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Photodegradation of sugar cane bagasse acidolysis lignins

Reinaldo Ruggiero[a,*], Antonio E.H. Machado[a], Christian Gardrat[b], William Hoareau[b], Stéphane Grelier[b], B. Siegmund[c], Alain Castellan[b,*]

[a] *Laboratorio de Fotoquimica e Quimica de Lignocelulosicos (LFQL), Grupo de Materiais Lignocelulosicos (GML), Universidade Federal de Uberlândia, P.O. Box 596, Uberlândia, Brazil*
[b] *Laboratoire de Chimie des Substances Végétales, Université Bordeaux 1, F-33405 Talence, France*
[c] *Station de la Bretagne BP 20, 97408 Saint-Denis Messageries Cedex 9 Réunion, France*

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Abstract

Acidolysis lignins of unbleached (SCB) and peroxide bleached (PB-SCB) sugar cane bagasse fibers were submitted to UV irradiation to approach photodegradation of materials made from these fibers. Similar degradation was observed by UV–vis absorption on dilute solution (0.04 g mL^{-1}) of lignins after irradiation at 254 nm (low pressure mercury lamp) or at wavelengths higher than 300 nm (medium pressure mercury lamp filtered by Pyrex glassware). Irradiation of PB-SCB and SCB lignins reveals that the bleaching process increases the sensibility of lignin to light, as revealed by fluorescence emission and UV–vis absorption. In other hand, efficient fragmentation of these two lignins was observed by size exclusion chromatography. ^{1}H and ^{31}P RMN spectroscopic analyses before and after irradiation were performed to observe the behavior of phenolic units in the lignin samples. They show an important decrease of the syringyl, guaiacyl and biphenyl phenolic elements, whereas *p*-hydroxyphenyl ones are less degraded. This point appears very important to promote the use of sugar cane bagasse fiber base materials when they have to be exposed to daylight.

Keywords: Lignin; Acidolysis lignin; Sugar cane bagasse; Photoreactivity; UV–vis absorption; Fluorescence emission; Size exclusion chromatography; ^{31}P NMR spectrometry

1. Introduction

Lignocellulosic materials are sensible to irradiation especially in the range from 300 to 400 nm and up to 500 nm for some wood species [1]. One visible observation of this phenomenon is photoyellowing of high yield pulp or clear woods [2–4]. It is generally accepted that photodegradation of lignocellulosics is mainly due to photooxidation of lignin [2]. Lignin polymer absorbs light in the longest wavelengths and collects the light from other polymers by energy transfer. The photodegradation mechanisms are not completely known but studies on models have highlighted some steps. Phenoxy radicals, which are key intermediates, are formed through different pathways: abstraction of phenol hydrogen by excited α-carbonyl [5] or singlet oxygen [6], direct oxidation of phenols absorbing near-UV light [7], photocleavage of phenacyl-aryl ethers [8] and breakdown of the β-*O*-4 bond in arylglycerol-β-aryl ethers [9]. Colored species like *o*-benzoquinones, formed by oxidation of phenoxy radicals [10] and the hydroquinone/benzoquinone redox systems [11–15] have been considered in the coloration process of lignocellulosics [11,12]. By contrast, phenolic structures such as coniferyl alcohol [16] and stilbene elements [17,18], which are conjugated phenols, were found to play a minor role in photoyellowing of lignin-rich pulps. Biphenyl structures were found to be important chromophores in photophysical

* Corresponding authors. Tel.: +55 34 3239 4143 (R. Ruggiero)/+33 5 4000 6280 (A. Castellan); fax: +55 34 3239 4208 (R. Ruggiero)/+33 5 4000 6439 (A. Castellan).
E-mail addresses: reinaldo@ufu.br (R. Ruggiero), a.castellan@lcsv.u-bordeaux1.fr (A. Castellan).

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and photochemical behavior of lignocellulosics. The increase of fluorescence in lignin and high yield pulps was attributed to the presence of reduced biphenyl units [19]. Dibenzodioxocin (DBDO) structures, which include a large part of the biphenyl structures of lignins [20–22], were recently shown to be photoreactive [23,24], due to the presence of both photoreactive α-*O*-4 and β-*O*-4 linkages.

