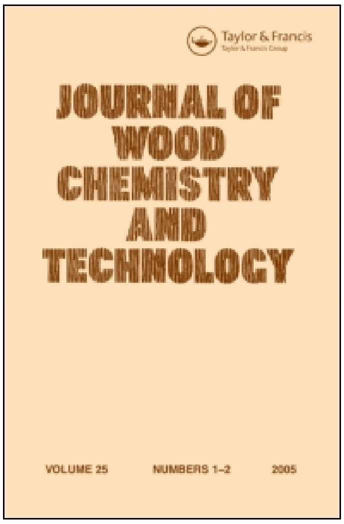

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Lawrence A. Dunn[a]; Roger H. Newman[b]; Jacqueline A. Hemmingson[b]
[a] Chemistry Department, University of Tasmania, Hobart, Tasmania, Australia [b] DSIR Chemistry, Private Bag, Petone, New Zealand

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BLEACHING OF EUCALYPT PULPS STUDIED BY CARBON-13 N.M.R. SPECTROSCOPY

Lawrence A. Dunn
Chemistry Department, University of Tasmania,
GPO Box 252C, Hobart, Tasmania, Australia

Roger H. Newman and Jacqueline A. Hemmingson
DSIR Chemistry, Private Bag, Petone, New Zealand

ABSTRACT

Cross polarization, magic-angle spinning, interrupted decoupling and paramagnetic doping techniques have been combined to provide the sensitivity needed for detection of chemical functional groups involved in pulp bleaching reactions. Cold soda pulp and stone groundwood pulp were bleached by calcium hypochlorite and hydrogen peroxide respectively. These treatments had little effect on ketonic structures and no effect on etherified aryl units, but hypochlorite degraded most lignin units not linked in beta-O-4 ethers. This work provides direct confirmation of published predictions based on bleaching of model compounds in solution.

INTRODUCTION

Alkaline hydrogen peroxide is widely used as a non-polluting bleaching agent for pulp. Calcium hypochlorite is less frequently used, but is relatively cheap. There are similarities between the bleaching mechanisms of hydrogen peroxide and hypochlorite[1,2]. In both cases, pulp brightening has been attributed to reactions of the anionic oxidants with various conjugated carbonyl structures present in lignin, e.g., quinones and cinnamaldehyde structures. Both reagents degrade aryl-carbonyl structures in lignin. Both can form free radicals which react with the phenolic structures in lignin.

In both cases, a number of mechanisms have been postulated through studies of reactions with model compounds in solution. Many of the results were reported in papers by Richtzenhain and Alfredsson[3-5] on hypochlorite bleaching, and by Gellerstedt *et al.*[6-8], and Omori and Dence[9] on hydrogen peroxide bleaching. We have now used solid-state NMR to test some of the conclusions through direct observation of chemical changes in pulp. We chose for the study commercial pulps made from a mixture of eucalyptus species. We used ^{13}C nuclear magnetic resonance spectroscopy with cross polarization and magic-angle spinning (CP/MAS NMR), and added interrupted decoupling (ID) and digital resolution enhancement (RE) to reveal details in bands of signals assigned to non-protonated carbon.

RESULTS AND DISCUSSION

Calcium hypochlorite bleaching of cold soda pulp

Comparison of normal CP/MAS NMR spectra (Figs. 1a and 1b) showed no gross changes in the chemical composition of the pulp. Signal area measurements indicated a small decrease in the lignin content, from 26% to 24% by weight of dry matter; but this change is close to the level of uncertainty in NMR estimation of lignin contents.

The ID NMR spectrum of the cold soda pulp showed peaks at $\delta = 137$ and 153 ppm, assigned to the non-protonated carbon in lignin syringyl units; C-1 and C-4 at 137 ppm, C-3 and C-5 at 153 ppm. A shoulder on the right-hand side of the latter peak was assigned to C-3 and C-4 in guaiacyl groups plus C-3 and C-5 of non-etherified syringyl groups, which are expected to contribute signals in the vicinity of $\delta = 148$ ppm. These signal assignments are based on literature data and were made in a previous publication[10]. The RE plot (Fig. 2a) revealed a peak at $\delta = 148$ ppm, but this peak was absent from the spectrum of the bleached pulp

