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### Reactivity of Lignin and Lignin Models Towards UV-Assisted Peroxide

Yan-Ping Sun<sup>a</sup>; Adrian F. A. Wallis<sup>a</sup>; Kien Loi Nguyen<sup>b</sup>

<sup>a</sup> CSIRO Forestry and Forest Products, Victoria, Australia <sup>b</sup> Australian Pulp and Paper Institute, Monash University, Victoria, Australia

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**REACTIVITY OF LIGNIN AND LIGNIN MODELS TOWARDS  
UV-ASSISTED PEROXIDE**

Yan-Ping Sun and Adrian F. A. Wallis  
CSIRO Forestry and Forest Products, Private Bag 10,  
Clayton South MDC, Victoria 3169, Australia

Kien Loi Nguyen  
Australian Pulp and Paper Institute, Monash University,  
Clayton, Victoria 3168, Australia

**ABSTRACT**

The comparative reactivities of a series of guaiacyl and syringyl lignin model compounds and their methylated analogues towards alkaline peroxide and UV-alkaline peroxide were investigated. The overall reaction was followed by monitoring the reduction of the substrate as a function of time, and in every case, the reaction showed pseudo-first-order kinetics. The reaction rates of most lignin models having identical sidechains with alkaline peroxide and with UV-alkaline peroxide were in the order syringyl > guaiacyl > 3,4,5-trimethoxyphenyl > veratryl. Thus phenols react faster than their methyl ethers, and an extra *ortho* methoxyl group promotes the reaction. Lignin models possessing electron-donating sidechains had generally higher reaction rates than those with electron-withdrawing sidechains. The reaction rates of the series of benzoic acids were 2-4 times higher at pH 11 than at pH 5. UV-peroxide degradation of a eucalypt kraft lignin was faster than that of a pine kraft lignin, and degradation was 1.4-1.6 times faster at pH 11 than at pH 5. The data are consistent with the formation of higher amounts of reactive radicals under alkaline conditions, and aromatic rings with greater electronegativities promoting reactions with the radicals.

## INTRODUCTION

The combination of UV light and hydrogen peroxide, an advanced oxidation system, has recently gained prominence in the treatment of water<sup>1</sup>. The process is able to degrade a variety of recalcitrant organic compounds, which has led to the installation of many UV-peroxide plants for water treatment<sup>2</sup>. We have found that UV irradiation has beneficial effects on the peroxide bleaching of kraft pulps from eucalypt<sup>3-5</sup> and radiata pine<sup>6</sup> wood, and high brightness pulps were obtained with totally-chlorine-free (TCF) sequences. Other studies have shown that UV-peroxide is an efficient delignifying system for organosolv pulp from *Eucalyptus grandis* wood<sup>7,8</sup>. The UV-peroxide system has also been successfully applied to the oxidation of kraft black liquors<sup>9</sup>. The present study was undertaken to examine the chemistry of delignification with UV-peroxide.

Reaction of UV light with hydrogen peroxide gives hydroxyl radicals with a quantum yield of two hydroxyl radicals formed per quantum of radiation absorbed (eq 1)<sup>1</sup>. The rate of photolysis of aqueous hydrogen peroxide is pH dependent and increases when more alkaline conditions are used.



The hydroxyl radical is a very powerful oxidant, thus capable of oxidising most organic compounds, chiefly by hydrogen abstraction<sup>1</sup>. It can also react with hydrogen peroxide and its anion to form the perhydroxyl radical and superoxide radical anion, respectively (eq 2 and 3). Reaction (3) is much faster than reaction (2)<sup>10</sup>, which means that alkaline conditions favour the formation of peroxy radicals.



Lachenal *et al.*<sup>11</sup> proposed that the active species in the delignification of chemical pulps with hydrogen peroxide were radical decomposition products of peroxide, *i.e.* hydroxyl and perhydroxyl radicals. Hydroxyl radicals were found to attack aromatic rings of lignin through hydroxylation, demethoxylation, dealkoxylation and sidechain displacement reactions, and to oxidise lignin sidechains<sup>12</sup>.

