

Investigation of the photo-oxidative chemistry of acetylated softwood lignin

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Received 22 August 2003; received in revised form 21 November 2003; accepted 26 November 2003

Abstract

Lignin was isolated from a spruce bleached chemithermomechanical pulp (BCTMP) with a mild acid hydrolysis and acetylated. Nonacetylated and acetylated lignins were impregnated onto cellulosic testsheets and photolyzed by two different light sources. Optical reflective studies indicated that the irradiated lignin underwent a two-phase photodiscoloration process with the acetylated lignin exhibiting reduced color formation. To examine the chemical processes initiated by irradiation, the photolyzed nonacetylated and acetylated lignins were extracted from the cellulosic testsheets and analyzed by using nuclear magnetic resonance (NMR). The results indicated that the photobehavior of the acetylated lignin exhibited substantially decreased reactivity during the light irradiation. The extent of lignin acetylation prior to photolysis was shown to be a very important parameter in controlling the overall photoreactivity of the acetylated materials. Aliphatic hydroxyl groups in lignin were observed to extensively degrade during photolysis, whereas the amounts of C5 condensed phenolics, guaiacyl phenolics, acids, and *p*-hydroxyphenyl increased.

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Keywords: Photoyellowing; Mechanical pulp; Lignin; Acetylation; Guaiacyl phenolics

1. Introduction

The need to develop environmental compatible industrial processes based on renewable resources is an important societal goal. The conversion of wood into pulp fibers using mechanical energy is an example of an environmental green chemical process. Typically, mechanical pulping and bleaching provide pulp yields of greater than 90% by utilizing all three of the major wood polymers, i.e. cellulose, hemicellulose, and lignin. Increased usage of mechanical pulps is limited due to their well-known tendency to rapidly undergo photodiscoloration when exposed to near UV light sources such as office lighting or sunlight [1,2]. Research studies have now clearly demonstrated that the photoyellowing process is initiated by the absorption of 300–400 nm light by several lignin functionalities including phenacyl- α -O-aryl ethers, extended conjugated phenolic structures, diguaiacyl stilbenes, hydroquinones, and quinones [3–8]. The initial

photoabsorption process generates a series of reactive radical intermediates that result in the oxidation of lignin yielding chromophoric products including *ortho*- and *para*-quinone lignin derivatives [5,9–11].

A number of photostabilization treatments are currently being pursued to photostabilize mechanical pulp, and they can be broadly described as either additive or fiber modification technologies [12–16]. One of the most promising fiber modification methods of halting the photoyellowing process involves acetylation of mechanical pulp employing acetic anhydride and an acid catalyst [16–19]. Although the treatment acetylates pulp polysaccharides and lignin, the photostabilization effects are generally attributed to the acetylation of lignin. Model compound studies investigating the chemistry of acid catalyzed lignin acetylation indicate that phenolics are preferentially acetylated over aliphatic hydroxyl groups when employing structures such as 1-(4-hydroxy-3-methoxyphenyl)-2-(2-methoxyphenoxy)-1,3-propanediol [20]. These and other model compounds studies have suggested that the acetylation of free-phenolics in lignin (see Fig. 1) plays a key role in the overall photostabilization effect of acetylated mechanical pulp.

