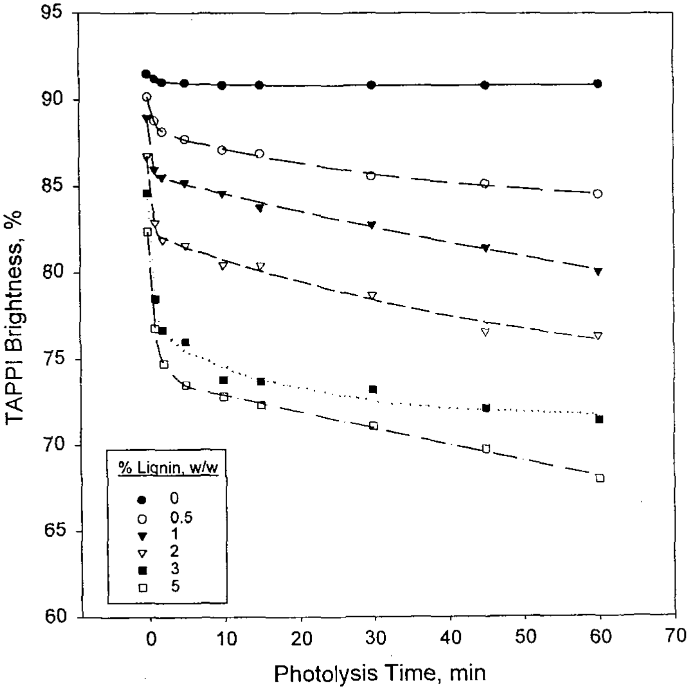

FIGURE 1. Brightness of the test sheets treated with several levels of applications of lignin (0.5–5% by weight) as a function of photolysis time.

The photoreversion properties of the 3% lignin-cellulose test sheets were then evaluated against BCTMP and acid-hydrolyzed BCTMP test sheets. In addition, the extracted lignin (3% by weight) was applied to sheets prepared from the acid-hydrolyzed BCTMP pulp. Figure 2 summarizes the changes in TAPPI brightness when these sheets were irradiated with a 300–400 nm light source for varying time periods. All test sheets exhibited comparable brightness reversion properties consisting typically of a fast reversion phase (*ca.* first 15 min of irradiation) and a succeeding slower phase. These results suggest that the acid-hydrolysis conditions used to isolate lignin for BCTMP do not significantly alter its photoreversion properties although certainly the acidic isolation conditions presumably modify the lignin isolated.

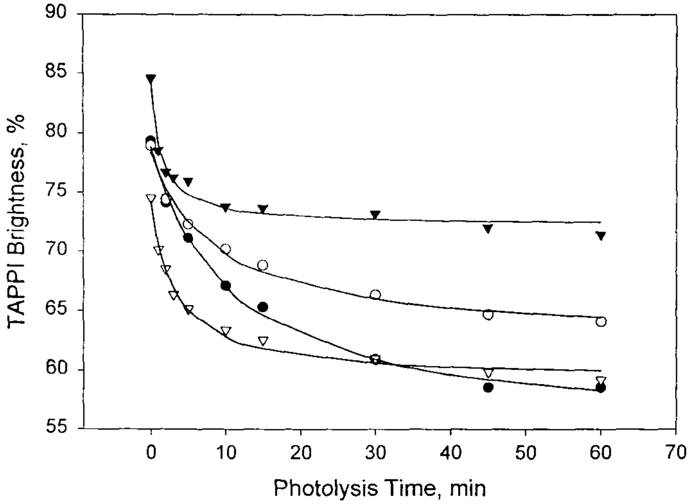

FIGURE 2. TAPPI Brightness as a function of photolysis time for testsheets prepared from: (●) BCTMP; (○) acid-hydrolyzed BCTMP (in an aqueous dioxane solution (pH 2.0) for 60 min under argon); (▼) cellulose test sheet treated with 3% BCTMP lignin; (▽) Acid-hydrolyzed BCTMP treated with 3% BCTMP lignin.