Hydroxyl radicals can also generate phenoxyl radicals which undergo coupling reactions, although hydroxyl radicals are not able to cause opening of the lignin aromatic rings<sup>12</sup>. In contrast, the major reaction of superoxide radical anions in alkaline solution with lignin is the scission of aromatic rings with the formation of aliphatic acids, although in acidic media the major attack by perhydroxyl radicals is through demethoxylation reactions<sup>13</sup>. Both singlet oxygen, and superoxide anion radicals have been detected in UV-irradiated alkaline peroxide solutions used for bleaching of pulps<sup>14</sup>.

Extensive studies of the reactions of lignin model compounds with hydrogen peroxide under acidic conditions (pH 4.5) were carried out by Tatsumi and Terashima. They found that the reactivities of lignin models towards alkaline peroxide at pH 10 differed from those of UV-peroxide at pH 4.5<sup>15</sup>. When treated at the latter pH with UV-peroxide, veratric acid underwent hydroxylation reactions, and hydroxyl groups displaced ring-substituted hydroxyl, methoxyl and carboxyl groups, resulting in a large number of reaction products<sup>16-18</sup>. However, oxidation reactions leading to ring-opened products were minor pathways under acidic conditions. The rate of degradation of vanillic acid with UV-peroxide was found to be greater at pH 9 than at pH 6<sup>19</sup>. Irradiation with UV alone gave dimeric products formed by oxidative coupling, whereas in the presence of peroxide no dimeric compounds resulted<sup>19</sup>. UV-peroxide conditions were also able to cleave  $\beta$ -ether<sup>18</sup> and biphenyl<sup>20</sup> bonds in lignin model compounds.

The rate of degradation of lignin preparations with UV-peroxide measured by the reduction in UV absorption was at least 7 times faster at pH 10 than at pH 5<sup>21</sup>. Hydroxyl radicals were the main reactive species at pH 5, whereas under alkaline conditions active oxygen species, *e.g.* superoxide radical anion and singlet oxygen, were produced<sup>21</sup>. The degradation is promoted by phenolic and  $\alpha$ -carbonyl groups in lignin, and is retarded by carboxyl groups attached to aromatic rings<sup>21</sup>.

Our preliminary findings have shown that acetoguaiacone was degraded faster than (*E*)-ferulic acid with UV-peroxide, and that both compounds were degraded faster under alkaline conditions than acid conditions<sup>22</sup>. Furthermore, ESR signals from the compounds, indicative of phenoxyl radicals, were strongly dependent on the concentration of alkali and hydrogen peroxide<sup>23</sup>. In the present study, the work has been extended to include a more detailed comparison of the reactivities with UV-peroxide of a series of guaiacyl and syringyl lignin model compounds and their methylated analogues with varying sidechains. The results

from the model compound reactions were verified by reaction of pine and eucalypt kraft lignins with UV-peroxide.

## **RESULTS AND DISCUSSION**

A range of aqueous alkaline solutions of guaiacyl, syringyl, veratryl and 3,4,5-trimethoxyphenyl lignin model compounds (**1-4, a-h**) were reacted at pH 11 and 40°C with alkaline peroxide with UV irradiation at 254 nm, and with alkaline peroxide alone. A substrate:peroxide ratio of 1:10 was used, to ensure availability of peroxide throughout the reaction. Water was chosen as the solvent for the models, because organic solvents can interfere with the radical processes and thus complicate the interpretation of the results<sup>24</sup>. Reactions of the 3,4,5-trimethoxyphenyl compounds **4c** and **4e** were not carried out, because of their insolubility in aqueous solution. To test the effect of pH on the reaction, the benzoic acids **1f-4f** were also reacted at pH 5. Unlike most of the lignin models, the benzoic acids were soluble in the acidic reaction medium.