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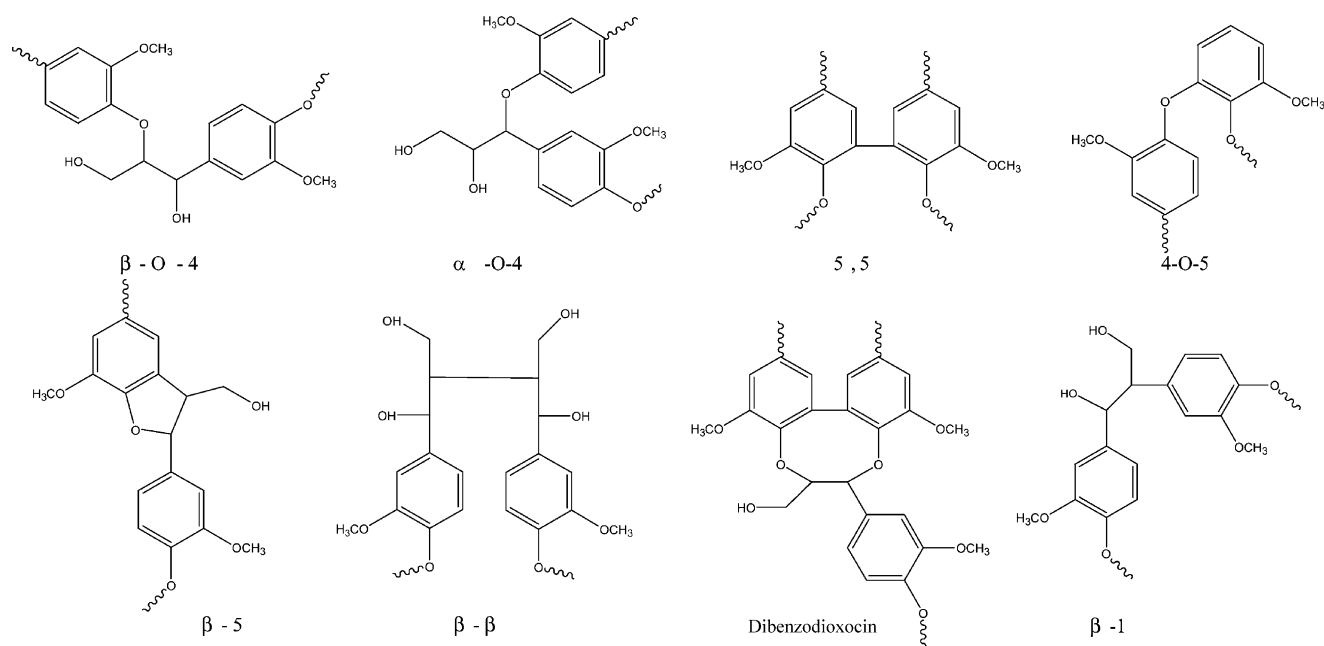


Fig. 1. Predominant softwood interunit lignin subunit linkages.

Model compounds studies have also demonstrated the *ortho*-quinone lignin-like structures were predisposed towards the Thiel–Winter type reaction when acetylated with acetic anhydride [21]. The conversion of *ortho*-quinoidal structures to their corresponding tri-acetate derivative is believed to be beneficial towards reducing the photoyellowing properties of mechanical pulps. To further investigate the fundamental photostabilization effects of acetylated lignin, Pu et al. have examined acid catalyzed acetylation of lignin in solution and quantified the Thiel–Winter reaction with lignin [22]. Heitner et al. have examined the photoreactivity of acetylated lignin in solution and concluded that lignin acetylation decreases the extent of photodegradation by hindering the cleavage of the β-O-aryl ether groups and this hinders the production of phenoxy radicals and lignin chromophores [23]. This paper further examines the photoyellowing chemistry of acetylated and nonacetylated mechanical pulp lignin absorbed on cellulosic testsheets employing differing light sources. Changes in lignin structure before and after photolysis were evaluated by NMR.

2. Materials and methods

All chemicals were commercially purchased and used as received, except *p*-dioxane which was purified by distillation over sodium borohydride before use. A commercially produced spruce bleached chemithermomechanical pulp (BCTMP), bleached to TAPPI brightness 79.1% via a two-stage hydrogen peroxide process was employed in this study. Testsheets (150 g/m²) were prepared from Whatman filter paper (Qualitative, No. 5) according to TAPPI procedure T 272 sp-97 [24].

2.1. Lignin isolation

Before isolation of lignin, the pulp was extensively washed, air-dried, and soxhlet extracted with acetone for 24 h. Air-dried pulp (150 g) was then refluxed in a 0.01N HCl dioxane–water (3:1, 8.5:1.5) solution under argon for 1 h [25]. The extracted pulp was filtered and washed with fresh *p*-dioxane (3 × 200 ml). The combined aliquots were neutralized with an aqueous saturated solution of sodium bicarbonate and then concentrated under reduced pressure at ~40 °C. The concentrated solution was added to 700 ml of a 0.006N aqueous HCl and the precipitated lignin was centrifuged, washed with acidic water (pH 2–3), and freeze dried. The lyophilized lignin was subsequently dried under high vacuum at 40 °C for 24 h.