Sugar cane bagasse is the solid residue left after juice extraction from sugar cane stalk. A large part of bagasse is usually burnt for energy supply. It can be also used to elaborate board materials; their photostability is questionable for outdoor uses. In our present interest in finding ways to transform sugar cane bagasse fibers into useful materials, such as board and composites [25,26], the photochemical behavior of these fibers to UV–vis irradiation and more specifically of its lignin part needs basic knowledge. The present work describes a study of photodegradation of lignin under UV light irradiation after extraction by soft acidolysis procedures from sugar cane bagasse, bleached and non-bleached with hydrogen peroxide. This study should bring new information on the photodegradation of these annual plant fibers, which display different lignin structures than wood fibers, due to their high content of *para*-hydroxyphenyl units. Mild acidolysis lignins, used in this study, are usually representative of native lignins found in plant cells.

2. Experimental

2.1. Fibers and acidolysis lignins

The sugar cane fibers (CIRAD, Reunion Island, France) were extracted (soxhlet) with cyclohexane/ethanol (1:1, v/v) for 48 h and then with water for 24 h. The fibers were dried in an air-circulated stove (60 °C) until constant weight. For the bleached fibers, the fibers (50 g) in a polypropylene bag were treated with a mixture of $Na_2SiO_3{\cdot}5H_2O$ (3.15 g), $MgSO_4{\cdot}7H_2O$ (0.25 g), DTPA (0.125 g) and NaOH (0.75 g) in 280 mL of water. Hydrogen peroxide (35%, 2.6 mL, 2% by reference to dry fiber) was added to the mixture and heated at 55 °C for 2 h. The fibers were filtered and washed with water. The bleaching procedure was repeated once. Then, the fibers were washed with dilute hydrochloric acid and water to bring the pH near 5 and finally dried in an air-circulated stove (60 °C) until constant weight. Before lignin isolation, the fibers were ground to powder (1 mm diameter) with a Forplex grinder.

The lignin isolation procedure was adapted from Gellerstedt et al. [27]. The ground dry fibers (100 g) were mixed with a solution (1 L) of dioxane and (0.1N) aqueous hydrochloric acid (8.5:1.5, v/v) and heated under nitrogen at 100 °C for 2 h. The solid was filtered and washed with a fresh dioxane–water solution (3 × 500 mL, 8.5:1.5) without hydrochloric acid. The combined filtrates are partially evaporated under vacuum (30 mbar). Complete elimination of dioxane is obtained after addition of water and evaporation under vacuum. These conditions maintain the pH solution above 1, avoiding excessive depolymerization of lignin. The precipitated lignin was centrifuged and dried under vacuum over phosphorous anhydride. The purity of bagasse lignin was estimated by Klason lignin determination corrected for soluble lignin contribution [28]. The purity of bleached and unbleached acidolysis lignins were found near 90% and their yields, calculated by reference to fiber lignin content, were estimated at about 10%.

2.2. Physical methods

A Minolta CR-310 colorimeter was used to measure color (CIE-LAB system) of peroxide bleached and unbleached sugar cane bagasse fibers (L^* = 84.1, a^* = 1.2, b^* = 20.7 and L^* = 74.3, a^* = 1.6, b^* = 20.4, respectively). UV–vis spectra were recorded on a Perkin-Elmer Lambda 18 spectrometer. Fluorescence spectra were measured with a Hitachi F4500 apparatus at room temperature (≈25 °C). The slits on the excitation and emission beams were fixed at 2.5 nm and the excitation wavelength at 285 nm. The emission spectra were corrected for instrumental response. The solutions were not degassed and the concentrations were set at 0.04 mg mL^{-1}.

Size exclusion chromatography (SEC) measurements were performed on a Spectra Physics P 100 pump equipped with three Tosohaas TSK gel columns (G 2000 HXL, G 3000 XXL and G 4000 HXL) and a UV detector Spectra Physics UV 150 set at 280 nm using tetrahydrofuran (HPLC grade) as eluent at a flow rate of 0.5 mL min^{-1}. The system was calibrated with polystyrene standards.