The reactions were monitored by measuring the loss of starting material by high performance liquid chromatography (HPLC) as a function of reaction time. In every case, the disappearance of the lignin model compounds initially followed pseudo-first-order kinetics, as shown for acetoguaiacone (**1g**), acetosyringone (**2g**), acetoveratrone (**3g**) and 3,4,5-trimethoxyacetophenone (**4g**) in Figure 1. In some cases, the slopes of the line decreased towards the end of the reactions, probably resulting from decreasing hydrogen peroxide concentrations caused by reactions with the substrates and decomposition of the peroxide. Similar phenomena were experienced by Sundstrom *et al.*<sup>25</sup> for the reaction of various aromatic compounds with UV-peroxide.

Pseudo-first-order rate constants were calculated for reaction of lignin models with alkaline peroxide, optionally with UV irradiation (Table 1). Inspection of the data shows that irradiation of the reactions with UV at 254 nm enhanced the reaction rates. The rates for reaction of benzoic acids **1f-4f** with UV-peroxide at pH 11 were 2-4 times higher than those measured at pH 5. This is consistent with the enhanced formation of reactive radicals with UV irradiation, particularly under alkaline rather than acid conditions.

For most substituted lignin models having identical sidechains, the reaction rates with UV-alkaline peroxide and with alkaline peroxide were in the order

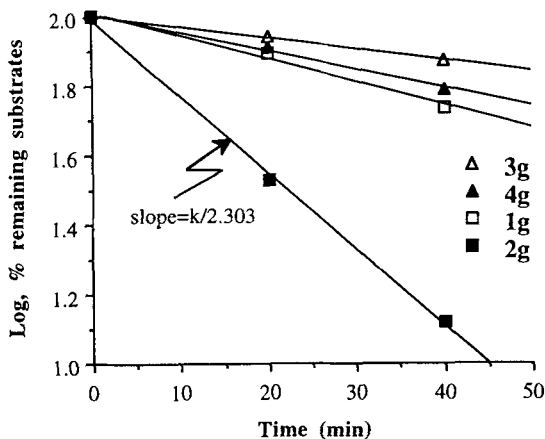


FIGURE 1. First-order rate plot of the reactions of acetoguaiacone (**1g**), acetosyringone (**2g**), acetoveratrone (**3g**) and 3,4,5-trimethoxyacetophenone (**4g**) with UV-alkaline peroxide at pH 11 and 40°C.

syringyl (**2**) > guaiacyl (**1**) > 3,4,5-trimethoxyphenyl (**4**) > veratryl (**3**) (Table 1). Notable exceptions were UV-peroxide reactions of the unsubstituted compounds, where syringol (**2a**) reacted slower and veratrol (**3a**) reacted faster than as expected from the general trend. Other veratryl compounds which did not conform to the trend included veratryl alcohol (**3d**), veratrylpropene (**3e**) and veratric acid (**3f**), all of which reacted comparatively rapidly with UV-peroxide. The reactions of lignin models with alkaline peroxide without UV irradiation conformed to the reactivity trend more than reactions which were irradiated with UV. With the exception of the aldehydes **3b** and **4b**, non-phenolic lignin models reacted slowly with alkaline peroxide without UV assistance.

The above results show that phenols react faster than their methyl ethers, and the series **2** and **4** with an additional methoxyl group reacted faster than **1** and **3** respectively. It is generally recognised that syringyl compounds are more reactive to alkaline hydrogen peroxide treatment<sup>26</sup>, oxygen oxidation<sup>27</sup> and alkaline degradation<sup>28</sup> than are guaiacyl compounds. This is understood as being a result of the greater electronegativity of the syringyl ring than the guaiacyl ring, caused by the additional methoxyl group in the syringyl models donating electrons to the