2.2. Lignin acetylation

Lignin acetylation was carried out following literature method [22]. In brief, lignin (0.200 g) was dissolved in refluxing *p*-dioxane (200 ml) and acetic anhydride (40 ml) for selected time periods. After cooling, the acetylated lignin solution was concentrated and dried under reduced pressure. The crude acetylated lignin was dissolved in chloroform (3 ml) and the solution was added with stirring to diethyl ether. The precipitated acetate was centrifuged, collected, and dried under high vacuum for 24 h (~70% recovery).

2.3. Photo irradiation

Nonacetylated lignin (0.045 g) was dissolved in a 9:1 dioxane:water solution (10 ml), uniformly applied onto

filter paper testsheets and subsequently air-dried in the dark. Acetylated lignin samples were processed in the same manner except that chloroform was employed as the solvent. The treated testsheets were attached to a merry-go-round apparatus and photolyzed in a Rayonet Photochemical Reactor (Model RPR-100, The Southern New England Ultraviolet Company, Branford, CT, USA). The first series of photolysis experiments employed 16 RPR 5750 UV-Vis fluorescent lamps that emit light in UV-Vis range (λ : 350–700 nm) with $\lambda_{\text{max}} = 575$ nm. This light source is frequently employed as model source for office lighting since it is a comparatively close spectral match to many commercial lighting sources. A second series of photolysis experiments employed 16 RPR 3500 UV fluorescent lamps that emit Gaussian distribution of light from ~ 300 to 400 nm with $\lambda_{\text{max}} = 350$ nm [19]. The merry-go-round was rotated slowly for uniform irradiation. A fan located at the bottom of the photochemical reactor was employed to maintain a photolysis temperature of $\sim 30^\circ\text{C}$. Each side of the testsheet was irradiated for half the photolysis period. At selected time periods, the testsheets were removed from the reactor for brightness measurements. Prior to measuring optical properties, the testsheets were kept at constant temperature of 23°C and relative humidity of 50% in the darkness for 4 h.

TAPPI brightness measurements of the testsheets were determined as a function of photolysis period with a Brigh-timeter Micro S-5 reflectometer (Technidyne Corporation, New Albany, Indiana, USA) according to standard TAPPI Test method T 452 om-98. This procedure basically determines the percentage of light reflected from a light source with $\lambda_{\text{max}} = 475$ nm. All reported brightness values for the untreated testsheets represent an average of eight separate measurements and have a standard derivation of ± 0.6 . The degree of color reversion was expressed as the postcolor (PC) number following standard literature methods employing TAPPI brightness measurements [19]. The PC number was calculated according to the following equations:

$$\text{PC} = \left(\left(\frac{k}{s} \right)_{\text{after}} - \left(\frac{k}{s} \right)_{\text{before}} \right) \times 100 \quad (1)$$

$$\frac{k}{s} = \frac{(1 - R_\infty)^2}{2R_\infty} \quad (2)$$

where k and s refer to the experimentally determined absorption and scattering coefficients of the testsheets, respectively, and R_∞ the TAPPI brightness as a fractional value. The relationship between TAPPI brightness and chromophore concentration is nonlinear, whereas PC values respond linearly to chromophore concentration in the testsheets. The larger the PC value the greater the number of chromophore bodies in the testsheet.

2.4. Extraction of the photolyzed lignin

The photolyzed nonacetylated lignin testsheets were initially extracted with 9:1 dioxane:water solution (3×60 ml),

followed by extraction with DMF (3×60 ml). The extracts were concentrated under reduced pressure and then added dropwise with stirring into anhydrous diethyl ether (150 ml). The lignin precipitate was centrifuged, the liquid phase was decanted and the concentrated lignin precipitate was dried under reduced pressure. The photolyzed acetylated lignin testsheets were processed in an analogous manner except that CHCl_3 was employed for the first extraction. Typically, this procedure provided greater than 73% recovery of irradiated lignin.