Characterization of post-photolyzed lignin. To study the photodegradation of BCTMP lignin, the irradiated test sheets were extracted with *p*-dioxane. Table 1 summarizes the mass recovery of lignin after irradiation. In general, the mass recovery of lignin was above 90% but did decrease as the photolysis time was increased, suggesting that lignin photoproducts might be chemically and/or physically incorporated into the cellulose matrix and/or volatile photoproducts (e.g., methanol) were formed and lost during concentration of the solvent extract.

^{1}H NMR analysis. NMR analysis of lignin is a facile means of analyzing many of the structural components of lignin. Lundquist[7] has shown that underivatized lignin can be quantitatively analyzed for a variety of functional groups by ^{1}H NMR. The ^{1}H NMR spectrum of the lignin extracted from BCTMP

is shown in Figure 3. This spectrum has structural features similar to the one corresponding to lignin isolated from softwood pulp by Lundquist[13] and Akerback *et al.*[14]

Applying this procedure to the lignins recovered from the irradiated BCTMP, the methoxyl, aromatic, condensed and non-condensed phenolic, formyl, and acidic group contents were readily determined. The results of these analyses are summarized in Figures 4 to 6.

Figure 4A shows that the uncondensed phenolic units in BCTMP lignin are consumed rapidly in the early stages of the photolysis experiment. Interestingly, the loss of uncondensed phenolics is accompanied by an increase in the overall amounts of condensed phenolics (see Figure 4B). It is well known that unstable phenolic radicals can easily undergo dimerization[15] and a comparable mechanism is most likely contributing to the formation of condensed phenolics observed in Figure 4B. The loss of aromatic protons (see Fig. 5A) as the lignin samples are irradiated is also consistent with a condensation mechanism, although other mechanism(s), such as, the photooxidative conversion of aromatic to non-aromatic structures, could also contribute to this phenomenon. The loss of methoxyl groups (see Fig. 5B) during photolysis has been previously noted by Leary[16] when mechanical pulp was irradiated; our results are consistent with his finding.

Accompanying the photoinitiated loss of phenolic groups is an increase in the carboxylic acid content of the photolyzed lignin as shown in Figure 6. The increase in carboxyl groups (see Fig. 6A) during photolysis is supportive of the overall oxidative mechanisms that have been suggested to account the photoyellowing of mechanical pulp. The loss of formyl groups (see Fig. 6B) during photolysis can be attributed, at least in part, to their direct oxidation to the corresponding carboxylic acid.

FT-IR spectroscopy. FT-IR analysis of the isolated lignin samples provided an alternate means of characterizing the changes in lignin during

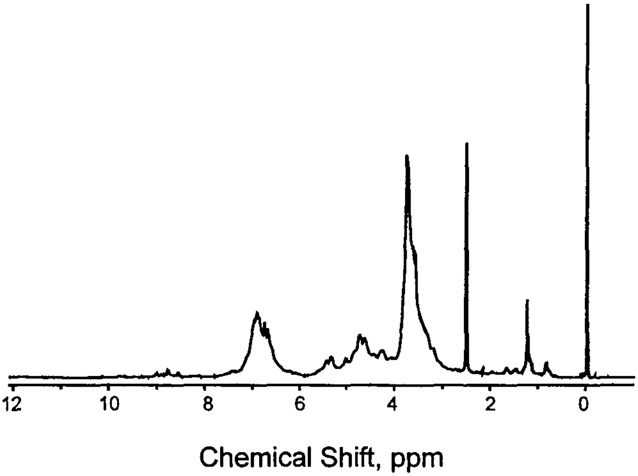

FIGURE 3. NMR spectrum of the unirradiated lignin (15 mg) isolated from softwood BCTMP in dry DMSO-d_6 (0.50 mL).

photolysis. As shown in Figure 7, several FT-IR signals of lignin are modified during irradiation.

The signal at 1726 cm^{-1} is very prominent in the irradiated lignin but in the IR spectra of non-photolyzed lignin this signal is substantially diminished. This IR band has been assigned to the carbonyl group in carboxyl and unconjugated carbonyl groups (conjugated carbonyl absorbs at 1715-1680 cm^{-1}).[17-18] Agarwal *et al.*[19] have noted similar trends when using FT-IR to characterize photoyellowed TMPs. Our results suggest that the lignin isolated from softwood BCTMP undergoes a rapid oxidation in the early phase of brightness reversion.