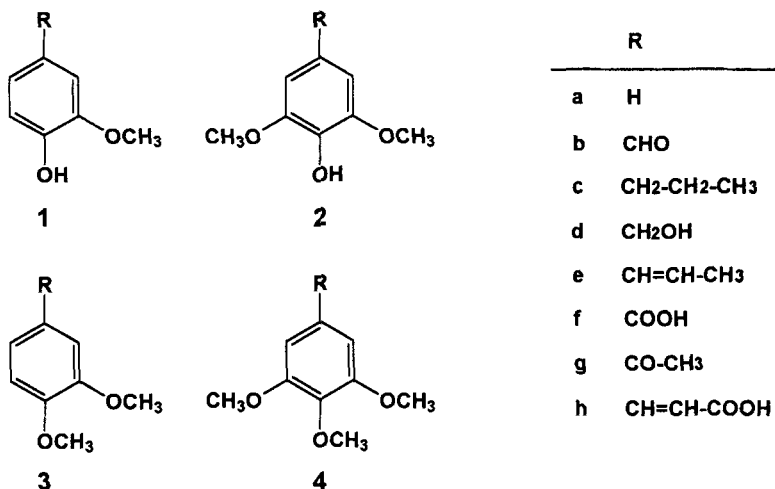
TABLE I

Observed pseudo-first -order rate constants for reaction of lignin models with UV-alkaline peroxide or alkaline peroxide\*

Substituent	Rate constants $10^3 k(\text{obs})$ ( $\text{min}^{-1}$ )			
	Guaiacyl (1)	Syringyl (2)	Veratryl (3)	Me-syringyl (4)
-H (a)	44.4 (1.54)	31.5 (14.6)	40.4 (0.77)	26.4 (3.07)
-CHO (b)	253 (177)	** (297)	48.1 (14.5)	195 (19.0)
-CH <sub>2</sub> -CH <sub>2</sub> -CH <sub>3</sub> (c)	44.8 (4.61)	57.3 (25.3)	9.19 (1.92)	***
-CH <sub>2</sub> OH (d)	33.7 (1.53)	47.8 (12.2)	23.8 (0.73)	21.8 (0.50)
-CH=CH-CH <sub>3</sub> (e)	30.6 (8.18)	74.8 (28.1)	38.2 (0.25)	***
-COOH (f)	19.6 (0.39)	27.2 (1.54)	22.1 (0.04)	7.90 (0.12)
-COOH (pH 5) (f)	6.52	7.29	8.29	3.45
-CO-CH <sub>3</sub> (g)	16.8 (4.22)	47.7 (9.21)	8.75 (0.50)	12.0 (1.15)
-CH=CH-COOH (h)	12.3 (1.15)	28.8 (8.83)	11.6 (0.19)	11.8 (0.04)

\* Rate constants for alkaline peroxide in brackets \*\* Rapid reaction

\*\*\* Not carried out due to incomplete solubility



aromatic ring, thus rendering the syringyl ring more susceptible to electrophilic reactions. The higher reactivity of phenols than their methyl ethers in alkaline solution is consistent with the stronger electron donating power of the phenoxyl anion compared with that of the methoxyl group. The reasons for the exceptions to the reactivity trend noted above are difficult to rationalise. Evidently, increased knowledge of the complex reactions taking place in the UV-peroxide system is required before a full understanding of the relative reactivities of lignin sub-structures is obtained.

The difference in reactivity of the compounds towards alkaline peroxide and UV-alkaline peroxide is also reflected in the structure of the sidechain. Within a series of compounds with identical aromatic nuclei, electron-donating substituents, *e.g.* propyl, generally gave higher reaction rates than the electron-withdrawing substituents *e.g.* carboxyl groups (Table 1), for the reason outlined above. The exceptions were compounds with aldehyde substituents (**b** group) and those with propenyl substituents (**e** group) which reacted more quickly than expected. Vanillin (**1b**) and syringaldehyde (**2b**) were consumed in the first few minutes, and gave purple-red and dark purple coloured solutions, respectively, due to rapid formation of quinonoid products from Dakin reactions<sup>29,30</sup>. This was



confirmed by gas chromatography-mass spectrometry (GC-MS) examination of the product mixture, which revealed that hydroquinones and aliphatic hydroxyacids arising from scission of the aromatic ring were present. Veratraldehyde (**3b**) and 3,4,5-trimethoxybenzaldehyde (**4b**) were oxidised to their corresponding acids **3f** and **4f** by peroxide (HPLC and GC-MS examination), and these were subsequently degraded further (Figure 2). The main reactions of the propenyl compounds **1e-3e** were those resulting from oxidation of the propenyl sidechains (GC-MS examination).