^{1}H NMR spectra were recorded on a Bruker DPX-300 spectrometer using 60 mg of acetylated lignin dissolved in $CDCl_3$ (0.75 mL) using 5 mm tubes. For each sample, 1024 scans were collected. Spectra were calibrated from the signal of residual chloroform (7.26 ppm). Quantitative ^{31}P NMR spectra were recorded on a Bruker DPX-200 spectrometer operating at 81 MHz. An inverse gated decoupling sequence was used with a pulse width of 90° and a relaxation delay between pulses of 5 s. About 1000 transients were acquired to ensure high signal/noise ratio.

2.3. UV irradiations

The photodegradation of bleached (PB-SCB) and unbleached (SCB) bagasse lignins in dilute solution (mixture of dioxane 0.45 vol.%, water 0.05 vol.% and ethanol 0.5 vol.%; lignin concentration 0.04 mg mL^{-1}), was monitored by UV–vis absorption spectroscopy or fluorescence emission, in a 10 mm quartz cell, at different times. The irradiations were performed using 254 nm emission, given by a low pressure mercury lamp (Vilbert-Lourmat T-8C for TLC detection), or light with wavelengths longer than 300 nm given by a setup, which includes two parallel medium pressure mercury lamps (400 W), a fan directed towards the sample to maintain temperature at ≈30 °C and a Pyrex container surrounding the sample cell, to eliminate wavelengths below 300 nm.

Solutions with higher lignin content (0.4 mg mL^{-1}, 200 mL, mixture of dioxane 0.45 vol.%, water 0.05 vol.% and ethanol 0.5 vol.%) were used for NMR and SEC characterization before and after irradiation.

2.4. Lignin derivatization

All the recovered lignin fractions were acetylated according to a procedure described elsewhere [29]. Acetylation gives soluble material in THF, the eluent used for size exclusion chromatography. Moreover, acetylation of lignins allows differentiation of aliphatic and aromatic hydroxyl groups by ^{1}H NMR spectroscopy. The lignins samples (80 mg), dissolved in pyridine (1 mL), were reacted with acetic anhydride (1 mL) under stirring at 60 °C for 25 h. Then, methanol (20 mL) was added and the mixture was refluxed for 3 h. The mixture was evaporated in presence of toluene (twice) and methanol. The lignin was dried over phosphorous anhydride under vacuum.

Prior to ^{31}P NMR analysis, the lignins were derivatized using a method published by Argyropoulos et al. [30–32]. A solvent mixture composed of pyridine and $CDCl_3$ (1.6:1, v/v), dried on molecular sieves, is used as stock solution. In addition, a solution of chromium(III) acetylacetonate in pyridine/$CDCl_3$ (5 mg mL^{-1}) was used as relaxation reagent stock solution. The lignins are phosphitylated with 2-chloro-4,4′,5,5′-tetramethyl-1,3,2-dioxaphospholane. Cholesterol (43 mg mL^{-1}) was used as internal standard. A 30 mg of lignin sample was dissolved in 0.5 mL of DMF in a 2 mL vial sealed with a Teflon-faced septum. Then, 0.3 mL of pyridine/$CDCl_3$ stock solution was added, followed by addition of 0.1 mL of internal standard and relaxation reagent solutions. The phosphitylation reagent (0.1 mL) was added to this mixture, and the flask, tightly closed, was shaken to ensure thorough mixing. After derivatization, the mixture was transferred to a 5 mm tube for ^{31}P NMR measurements.

3. Results and discussion

The lignin structures of nonwood plant fibers and wood fibers are different. Particularly, cinnamic acid derivatives are present in the former [33]. Therefore, it seems to be interesting to approach the sugar cane bagasse lignin photoreactivity. Treatment of lignocellulosics by alkaline hydrogen peroxide is known to degrade specifically enones of lignin, such as cinnamaldehydes and quinones [34,35]. This fiber bleaching treatment might be appropriate for some applications needing a clear visual aspect of the material. For all these reasons the photostability of acidolysis SCB and PB-SCB lignins were evaluated in dilute solutions (0.04 mg mL^{-1}) at two different irradiation wavelengths: λ = 254 nm (using a low pressure mercury lamp) and λ > 300 nm (using two medium pressure mercury lamps through Pyrex glassware). For structural analysis by SEC and NMR, the irradiations were performed in more concentrated solutions (0.4 mg mL^{-1}).