As reported by Schultz,[18] quantitative analysis of IR spectra can be made based on the signal at 1600 cm^{-1}. This signal, attributable to the aromatic C-H stretch, provides a facile means of correlating signals by measuring relative signal intensities. The ratios of absorbancy at 1726 cm^{-1} to that at 1600 cm^{-1} for the untreated and photolyzed lignins are summarized in Figure 8. Unfortunately,

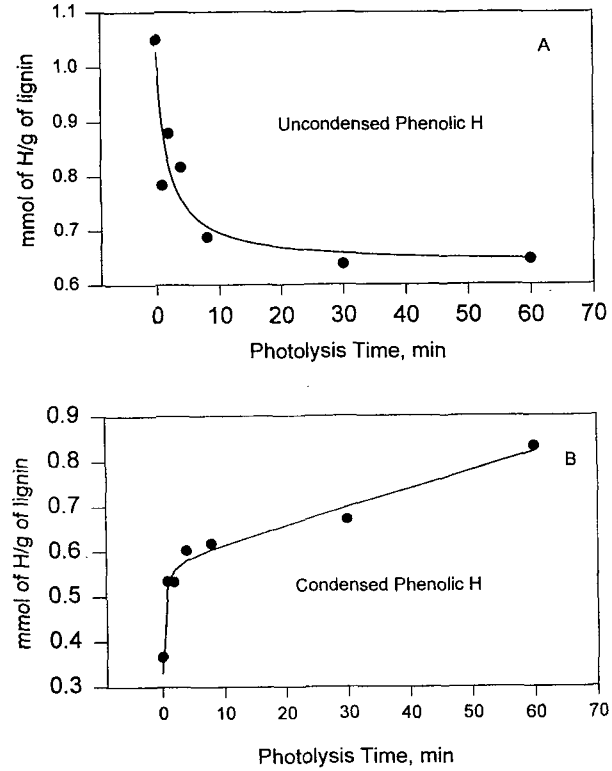

FIGURE 4. Changes in the phenolic proton contents of uncondensed (A) and condensed (B) lignin units as a function of photolysis time.

these results can be viewed as only semiquantitative since the NMR analysis suggests that a portion of the aromatic C-H groups in lignin decreases upon photolysis.

Nonetheless, the FT-IR analyses are consistent with the NMR spectroscopic results, suggesting that acidic carboxyl groups increase with increasing irradiation time. Both spectroscopic techniques suggest that there is a fast and slow phase in the photooxidation of lignin.

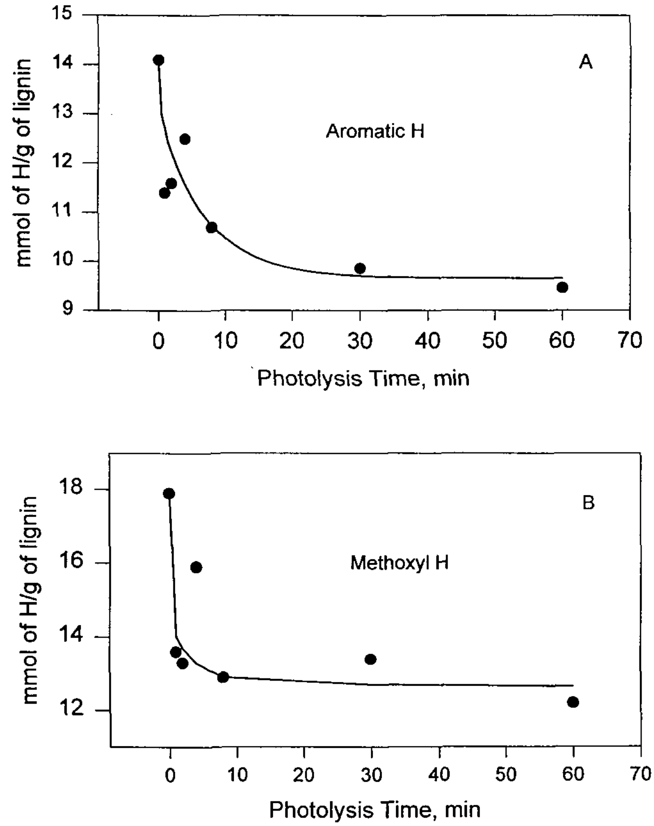

FIGURE 5. Changes in the proton contents of the aromatic (A) and methoxyl (B) groups in lignin as a function of photolysis time.