Tatsumi and Terashima<sup>15</sup> found that reaction of guaiacyl lignin model compounds with UV-peroxide at pH 5 was in the order vanillyl alcohol (**1d**) > vanillin (**1b**) > vanillic acid (**1f**) > acetoguaiacone (**1g**), whereas the order for veratryl compounds was veratric acid (**3f**) > veratryl alcohol (**3d**) > veratraldehyde (**3b**) > acetoveratrone (**3g**). This is similar to the order found for UV-peroxide reactions at pH 11 (Table 1), with the exception of the aldehydes **1b** and **3b** which reacted faster at pH 11, and veratryl alcohol, which reacted slightly faster than veratric acid at pH 11. The enhanced reactivity of vanillin is because the Dakin reaction proceeds only under alkaline conditions, and these conditions evidently favour the oxidation of veratraldehyde to veratric acid.

Syringic acid (**2f**) reacted slowly with alkaline hydrogen peroxide, and in accord with the principles outlined above, vanillic acid (**1f**), veratric acid (**3f**) and 3,4,5-trimethoxybenzoic acid (**4f**) reacted even more slowly (Table 1). This is contrary to the observations of Tatsumi and Terashima<sup>15</sup>, who found that syringic acid was degraded rapidly under alkaline peroxide conditions. In the presence of UV irradiation, all of these acids were consumed rapidly, in the order of syringic acid > veratric acid > vanillic acid > 3,4,5-trimethoxybenzoic acid (Table 1).

Reactions of pine and eucalypt kraft lignins with UV-peroxide were carried out both in aqueous solutions at pH 11 and in 40% aqueous methanol solutions at pH 5 and pH 11, and were monitored by UV spectroscopy (Figures 3 and 4). Aqueous methanol solutions were used for the pH comparison because the lignin samples were insoluble in water at pH 5. The UV absorbances of the lignin samples decreased with time of reaction with UV-peroxide, indicative of degradation of the lignin. However after reaction of an aqueous solution of the pine kraft lignin sample with UV-peroxide at pH 11 for 40 min, enhanced UV absorption at 280 nm resulted (Figure 3), and for the eucalypt kraft lignin at pH 5 in aqueous methanol solution, there was an initial enhancement of absorption at

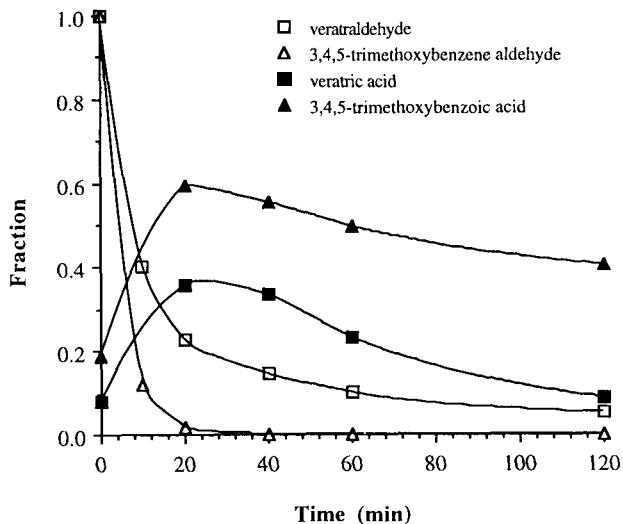


FIGURE 2. Formation of veratric acid (**3f**) and 3,4,5-trimethoxybenzoic acid (**4f**) from reaction of veratraldehyde (**3b**) and 3,4,5-trimethoxybenzaldehyde (**4b**), respectively, with UV-alkaline peroxide at pH 11 and 40°C.

250 nm. These changes probably occur through hydroxylation reactions by UV-peroxide.