3.1. UV–vis absorption and fluorescence emission

The action of H_2O_2 in alkaline medium on sugar cane fibers induced a bleaching effect, less efficient than for wood fibers, due to the presence of cinnamic acid [33]. This is illustrated by comparison of color data of PB-SCB and SCB fibers (see Section 2) to peroxide bleached poplar alkaline peroxide mechanical pulp (L^* = 94.7, a^* = −1.0, b^* = 5.7) [36]. The luminance (L^*) of fibers increases drastically by action of hydrogen peroxide in alkaline medium giving the brighter aspect to the bleached fibers. The a^* color coordinate decreases slightly indicating degradation of some reddish chromophores such as *ortho*-quinones by action of hydrogen peroxide, whereas the b^* color coordinate remains constant, likely due to the presence of cinnamic acids (vide supra). UV–vis absorption spectrum of non-irradiated bleached sugar cane bagasse lignin (PB-SCB), comparatively to unbleached one (SCB) (Figs. 1 and 2), shows higher absorption at 314 nm; this observation might be assigned to ether-bonded ferulic acid [33,37]. The action of hydrogen peroxide on coniferaldehyde residue does not give ferulic acid (FA) structures [34]. So, higher proportion of FA in PB-SCB is likely due to the isolation procedure. It does not give the same fraction of plant cell, due to a more hydrophilic character of bleached lignin. SCB and PB-SCB lignins display similar acidic content measured by ^{31}P NMR, as we shall see later, indicating that ferulic acid component is not the only acidic group present in lignin fractions. Similar absorptions at wavelengths longer than 400 nm are observed for both lignins, which is in opposition to the visual aspect of color fibers. This fiber color represents a small proportion of the whole absorption and is mainly due to an important difference noted for luminance L^* instead of b^* coordinate.

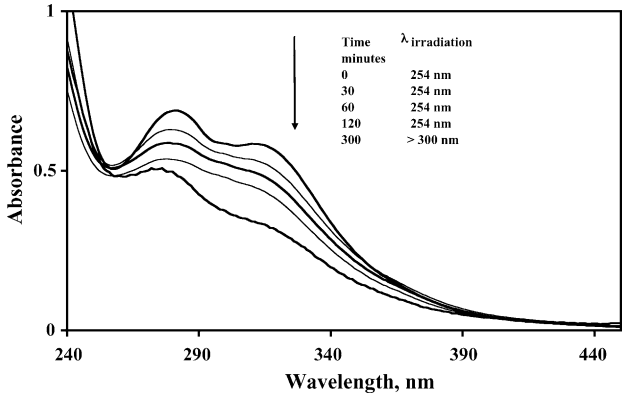

Fig. 1. Absorption spectra of SCB after irradiation with low medium pressure mercury lamp (λ ≈ 254 nm) and medium pressure mercury lamp (λ > 300 nm) in non-degassed solution (solvent mixture: dioxane 0.45 vol.%, ethanol 0.5 vol.% and water 0.05 vol.%; lignin concentration ≈0.04 mg L^{-1}; path length 1 cm; temperature ≈25 °C) for 0, 30, 60, 120 and 300 min.

