Cyanamide activation of peroxide bleaching: a lignin model compound study

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ABSTRACT

The effect of cyanamide (H_2NCN) on hydrogen peroxide oxidation of lignin model compounds was studied. Results showed that cyanamide addition significantly enhanced the rate of model oxidation. However, it also increased oxidant decomposition, limiting the final extent of model oxidation. When peroxide was applied alone, the different lignin models reacted to widely varying degrees. In the presence of cyanamide, however, all models were significantly degraded to a comparable extent. Results are consistent with formation of an intermediate peroxyimidic acid. This strong oxidant then either rapidly degraded the added lignin model (directly or via decomposition products) or oxidized the peroxide, leading to undesirable degradation of the oxidant.

Application:

Addition of cyanamide during peroxide bleaching enhances lignin removal. A model compound study was undertaken to investigate why.

HYDROGEN PEROXIDE IS BEING used increasingly during the bleaching of chemical pulps, both for final brightening of the pulp *(1)* and, more recently, for lignin removal *(2)*. Addition of cyanamide (H_2NCN) during peroxide bleaching has been shown to increase both the brightness and the degree of delignification of the pulp, without also reducing pulp strength *(3, 4)*. The increased delignification has been attributed to formation of a peroxyimidic acid intermediate. This intermediate, formed by combination of peroxide and cyanamide, is a stronger oxidant than hydrogen peroxide alone.

Here, we report on a model compound investigation into the chemistry of cyanamide-activated peroxide (peroxide/cyanamide) delignification. The initial investigations used apocynol as a lignin model and monitored degradation of model compound and oxidant under various conditions. Subsequently, a range of simple lignin model compounds was used to determine the reactivity of cyanamide-activated peroxide toward various lignin structures.

EXPERIMENTAL

Model compound preparation

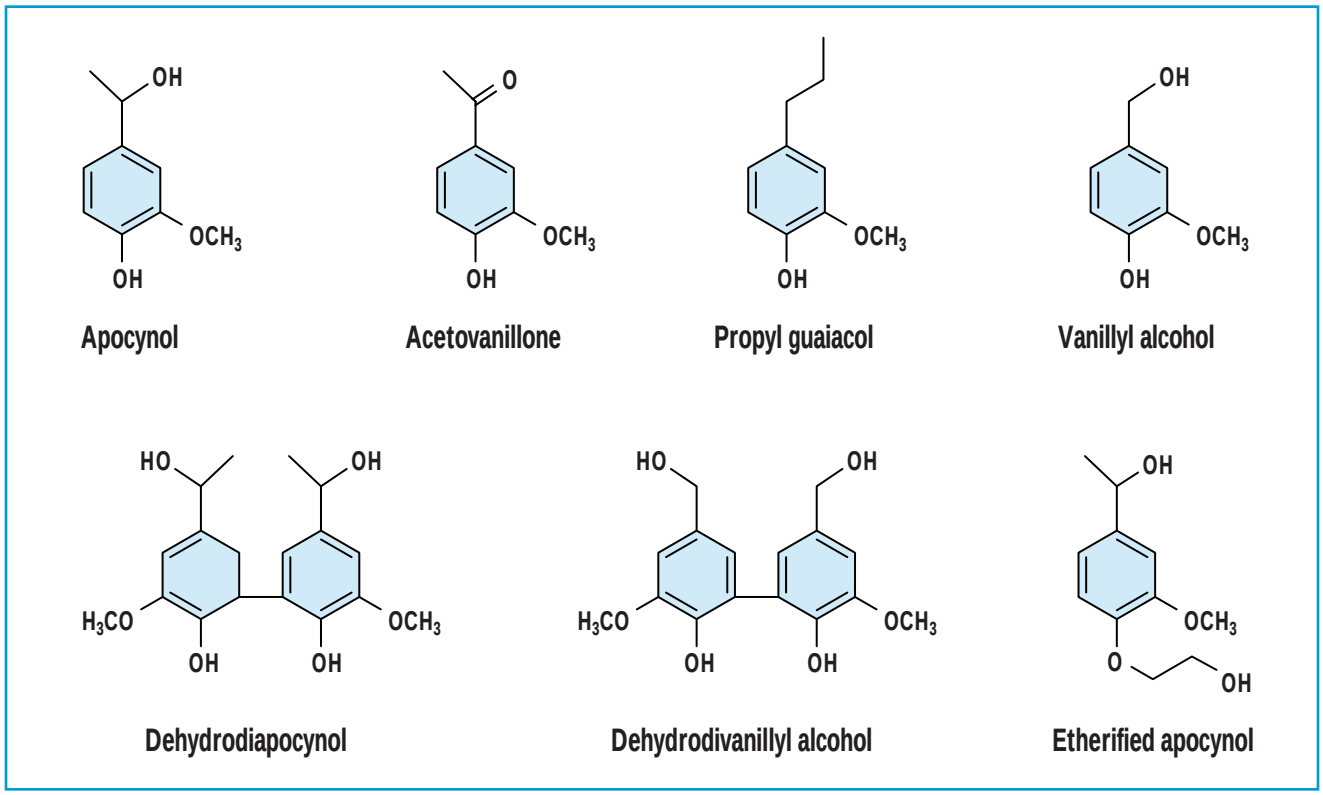
Figure 1 shows the structures of the seven model compounds used in this study. Apocynol was prepared by hydrogenation of acetovanillone; propyl guaiacol by hydrogenation of isoeugenol *(5)*; vanillyl alcohol by reduction of vanillin with $NaBH_4$; dehydrodiapocynol from acetovanillone by oxidative coupling using $Na_2S_2O_8/FeCl_3$ *(6)* followed by reduction with $NaBH_4$; dehydrodivanillyl alcohol by catalytic hydrogenation of dehydrodivanillin *(6)*; and the etherified apocynol from acetovanillone by alkylation with excess dibromoethane, hydrolysis of the resulting bromide with aqueous K_2CO_3, and reduction with $NaBH_4$ *(7)*.