UV-VIS spectroscopy. Absorption spectra (Figure 9) of BCTMP lignin that was photolyzed for varying time periods were measured in a 9:1 dioxane-water mixture. These observed absorption bands are in good agreement with the results of studies reported by Lin *et al.*[20] for softwood MWL lignin. The change in the 280 nm absorption band during UV irradiation is given in Table 2. This absorption band decreases as the photolysis time is increased. There is no shift in absorption maximum, suggesting that the photoinduced products do not

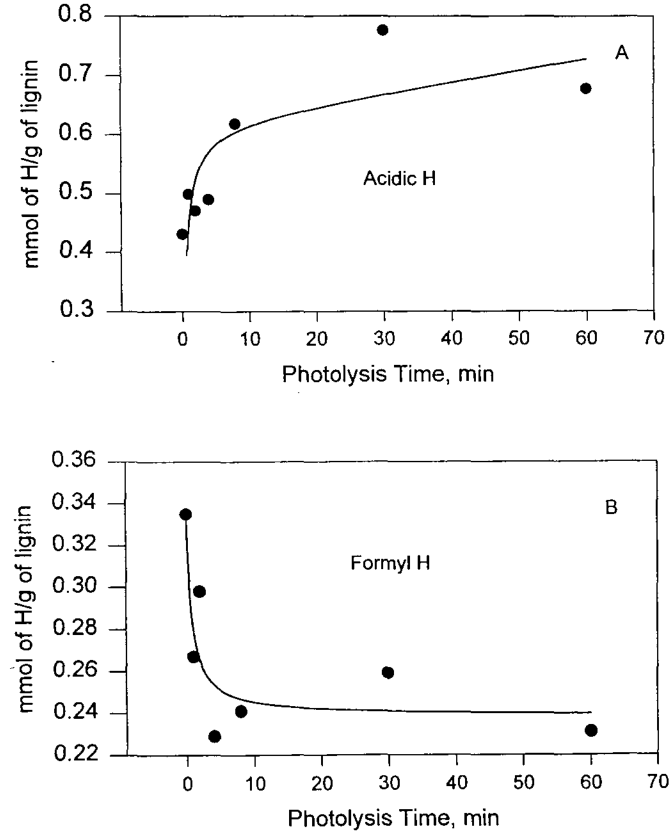

FIGURE 6. Changes in the proton contents of the acidic (A) and formyl (B) groups in lignin as a function of photolysis time.

contributed to this band. The decrease in absorbance at 280 nm may be related to the brightness loss, that is, the formation of chromophores. The maximum at 280 nm is attributed to the absorption of phenylpropane groups,[21-22] a basic structural unit of lignin. The elimination of the phenylpropane structure during photolysis is consistent with the formation of carboxylic acid and the loss of aromatic protons indicated by NMR spectroscopic part of this study.

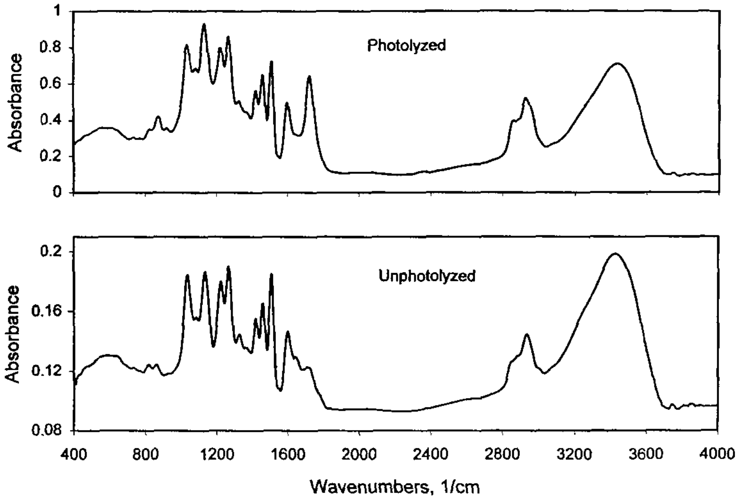

FIGURE 7. FT-IR spectra of unphotolyzed and photolyzed (60 min) lignin.