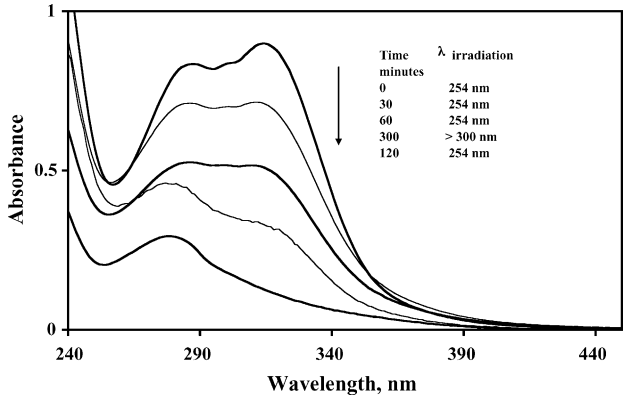

Fig. 2. Absorption spectra of PB-SCB after irradiation with low medium pressure mercury lamp ($\lambda \approx 254$ nm) and medium pressure mercury lamp ($\lambda > 300$ nm) in non-degassed solution (solvent mixture: dioxane 0.45 vol.%, ethanol 0.5 vol.% and water 0.05 vol.%; lignin concentration ≈ 0.04 mg L^{-1}; path length 1 cm; temperature $\approx 25\,^{\circ}C$) for 0, 30, 60, 120 and 300 min.

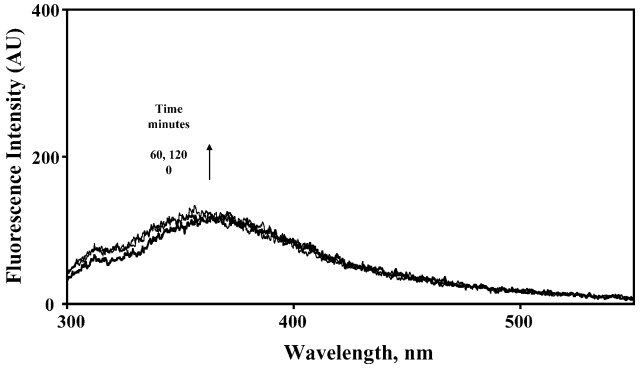

Fig. 3. Fluorescence spectra of SCB after irradiation with low medium pressure mercury lamp ($\lambda \approx 254$ nm) in non-degassed solution (solvent mixture: dioxane 0.45 vol.%, ethanol 0.5 vol.% and water 0.05 vol.%; lignin concentration ≈ 0.04 mg L^{-1}; path length 1 cm; temperature $\approx 25\,^{\circ}C$; λ_{exc} 285 nm; f_{exc} 2.5 nm; f_{em} 2.5 nm; temperature $\approx 25\,^{\circ}C$) for 0, 30, 60 and 120 min.

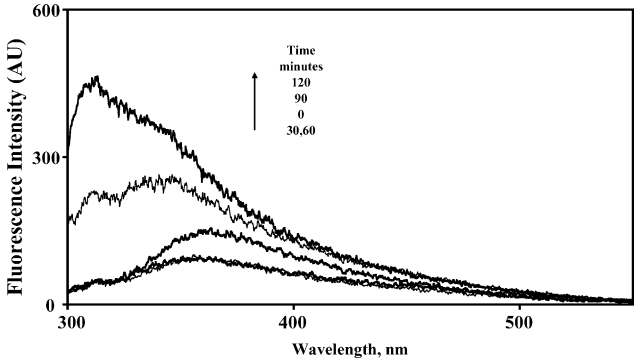

Fig. 4. Fluorescence spectra of PB-SCB after irradiation with low medium pressure mercury lamp ($\lambda \approx 254$ nm) in non-degassed solution (solvent mixture: dioxane 0.45 vol.%, ethanol 0.5 vol.% and water 0.05 vol.%; lignin concentration ≈ 0.04 mg L^{-1}; path length 1 cm; temperature $\approx 25\,^{\circ}C$; λ_{exc} 285 nm; f_{exc} 2.5 nm; f_{em} 2.5 nm; temperature $\approx 25\,^{\circ}C$) for 0, 30, 60, 90 and 120 min.

SCB and PB-SCB lignins in dilute solutions are degraded by UV irradiation (Figs. 1 and 2), the bleached sample being the most sensitive. The excitation at 254 nm gives similar results to irradiation with wavelengths filtered by Pyrex glassware, eliminating the short UV component ($\lambda < 300$ nm). These results indicate that there is no reactivity by upper excited states [38] of lignin. Light energy dissipation is operating by internal conversion to the lowest excited electronic state of the polymer before the photochemical degradation processes. Irradiation at 254 nm is comparatively more efficient for peroxide bleached lignin than for unbleached one. This is the reverse for Pyrex filtered light irradiations. For PB-SCB, the etherified ferulic acid structural elements, absorbing at 314 nm, appear to be photodegraded more rapidly, as indicated by the relative decrease of the band. Singlet oxygen (which can be formed by triplet state sensitization of lignin [39]) known to react with conjugated double bonds is probably involved in this process. The phenolic parts of the lignin polymer are also degraded, as will be seen later.