2.5. ^{31}P NMR spectroscopy

The ^{31}P NMR spectra were recorded on a 400 MHz Bruker Advance/DMX NMR spectrometer [26,27]. The samples were dissolved in a solvent of pyridine/ CDCl_3 (1.6/1, v/v) and phosphorylated with 2-chloro-4,4,5,5-tetra-methyl-1,3,2-dioxaphospholane. The spectra were recorded with an inverse gated pulse sequence, 25 s pulse delay, 250 acquisitions, and 4 Hz line broadening at room temperature. NMR spectral acquisition and analysis were controlled by Bruker's XWINNMR 2.1 software running on a Silicon Graphics Indigo (SGI) server using the Irix 7.0 operating system.

3. Results and discussion

3.1. Acetylation of lignins

Previous studies have shown that the extent of acetylation can be controlled by varying the reaction time [20,23]. Heitner et al. have found that acetylation of milled wood lignin with acetic anhydride at 100°C for 300 min fully derivatized both phenolic and side-chain aliphatic hydroxyl groups, whereas acetylation of milled wood lignin with acetic anhydride at 25°C for 120 h completely derivatized only the primary hydroxyl groups, leaving phenolic and benzylic hydroxyl groups partially acetylated [23]. Quantitative ^{31}P NMR spectra were used to quantify different hydroxyl groups present in lignins and to determine the degree of lignin acetylation. Figs. 2 and 3 show the aliphatic and phenolic hydroxyl group contents at different acetylation times. The acetylated lignin has a lower contents of aliphatic and phenolic hydroxyl groups than nonderivatized lignin. Acetylation for 10 min derivatizes around 92.9% of guaiacyl phenolic hydroxyl group, 58.6% of condensed phenolic hydroxyl group and 55.7% of aliphatic hydroxyl groups. Acetylation for 150 min derivatizes around 94.8% of guaiacyl phenolic hydroxyl group, 72.4% of condensed phenolic hydroxyl group and 82.2% of aliphatic hydroxyl groups. A relatively low or high level of lignin acetylation was accomplished by reacting isolated lignin in acetic anhydride/dioxane for 10 or 150 min, respectively.

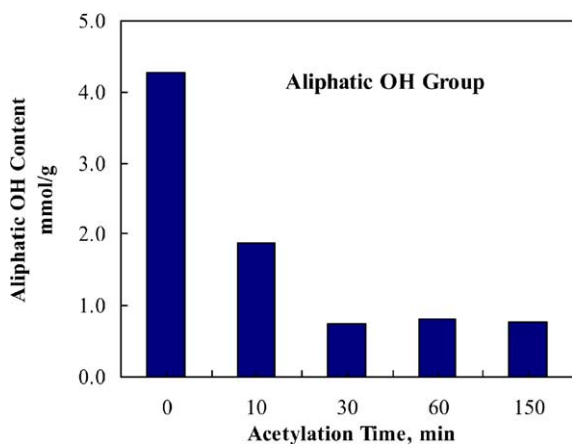


Fig. 2. Aliphatic OH group contents of lignins vs. acetylation time.

3.2. Photoreversion of nonacetylated and acetylated lignins

Nonacetylated and acetylated lignins (10 and 150 min acetylation time) were applied to filter paper testsheets and subjected to irradiation by two different light sources. The photodiscoloration properties of the irradiated testsheet were characterized by determining its brightness and PC values. Figs. 4 and 5 summarize the results of these measurements for acetylated and nonacetylated lignins when irradiated with RPR 5750 lamps (λ : 350–700 nm). The lignin sample that was extensively acetylated exhibits a significantly reduced tendency to undergo photoyellowing throughout the photolysis experiments. The results of irradiating lignin testsheets with RPR 3500 lamps (λ : 300–400 nm) are summarized in Figs. 6 and 7. These results indicate that photodiscoloration process is similar with the RPR 5750 lamps except that the intensity of the overall photoyellowing process significantly increases. The photoyellowing process consists of an initial rapid phase and a subsequent slower phase for both nonacetylated and acetylated lignins under near UV light source. This is consistent with the general behavior of