The change in UV absorbance at 280 nm of the kraft lignins with reaction time with UV-peroxide is shown in Figure 5. In aqueous solution at pH 11, there was an initial increase in absorption after 40 min, followed by a steady decrease. Degradation of the eucalypt kraft lignin was more complete than that of the pine kraft lignin; 90% degradation was achieved for the eucalypt lignin after 160 min, and for the pine lignin after 240 min. In aqueous methanol solution, degradation of both lignin samples with UV-peroxide was faster at pH 11 than at pH 5 (Figure 5.), although the degradation was not as extensive as in aqueous solutions. The degradation of the lignins followed pseudo-first-order kinetics, and gave rate constants for the pine lignin at pH 5 and 11 of  $3.08$  and  $4.99 \times 10^{-3} \text{ min}^{-1}$ , respectively, while the corresponding rates for the eucalypt lignin were  $6.01$  and  $8.64 \times 10^{-3} \text{ min}^{-1}$ . Thus the rate of UV-peroxide degradation of the lignins was 1.4-1.6 times faster at pH 11 than at pH 5, whereas for rice hull lignin there was a

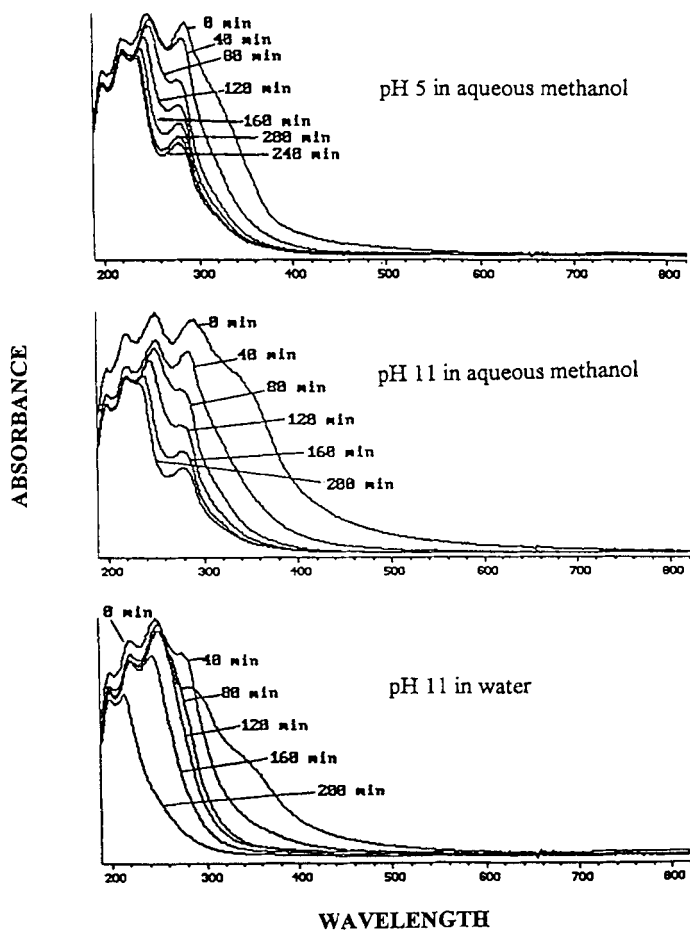


FIGURE 3. UV absorption spectra of pine kraft lignin treated with UV-peroxide at pH 11 (aqueous solution) and pH 5 and 11 (aqueous methanol solutions).

seven-fold increase<sup>21</sup>. The difference could be partly due to differences in the wavelength of UV radiation, and to differences in the lignin substrates. As the eucalypt lignin was degraded faster than the pine lignin, the eucalypt kraft pulps would be expected to be more responsive to UV-peroxide bleaching than would pine kraft pulps. The lignin results are consistent with those of the lignin model compounds, which showed that syringyl compounds and their methyl ethers