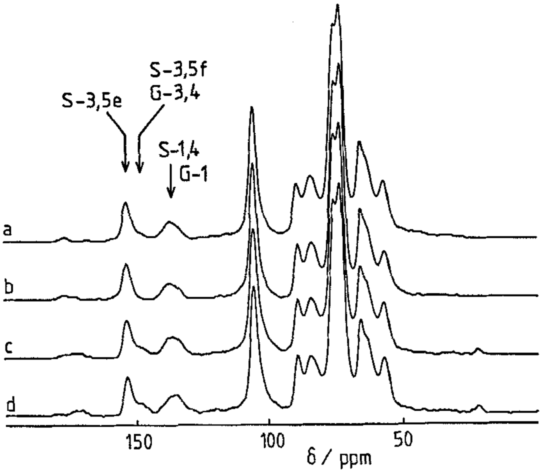


FIGURE 1. Normal CP/MAS NMR spectra of cold-soda pulp (a) before and (b) after bleaching with hypochlorite, and stone groundwood pulp (c) before and (d) after bleaching with hydrogen peroxide. S = syringyl, G = guaiacyl, e = etherified and f = free OH at the 4 position.

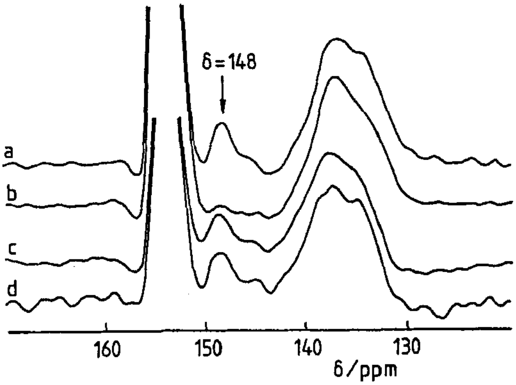


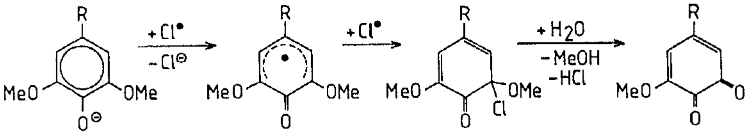
FIGURE 2. Resolution-enhanced CP/MAS-ID NMR spectra of cold-soda pulp (a) before and (b) after bleaching with calcium hypochlorite, and stone groundwood pulp (c) before and (d) after bleaching with hydrogen peroxide.

(Fig. 2b). Such RE spectra should not be used for quantitative analysis, because broader bands (in this case assigned to the guaiacyl component) can be suppressed relative to sharper bands. Syringyl/guaiacyl ratios were therefore estimated from ID spectra plotted without resolution enhancement. The method of Manders[11] was used. This involved forming linear combinations of the ID spectra of pulp and the ID spectrum of a softwood (in this case *Picea abies*) taken as representative of guaiacyl lignin. The results indicated an increase in the syringyl/guaiacyl ratio from 3.6 before bleaching to 4.4 after bleaching.

Hypochlorite bleaching is known to degrade non-etherified phenolic structures in model compounds[1-3]. The hypochlorite anions are too strongly nucleophilic to react directly with aromatic rings, and must first form free radicals[1,2];

$$OCl^- + HOCl \rightarrow OCl^{\cdot} + Cl^{\cdot} + OH^- \qquad [1]$$

The free radicals then oxidize the phenol to a quinone:



[2]

The quinone is then rapidly oxidized by hypochlorite anions. Studies of model compounds have shown that etherification of the phenol blocks this oxidation mechanism[3].

The increase in the syringyl/guaiacyl ratio could be explained in qualitative terms (a) by oxidation of non-etherified lignin units, if syringyl units are more likely to be etherified[12] or (b) by a greater reactivity of guaiacyl versus syringyl units due to the lack of a free 5-position in the latter. The NMR spectra alone do not provide adequate information for estimates of both the syringyl/guaiacyl ratio and the degree of etherification of syringyl or guaiacyl units. The method of Manders[11] simply ignores the possibility of non-etherified syringyl groups contributing to signals in the vicinity of $\delta = 148$ ppm. The best we can do is to place a lower limit on the proportion of lignin units affected by bleaching. If only guaiacyl units were oxidized, then the observed change in the syringyl/guaiacyl ratio could be explained by oxidation of 4% of the total lignin, i.e. about one fifth of guaiacyl units.

An estimate of 80% etherification of guaiacyl units has been obtained for *Pinus radiata* lignin in intact wood[13]. If the same degree of etherification is found in the guaiacyl units of hardwood lignin, then there would be a sufficient quantity of non-etherified units to account for the observed loss through oxidation.

The degradation of phenols must be regarded as a side reaction in the bleaching process, and perhaps an undesirable one in that chromophores are generated during the reaction. Degradation of free phenols is slower than the bleaching of the original quinone chromophores, because of the relatively slow production of free radicals and the additional steps shown in Eq. [2].