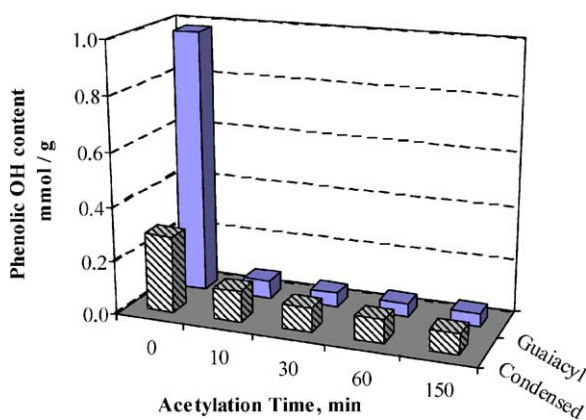


Fig. 3. Phenolic OH group contents of lignins vs. acetylation time.

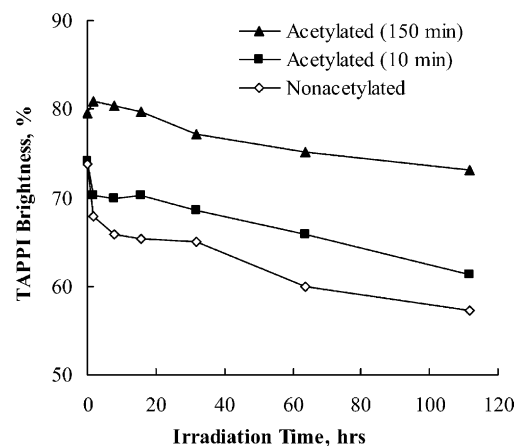


Fig. 4. Brightness of nonacetylated and acetylated lignin testsheets during irradiation with RPR 5750 UV-Vis lamps.

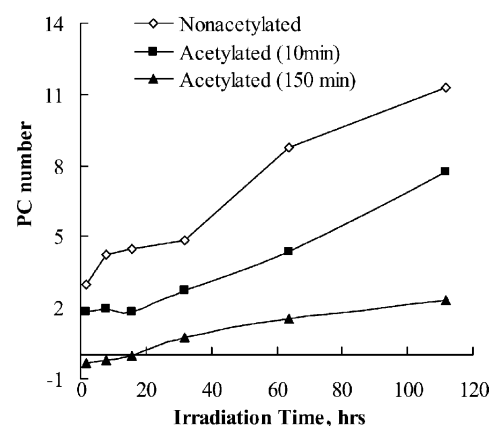


Fig. 5. PC number of nonacetylated and acetylated lignin testsheets during irradiation with RPR 5750 UV-Vis lamps.

the discoloration process of irradiated high yield pulp sheets that has been previously reported [25].

The nonacetylated lignin shows much lower brightness values and higher PC numbers than the acetylated lignin for

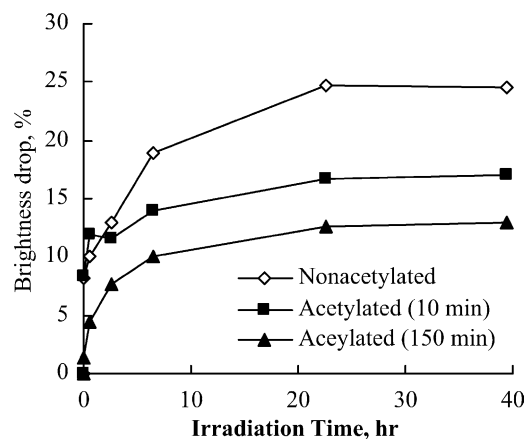


Fig. 6. Brightness drop for nonacetylated and acetylated lignin testsheets during irradiation with RPR 3500 UV lamps. Initial brightness: nonacetylated (74.5%), 10 min acetylated (76.9%), and 150 min acetylated (82.1%).