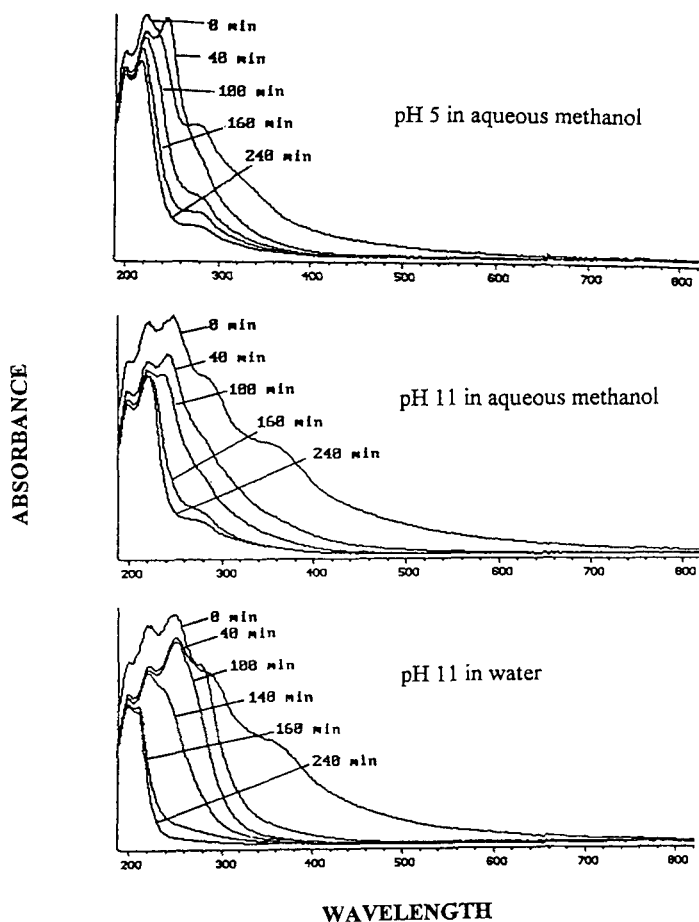


FIGURE 4. UV absorption spectra of eucalypt kraft lignin treated with UV-peroxide at pH 11 (aqueous solution) and pH 5 and 11 (aqueous methanol solutions).

(characteristic structures of hardwood lignins) were more reactive to UV-peroxide than guaiacyl and veratryl compounds, respectively.

#### Concluding remarks

The study has shown that the rate of peroxide oxidation of lignin model compounds is enhanced by UV irradiation at 254 nm, by the presence of electron

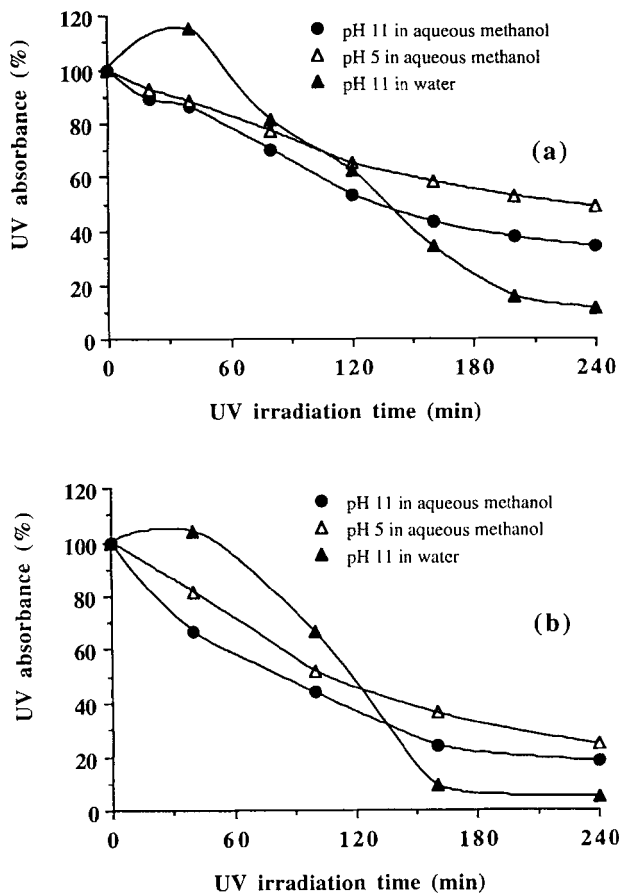


FIGURE 5. Change in UV absorbance at 280 nm of solutions of (a) pine kraft lignin and (b) eucalypt kraft lignin at pH 11 (aqueous solution) and pH 5 and 11 (aqu. methanol solutions) treated with UV-peroxide.

donating groups, and by reaction under alkaline rather than acidic conditions. Syringyl lignin models and their methyl ethers react faster with UV-peroxide than do guaiacyl and veratryl models, respectively, and hardwood lignin is more reactive to UV-peroxide than is softwood lignin.