Model reactions

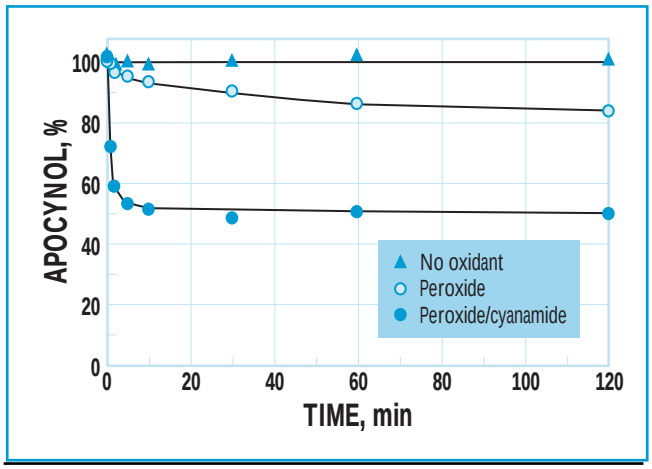
In a typical reaction, apocynol (20 mg, 0.119 mmole) and solutions of $MgSO_4$ (500 µL, 10 mg/mL) and DTPA (500 µL, 20 mg/mL) were placed in a 50-mL three-necked glass flask under a nitrogen atmosphere, diluted to 9.5 mL with pH 11 buffer ($NaOH/NaHCO_3$) and stirred. Hydrogen peroxide (500 µL, 1.19 mole/L) was added after the reaction had equilibrated to the desired temperature. In the peroxide/cyanamide reactions, 9.4 mL of buffer was used, and then the peroxide and H_2NCN (100 µL, 5.95 mole/L) were added simultaneously. Samples for residual model and oxidant were removed at intervals during the 2-hour reaction.

For analysis of the remaining model, a 500-µL aliquot was removed from the reaction vessel, added to a solution of sodium thiosulfate (1 mL, 60m*M*), and acidified to pH 2 with 5% H_3PO_4 to quench any remaining oxidant. The quenched reaction mixture was adjusted to pH 6 using 0.5*M* NaOH, and the internal standard, *o*-vanillin (0.024 mmole) in methanol (2 mL), was added. The sample was diluted to 5 mL with deionized water and an aliquot filtered through a 0.45-µm nylon syringe filter ready for high-pressure liquid chromatography (HPLC) analysis.

HPLC analyses were carried out using a reverse-phase C18 column (150 mm × 4.6-mm inside diameter, 5 µm, Alltech Econosphere) on a system comprising a pump (Waters Model 600), an autosampler (Gilson Model 231), and an ultraviolet/visible-light detector (Waters Model 400) set at 280 nm. Elution was performed for 5 min with 20% methanol in water containing 0.1% H_3PO_4, and then the methanol concentration increased linearly over 5 min to 80% methanol and held for a further 15 min. The flow rate was 1 mL/min.



1. Model compounds used in this study



2. Apocynol remaining vs. time for peroxide and peroxide/cyanamide oxidation (55°C, pH 11, 5:1 oxidant:model, 1:1 cyanamide:peroxide)

To determine residual oxidant, a 500-µL aliquot of the reaction mixture was added to aqueous solutions of $CoCl_2$ (1 mL, 15 mg/mL) and Na_4-EDTA (1 mL, 25 mg/mL), and the mixture was made up to 5 mL with deionized water. The absorbance of the resulting solution at 570 nm was used as a measure of oxidant concentration *(8)*.