The lower limit estimated for the proportion of lignin units oxidized corresponds to 0.05 mole of units per kg pulp. Oxidation to a quinone (Eq. [2]) would require 1 mole OCl^- per mole of phenol, and oxidation of the quinone to a dicarboxylic acid would require as much again. These two steps would therefore consume about 0.1 mole OCl^- per kg pulp. Further oxidation steps are possible[3], having a potential demand of several further moles of OCl^- per mole of free phenols. The initial concentration of available chlorine corresponded to 0.7 mole OCl^- per kg pulp. Our results therefore suggest that oxidation of non-etherified lignin units dominates the demand for oxidant in this bleaching process.

Carboxylate salts contributed a peak at $\delta = 177$ ppm. This assignment was confirmed by acidification of one pulp with HCl. The signal shifted to $\delta = 173$ ppm, i.e. to the chemical shift expected for carboxylic acids. Signal areas indicated an increase in concentration from 0.3 mole kg^{-1}

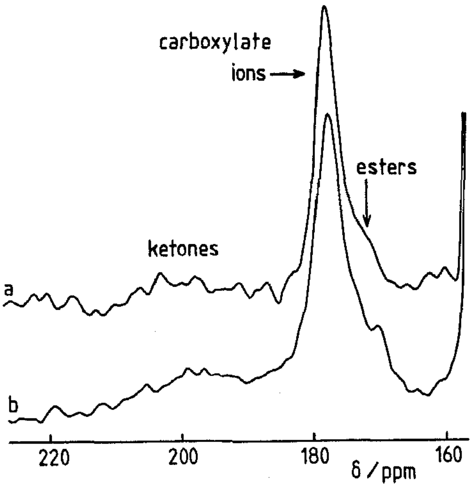


FIGURE 3. CP/MAS-ID NMR spectra of cold-soda pulp (a) before and (b) after bleaching with calcium hypochlorite.

before bleaching to 0.5 mole kg^{-1} after bleaching. This increase is consistent with oxidation of non-etherified lignin units to carboxylic acids.

A weak band from δ = 190 to δ = 210 ppm (Fig. 3) is attributed to ketonic functional groups. Clear resolution into contributions that could be assigned to aryl-α-carbonyl structures (expected at δ = 195 ppm) and non-conjugated carbonyl groups (expected at δ = 200 to 210 ppm) was not possible. The cold-soda pulp contained these groups at a level of about 0.09 mole kg^{-1}, rising to about 0.13 mole kg^{-1} after bleaching. As the band was too weak and diffuse for accurate integration, the apparent change was within experimental uncertainty. Studies of model compounds have shown that hypochlorite ions can react with aryl-α-carbonyl structures[4]. Such sidechain reactions would break down the polymeric structure of the lignin. Reactions with model aryl-α-carbonyl structures have been reported as slow compared with degradation of phenols[3,4].

This is consistent with our assignment of the weak signals to ketones in the bleached pulp.

Hydrogen peroxide bleaching of stone groundwood pulp

Comparison of normal CP/MAS NMR spectra (Fig. 1c and 1d) showed no gross changes in the chemical composition of the pulp. Signal area measurements indicated a small increase in the lignin content, from 26% to 30% by weight of dry matter. The increase is a little more than experimental uncertainty, and may indicate removal of material other than lignin during bleaching, or production of material associated with NMR signals in the region of $\delta = 150$ ppm.

The ID NMR spectrum of the groundwood pulp (Fig. 2) showed a signal at $\delta = 148$ ppm assigned to C-3 and C-5 in non-etherified syringyl units, at a level similar to that in the cold soda pulp (see above). These non-etherified units were not degraded by hydrogen peroxide. This observation differs from the results for hypochlorite bleaching, probably because hydrogen peroxide is stabilized in the commercial process by addition of silicate[6]. In the absence of stabilization, hydrogen peroxide can fragment[2] by a reaction analogous to that shown in Eq. [1], i.e. as shown in Eq.[3];

$$HOO^- + H_2O_2 \rightarrow HOO\bullet + OH^- + OH^\cdot \qquad [3]$$

The hydroperoxide anion is a strong nucleophile, and is unable itself to react with phenolic structures such as non-etherified lignin units[2].

Carboxylic acids and esters contributed a band of signals from about $\delta = 165$ to $\delta = 180$ ppm, with a maximum at $\delta = 173$ ppm. The concentration of carboxylic functional groups was consistently higher in the groundwood pulp than in the cold soda pulp, at 0.7 mole kg^{-1}. The additional signal strength was assigned to the acetyl groups of hemicelluloses, present in the groundwood pulp but not in the cold soda pulp. These acetyl groups also contributed a signal at $\delta = 22$ ppm, both before and after bleaching (Fig. 1). The concentration of carboxylic functional groups remained unchanged at 0.7 mole kg^{-1} after bleaching.