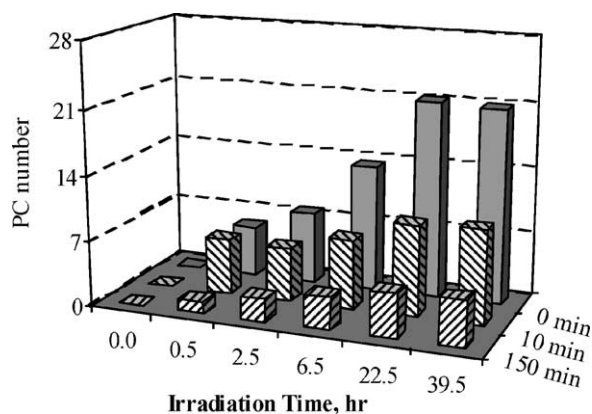


Fig. 7. PC number increase for nonacetylated and acetylated lignin test-sheets during irradiation with RPR 3500 UV lamps. (nonacetylated: 0 min).

both light sources, indicating that the acetylation treatment efficiently inhibits the photoyellowing of lignin. The lignin with an acetylation time of 150 min has a lower PC number than that with 10 min acetylation, suggesting that the greater the degree of lignin acetylation the more photostabilized the lignin becomes.

3.3. Structural characteristics

To explore the fundamental chemical parameters involved in the photostabilization of acetylated lignin, the samples irradiated with the RPR 3500 lamps (λ : 300–400 nm) were isolated, phosphorylated, and analyzed using quantitative ^{31}P NMR spectra. Fig. 8 summarizes the changes in aliphatic hydroxyl group content for the acetylated and nonacetylated lignin samples before and after photolysis. The differences in aliphatic hydroxyl groups at time zero were due to the extent of acetylation of aliphatic hydroxyl groups in lignin. Photolysis of nonacetylated lignin exhibits a decrease in aliphatic hydroxyl groups and after 40 h of irradiation 54% was removed.

The photoreactivity of nonacetylated lignin has been previously studied by Argyropoulos and Sun [28] and Li and Ragauskas [25]. They had observed the loss of aliphatic hydroxyl groups during irradiation and this effect was attributed to photoinitiated side-chain oxidation. The

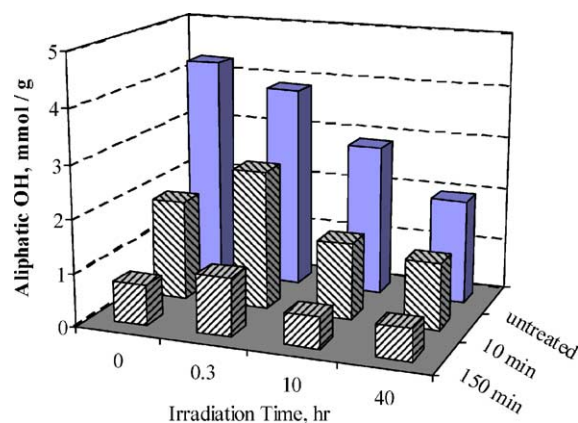


Fig. 8. Aliphatic hydroxyl content of nonacetylated and acetylated lignin before and after irradiation with RPR 3500 UV lamps.

acetylated lignin samples exhibits a slight increase in aliphatic hydroxyl after 0.3 h of irradiation followed by a gradual decrease in aliphatic hydroxyl groups. Prior studies by Heitner et al. had attributed an increase in aliphatic hydroxyl contents to be due to reactions between secondary lignin radicals and hydroxyl radicals [23]. The gradual loss of aliphatic hydroxyl groups for photolyzed acetylated lignin samples can be attributed, in part, to free radical ketyl oxidation of β -O-aryl ethers as summarized in Fig. 9 [29]. Around 56% of aliphatic hydroxyl groups were acetylated after 10 min of reaction and 82% after 150 min. The unacetylated aliphatic hydroxyl groups probably also result in the observed decrease of aliphatic hydroxyl groups during irradiation.