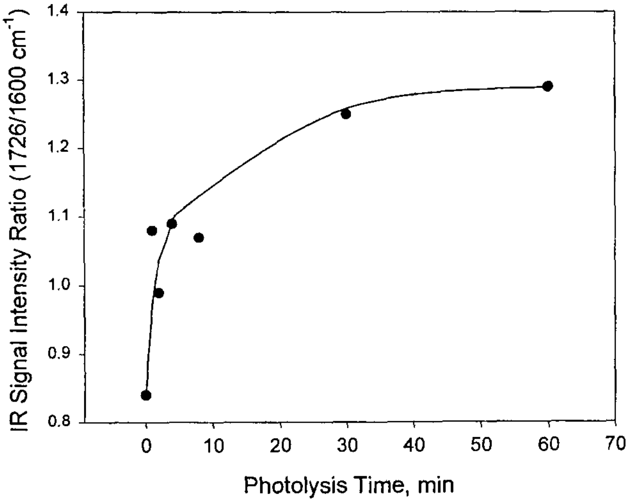

FIGURE 8. FT-IR relative intensity (1726/1600 cm^{-1}) as a function of photolysis time.

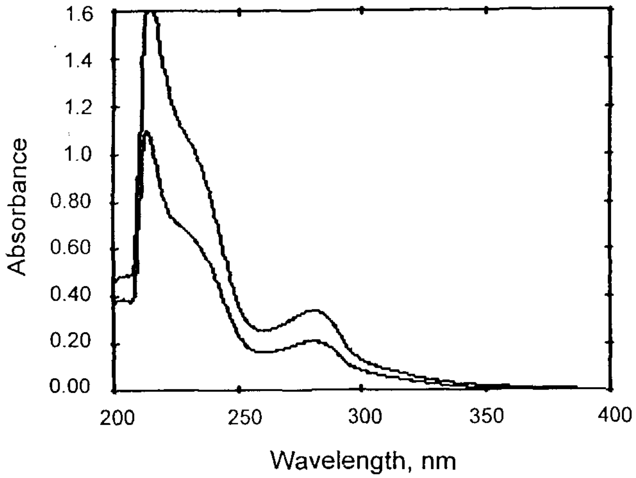

FIGURE 9. UV absorption spectra of unphotolyzed and photolyzed (60 min) lignin

TABLE 2: UV absorbance at 280 nm and Relative Emission (Em.) Intensity at 360 nm of the Extracted BCTMP Lignin as a Function of Photolysis Time.

Time, min	UV Abs.	Relative Em. Intensity
0.0	0.328	1.0
1.0	0.258	0.86
2.0	0.242	0.82
4.0	0.221	0.89
8.0	0.232	0.80
30.0	0.192	0.57
60.0	0.204	0.58

Emission spectroscopy. The solutions used in the UV-VIS absorption measurement were also employed in the measurement of emission spectra. The results are given in Table 2. The emission intensity at a maximum of 360 nm decreases as the photolysis time is increased. It is noted that photoproducts, such as quinone structures, have no emission at 280-nm excitation.[23] The absorbance at 280 nm also decreases as photolysis time is increased (see Table 2). If we assume that the decrease in absorbance at 280 nm is attributable to the degradation of lignin and that the photoproducts do not absorb at this wavelength, the conclusion can be made that the decrease in emission intensity is mainly attributable to the decrease in absorbance. This is because the fewer the number of photons absorbed by lignin, that is, smaller the number of excited molecules produced, the fewer the number of photons emitted.

CONCLUSIONS

Lignin isolated from softwood BCTMP under mild acidic hydrolysis conditions (pH 2) exhibits brightness reversion properties. As a result, the isolated lignin can be used as a model to study the brightness reversion of mechanical pulp. The increase in condensed lignin and carboxylic acids accompanying photolysis is attributed to the photooxidation of lignin, and is consistent with the observed decrease in the formyl, methoxyl, and uncondensed phenolic groups in lignin. The changes in functional groups during UV irradiation may play an important role in helping to establish the mechanism of brightness reversion of mechanical pulps.

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