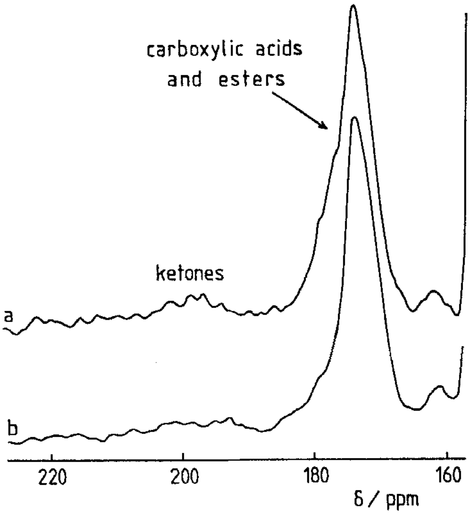


FIGURE 4. CP/MAS-ID NMR spectra of stone groundwood pulp (a) before and (b) after bleaching with hydrogen peroxide.

The groundwood pulp contained ketonic functional groups at a level of about 0.07 mole kg^{-1} (Fig. 4a). The level was about 0.08 mole kg^{-1} after bleaching (Fig. 4b), therefore the change is smaller than the experimental uncertainty in measuring the signal area of the weak signal. Aryl-α-carbonyl structures are known to react with alkaline hydrogen peroxide, yielding carboxylic acids and semi-quinones[7,9], but the reaction rate must be too slow for significant changes to occur in the commercial bleaching process.

Comparison with other NMR studies

CP/MAS NMR spectra have been used in studies of peroxide bleaching of chemimechanical pulp from balsam fir[14] and thermomechanical pulp from white spruce[15]. These studies provided NMR evidence for oxidative ring opening affecting about 5% of lignin units in the former case and

80% in the latter. The latter result is surprisingly high compared with the former result and our own observations.

However, the earlier studies involved softwood pulps and are therefore not directly comparable with our studies of hardwood pulp.

CONCLUSIONS

Bleaching with calcium hypochlorite resulted in oxidation of non-etherified lignin units. Bleaching with hydrogen peroxide left those units intact. The difference can be explained in terms of stabilisation of hydrogen peroxide against formation of free radicals. Non-etherified lignin units can account for the dominant demand for oxidant in bleaching of cold-soda *Eucalyptus regnans* pulp with calcium hypochlorite.

EXPERIMENTAL

Samples

Samples were taken from the alkaline washers (unbleached pulp) and proportioners (bleached pulp) of a commercial pulp mill. The cold soda pulp was bleached for about 2 hours at 25°C in a mixture of sodium hydroxide (1%) and calcium hypochlorite giving an available chlorine concentration of about 5%. The stone groundwood pulp was bleached for about 3 hours at 50°C in a mixture of hydrogen peroxide (2%), sodium hydroxide (2%) and sodium silicate (3%). The percentages are expressed relative to the weight of dry fibre. The bleached pulps had brightness values of 58-60% and 65% respectively.

Each pulp was air-dried, mixed with a solution of chrome alum, and air-dried again to bring the Cr^{3+} content of the pulp to 0.1% by weight. The Cr^{3+} was added to shorten proton spin-lattice relaxation time constants for rapid-pulsing NMR experiments[16]. Samples of between 0.11 g and 0.15 g pulp were packed in 7 mm diameter cylindrical sapphire rotors sealed with Kel-F caps.

NMR experiments

Samples were spun at 5 kHz in a Doty Scientific MAS probe, and NMR spectra were run at 50 MHz ^{13}C NMR frequency on a Varian XL-200 spectrometer. Normal CP/MAS NMR spectra were run with a 200 ms recovery delay, a 5 µs preparation pulse, a 2 ms cross-polarization contact time and 30 ms of data acquisition. Transients from at least 2000 acquisitions were averaged. Lignin contents were estimated from these spectra by the method of Hemmingson and Newman[10] with a spinning-sideband correction factor redetermined for MAS at 5 kHz. Interrupted-decoupling experiments were based on the pulse sequence of Harbison *et al.*[17] with an interruption interval of 42 µs. The number of acquisitions was increased to between 6×10^5 and 9×10^5. Other parameters were as for the normal CP/MAS NMR spectra. Resolution enhancement involved convolution of the raw data table with an exponentially-increasing function (time constant 3 ms) and a Gaussian decay function (time constant 6 ms).

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