## EXPERIMENTAL

### Chemicals

Unless otherwise stated, the lignin model compounds were obtained from commercial sources. Catalytic hydrogenation of eugenol, 4-allylsyringol and 4-allylveratrole gave compounds **1c**, **2c** and **3c**, respectively. Compound **2e** was prepared by the isomerisation of 4-allylsyringol with alkali<sup>31</sup>, and **3e** was obtained by methylation of isoeugenol with dimethylsulfate. Pine kraft lignin (Indulin AT) was obtained from Westvaco, Charleston, SC, USA. Eucalypt kraft lignin was prepared by acidification of eucalypt kraft black liquor to pH 1 with 1M sulfuric acid, and collection and washing of the resulting precipitate.

### UV-peroxide treatment of model compounds

A solution of a lignin model compound (0.3 mmol) in aqueous sodium hydroxide adjusted to pH 11 (45 mL) in an 80 mL quartz tube was heated to 40°C. Hydrogen peroxide (30%, 3 mmol) was added, and the tube was placed in the centre of a Rayonet photochemical reactor (Southern New England Ultraviolet Co., Middletown, CT, USA) with 10 mercury lamps emitting UV light at 254 nm, and the reaction was maintained at 40°C. Aliquots (2 mL) of the reaction mixture were withdrawn at 10-40 min intervals and diluted with the appropriate HPLC solvent to a total volume of 10 mL, and the resulting solution was analysed by HPLC. The reaction was monitored by following the disappearance of the starting material with time. In addition, the reactions were treated as above but in the absence of UV light.

The logarithm of the percentage of the reactants remaining was plotted against time, and gave in every case a straight line. The pseudo-first-order rate constants were determined from the slope of the line  $\times 2.303$ .

Portions of the reaction mixtures (5 mL) were acidified to pH 2 with 0.1M sulfuric acid, freeze dried, extracted with acetone (10 x 2 mL), and the combined extracts were dried over sodium sulfate. The solvent was removed *in vacuo*, and the residue was silylated with *N,O*-bis(trimethylsilyl)trifluoroacetamide for 1 h at 60°C, and the silylated mixture was analysed by GC-MS.

### UV-peroxide treatment of lignin

Lignin samples (5 mg) in 40% aqueous methanol solution adjusted to pH 5 or pH 11 (50 mL) in a 60 mL quartz tube were irradiated with UV at 254 nm at

40°C as above. The lignins were also irradiated at pH 11 in aqueous solution. The UV irradiation was performed in the Rayonet photochemical reactor described above. The reactions were monitored for UV absorbance of the solution with a Hewlett Packard 8452A Diode Array Spectrophotometer.

#### HPLC analysis

HPLC was carried out on a Millipore-Waters system comprising a model 501 pump, a 715 ULTRA WISP sample processor and a 484 UV detector coupled to a Waters 746 data module. An analytical Resolve™ 5 $\mu$  spherical C-18 column (150 mm x 3.9 mm i.d.) was used. Solvent elution was isocratic with acetonitrile:water (1:8-1:4, v/v) containing 1% acetic acid, or methanol:water (1:4-4:1, v/v) at a flow rate of 1 mL/min. The detector was operated at 280 nm.

#### GC-MS analysis

The GC-MS system consisted of a Hewlett Packard HP5890 series II gas chromatograph fitted with an autoinjector and an HP5971 mass selective detector. The column was a J & W bonded phase DB5 fused silica column (30 m x 0.25 mm ID) with a film thickness 0.25  $\mu$ m. GC conditions were: injector temp. 250°C, detector temp. 320°C, oven temp. 40°C for 3 min, programmed at the rate of 5°C/min to 180°C, 2 min at 180°C, 30°C/min to 300°C. Splitless injections of 1  $\mu$ L with a 0.3 min purge delay were used and full-scan ( $m/z$  30-550) electron impact (70 eV) mass spectra were collected.

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