Photolysis of acetylated lignin is found to significantly increase the content of guaiacyl phenolic hydroxyl groups (Fig. 10). In contrast, nonacetylated lignin initially exhibits a reduction of guaiacyl phenolic hydroxyl groups after 0.3 h irradiation, followed by an increase of guaiacyl phenolic hydroxyl content with extended irradiation. The latter results are consistent with prior photolysis studies of lignin. For example, Li and Ragauskas have reported that BCTMP lignin had a lower content of uncondensed phenolic units when irradiated at a short time range of 0–60 min [25]. Argyropoulos and Sun have reported that milled wood lignin had a higher content of uncondensed phenolic structures

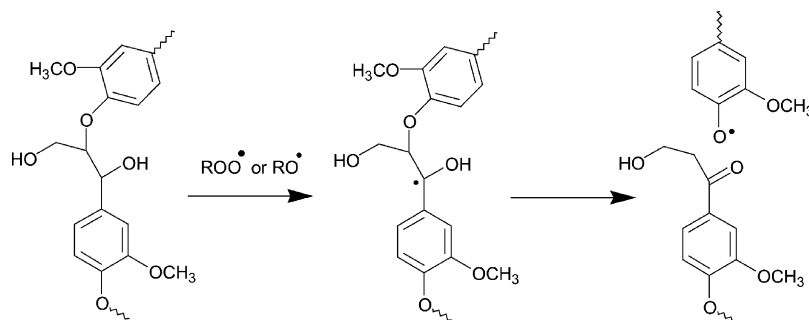


Fig. 9. Free radical ketyl oxidation of lignin.

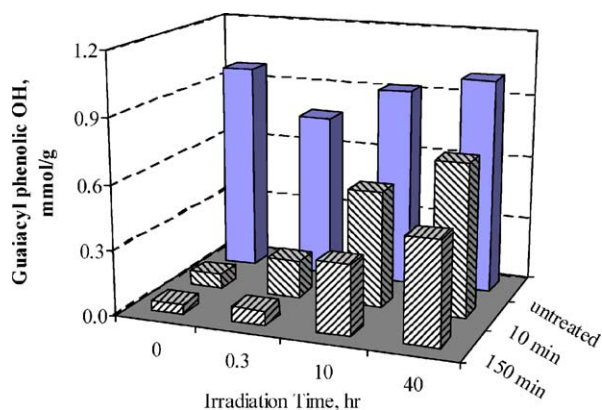


Fig. 10. Guaiacyl phenolic hydroxyl content of nonacetylated and acetylated lignin before and after irradiation with RPR 3500 UV lamps.

when irradiated at a longtime range of 0–24 h under an oxygen and nitrogen atmosphere [28].

The increase in noncondensed phenolics for acetylated lignin has not been previously reported and can be attributed to free phenoxy groups generated by free radical ketyl associated chemistry. The same chemical pathways undoubtedly contribute to the increased presence of *p*-hydroxyphenyl groups in photolyzed lignin as summarized in Fig. 11. The gradual increase in phenoxy content for the photolyzed acetylated lignins does illustrate limitations in employing acetylation of lignin as a photostabilization procedure, since the newly formed phenoxy groups represent new sites of potential oxidation to lignin.

Lignin phosphorylation and ^{31}P NMR analysis facilitates characterization not only of C5 noncondensed phenolics, but also C5 condensed phenolics. For BCTMP lignin, C5 condensed

phenolic structures refer to lignin phenolics structures such as 5,5, β -5, and 4-O-5 units (see Fig. 1). An increase of C5 condensed phenolic units was found for nonacetylated and acetylated lignins during irradiation as summarized in Fig. 12. The amounts of C5 condensed phenolics of acetylated lignin increased by >300% after 40 h irradiation. The

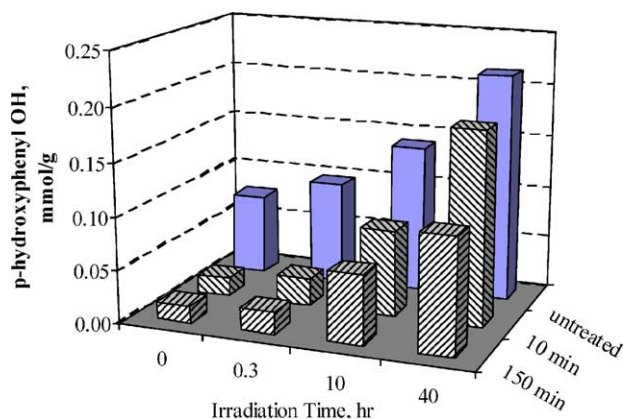


Fig. 11. *p*-Hydroxyphenyl content of nonacetylated and acetylated lignin before and after irradiation with RPR 3500 UV lamps.