The fluorescence emission of irradiated solutions was recorded for SCB and PB-SCB (Figs. 3 and 4). SCB emission was quite insensitive to irradiation; only a slight hypsochromic shift from 370 to 360 nm is observed (Fig. 3). This indicates that fluorescence emission is due to non-reactive chromophores such as etherified biphenyls [24], or fluorescence-emitting species are quenched by carbonyl derivatives such as quinones or cinamaldehydes, hiding the photochemical effect [40]. Irradiation of PB-SCB leads to a slight decrease of fluorescence emission for short irradiation time and then to intensity increase and shift to short wavelengths (Fig. 4). For PB-SCB, the fluorescence quenching by carbonyl derivatives is less important, due to their lower content after action of hydrogen peroxide in alkaline medium. The fluorescence emission, in this case, reveals the photodegradation process: e.g. *ortho*-quinone formation in the beginning of irradiation, followed by photochemical breakdown of enone structural elements [41], allowing the fluorescence of aromatic monomer chromophores of lignin to emit at short wavelengths [42].

3.2. Molecular weight distributions of PB-SCB and SCB before and after irradiation

The effect of UV light ($\lambda > 300$ nm) on unbleached and peroxide bleached lignins was evaluated by size exclusion chromatography (SEC) (Table 1) on acetylated samples. The acetylation procedure is necessary to make the polymer soluble in tetrahydrofuran.

Table 1
Weight-average (M_w), number-average (M_n) molar weights (g/mol) and polydispersity (M_w/M_n) of SCB and PB-SCB lignins before and after irradiations ($\lambda > 300$ nm)

Sample	SCB	Irradiated SCB	PB-SCB	Irradiated PB-SCB
M_w	2820	330	1410	290
M_n	1530	130	780	140
M_w/M_n	1.84	2.54	1.81	2.07

Table 2
Quantification of several hydroxyl groups (mmol/g) in SCB and PB-SCB lignins before and after irradiation ($\lambda > 300$ nm) from ^{31}P NMR analysis of their phosphitylated derivatives (see Section 2)

Lignins	Aliphatic OH	S-OH[a]	G-OH[b]	H-OH[c]	5,5′-Condensed	Total phenol	Acids
SCB	2.35	0.06	0.32	0.48	0.02	0.88	0.06
Irradiated SCB	1.35	0.01	0.03	0.29	nd[d]	0.33	0.03
PB-SCB	2.53	0.04	0.30	0.34	0.03	0.71	0.06
Irradiated PB-SCB	0.88	0.01	0.02	0.11	nd[d]	0.14	nd[d]

[a] S: syringyl.
[b] G: guaiacyl.
[c] H: *p*-hydroxyphenyl.
[d] nd: non-detected.

The lignin isolated by mild acidolysis from peroxide-bleached sugar cane bagasse fibers is more fragmented than the unbleached one (50% less). The polydispersity does not significantly change, indicating that the bleaching with hydrogen peroxide leads to some homogeneous chain fragmentation. By contrast, irradiation induces a profound fragmentation of both lignins. The molecular mass distribution decreases are about of 90 and 80% for SCB and PB-SCB, respectively, with the greatest polydispersity for the first one. Destine et al. already observed similar fragmentation [43] on spruce MWL, irradiated in dioxane in presence of oxygen. The main fragmentation mechanism involved peroxy free radicals abstracting hydrogen atoms from benzylic carbons to produce ketyl radicals, which in turn undergo β-aryl ether cleavage to form phenols and aromatic ketones [9]; the phenols being degraded by light, as observed by ^{31}P NMR (see below). The important polymeric fragmentation achieved by light irradiation in the two lignin samples results in low mass molecular elements monomers or dimers in accordance with absorption and fluorescence measurements, especially for the bleached lignin.

3.3. NMR of lignins

The ^{1}H NMR spectra of sugar cane acidolysis lignins were already presented [26]; the spectrum of peroxide bleached lignin is very similar (spectrum not shown), indicating a close similarity of the lignin backbone. Integration of acetyl signals allows relative quantification of hydroxyl groups in SCB and PB-SCB before and after irradiation. The ratio phenolic/aliphatic hydroxyl groups gives 0.38 and 0.32 for SCB and PB-SCB, respectively, before irradiation; and 0.24 and 0.23 after irradiation. ^{31}P NMR of phosphitylated lignins has been developed by Argyropoulos et al., and was found to be a very powerful tool for lignin characterization [30,31]. Lignin samples were derivatized with 2-chloro-4,4′,5,5′-tetramethyl-1,3,2-dioxaphospholane. This allows good quantification of aliphatic hydroxyl groups, syringyl, guaiacyl, *p*-hydroxyphenyl, condensed phenol units, and carboxylic acids. Quantification of the different hydroxyl groups of SCB and PB-SCB before and after irradiation is presented in Table 2.

The bleaching process induces an increase of aliphatic hydroxy content which might be due to alkaline hydrolysis of ester linkages between hemicelluloses and lignin at carbons α and γ of the propane chain. By contrast, phenolic content is lower in the bleached lignin than in the unbleached one. This likely reflects more differences in lignin origin from cell wall during extraction process, than chemical oxidation of phenols by hydrogen peroxide. It is known that the hydroxyphenyl component (H) is the less susceptible to give electron transfer to oxygen during the oxidation process, compared to G and S structures. However, *p*-hydroxyphenyl units are more degraded than guaiacyl ones.

The ratios between phenol and aliphatic hydroxy groups measured by ^{31}P NMR for bagasse lignin: 0.37 (non irradiated SCB), 0.28 (non irradiated PB-SCB), 0.24 (irradiated SCB) and 0.16 (irradiated PB-SCB) are consistent with those obtained by ^{1}H NMR for the acetylated bagasse lignins. The values given by ^{31}P NMR are more reliable, due to better separations of the signals and the difficulty to completely acetylate hydroxy groups in lignins for ^{1}H NMR measurements. The ratio indicates a more important decrease of phenolic hydroxyl groups than aliphatic ones. For aliphatic hydroxy groups, the decrease is 42 and 53% for SCB and PB-SCB, respectively, compared to 62 and 80% for the phenolic ones.

The main photodegradation process of phenolic structural elements of lignin is demethoxylation of the guaiacyl or syringyl rings; however, simple phenols might be photooxidized into quinones and muconic acids [10]. Examination of Table 2 indicates that phenolic groups in bleached lignin are much prone to photodegradation than in unbleached lignin. The presence of some peroxy structures in the lignin polymer, due to action of hydrogen peroxide, might increase phenol sensitivity, phenoxy radicals being more degraded by carbon-centered peroxy radicals than by oxygen [44]. Among phenols, G elements are more photodegraded than S and H phenylpropane units, respectively. Syringyl elements give very stable phenoxy radicals [45] with a structure related to hindered phenols such as BHT [46]. Guaiacoxy radicals are prone to be transformed in *o*-quinones by demethoxylation, whereas oxidation of H-phenoxy radicals appears to be more difficult. The presence of such large quantities of H phenolic elements in sugar cane bagasse lignin should bring higher photostability to these lignocellulosic fibers and materials made of them, compared to hardwood and softwood fibers based material.

4. Conclusion

Sugar cane bagasse fibers display lignin and carbohydrate contents close to those of hardwood fibers. Molecular analysis of acidolysis lignin of peroxide bleached and unbleached bagasse fibers have shown that both lignins are degraded by UV light, but among the photoreactive phenols, hydroxyphenyl units are the most resistant. This point appears very important to promote the use of sugar cane bagasse fiber base materials, when they are exposed to light because their high content in *p*-hydroxyphenylpropane units compared to hardwood and softwood should induce less photosensitivity to sunlight. The unique properties of these materials may encourage more research into finding alternative uses for it. This could be of great benefit. Photochemical studies on sugar cane bagasse fibers will be presented in a near future.

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