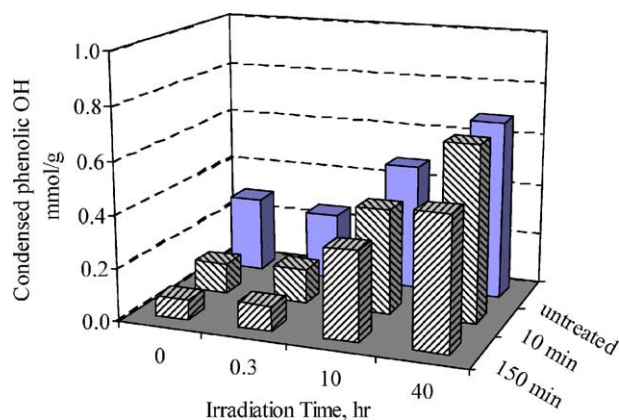


Fig. 12. Condensed phenolic hydroxyl content of nonacetylated and acetylated lignin before and after irradiation with RPR 3500 UV lamps.

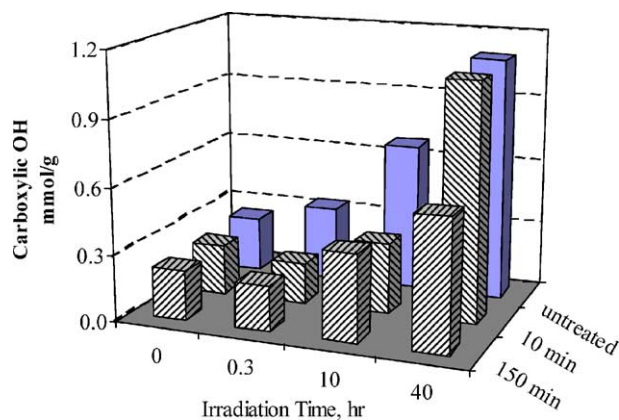


Fig. 13. Carboxylic acid content of nonacetylated and acetylated lignin before and after irradiation with RPR 3500 UV lamps.

increased formation of condensed phenolics during photolysis can be attributed to the formation of phenoxy radicals that undergo radical coupling reactions.

The data presented in Figs. 8 and 10–12 can be attributed to a series of radical oxidative chemical pathways initiated upon irradiation. Supporting this mechanism is the dramatic increase in carboxylate content for the photolyzed lignin samples as shown in Fig. 13. Indeed, from a carboxylate perspective the low level of lignin acetylation did not hinder acid formation after 40 h of irradiation. Only the extensively acetylated lignin sample exhibits a hindrance to oxidative formation of acid groups after prolonged photolysis. The reduced photoinitiated formation of carboxylate groups is reflective of the increased photostabilization of lignin after extensive acetylation.

4. Conclusion

This paper examines the photoyellowing properties of nonacetylated and acetylated mechanical pulp lignins under visible and/or near UV light sources. The behaviors

of the acetylated lignins exhibit substantially decreased photodiscoloration. Acetylation at a higher degree provides significantly greater reductions in the rate of light-induced chromophore formation than lignin acetylated at a lesser degree. Structural analysis studies indicate that aliphatic hydroxyl groups are extensively degraded during photolysis, whereas the amounts of C5 condensed phenolics, guaiacyl phenolics, acids, and *p*-hydroxyphenyl increase. The retarded photoyellowing of acetylated lignin may be attributed to a decreased photoreactivity of the derivatized lignin. Nonetheless, despite substantial esterification of the lignin it is clear that upon exposure to a near UV light a series of oxidative reactions are initiated that change the structure of acetylated lignin. Improvements in the photostability of acetylated lignin will need to address these chemical reactions.

Acknowledgements

The authors would like to thank the US Department of Agriculture, Improved Utilization of Wood Program (Grant # 99-35103-8603 and 98-35501-6911) and the member companies of the Institute of Paper Science and Technology for their support of this research.

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