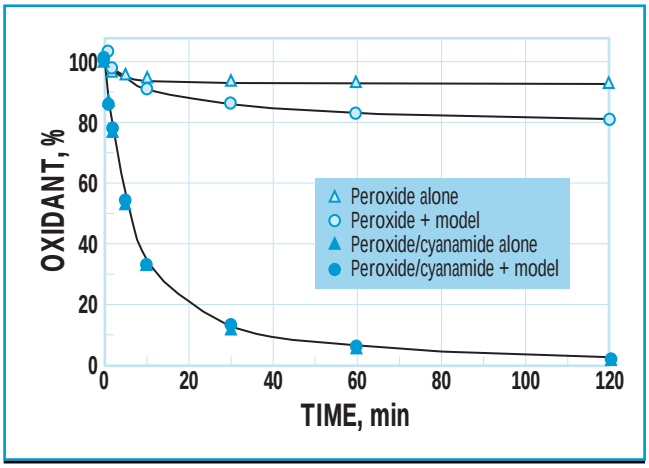
RESULTS AND DISCUSSION

Reactivity of peroxide/cyanamide

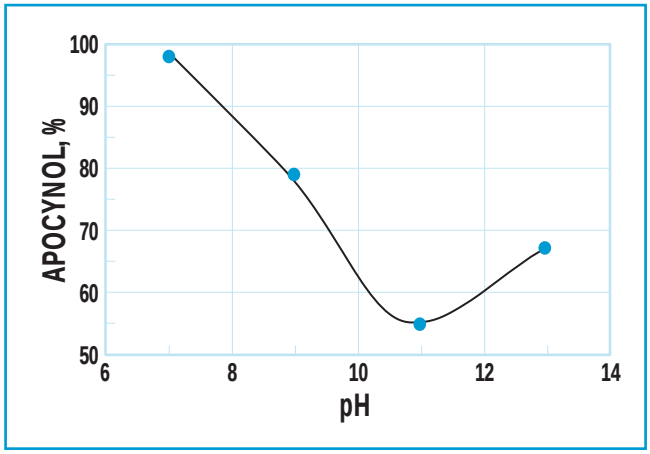
Figure 2 shows the degradation of apocynol at 55°C and pH 11 in the presence of (a) 5 mole equivalents of hydrogen peroxide and (b) 5 mole equivalents of H_2O_2 plus an equimolar amount of cyanamide. Unless otherwise indicated, all further experiments were carried out using this model:peroxide:cyanamide mole ratio of 1:5:5. Addition of cyanamide significantly enhanced apocynol oxidation, leading to 50% degradation of the model compound within 10 min, compared with 5% in the case of peroxide alone. However, when cyanamide was present, model compound degradation essentially stopped after 10 min.

To provide further insight into these results, oxidant degradation was measured for the peroxide and peroxide/cyanamide oxidations in the presence or absence of model compound. **Figure 3** shows that for oxidations involving only peroxide, addition of apocynol increased the degradation of oxidant from 5% to 19% in 2 hours. In the absence of apocynol, addition of cyanamide increased oxidant degradation to 98% after 2 hours, compared with 5% for peroxide alone. Degradation of oxidant for the peroxide/cyanamide oxidation in the presence of apocynol was essentially identical to that in the absence of apocynol. This quick decomposition of the oxidant in the peroxide/cyanamide reaction can explain why no further degradation of apocynol was seen after 10 min.

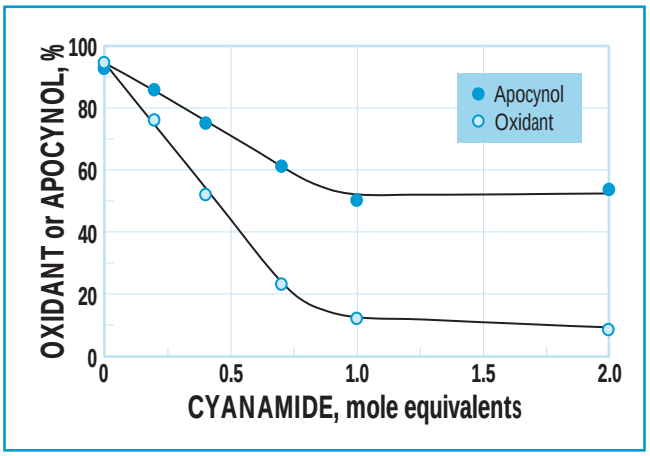
Effect of pH



3. Oxidant remaining vs. time for peroxide and peroxide/cyanamide oxidation in the presence and absence of apocynol (55°C, pH 11, 5:1 oxidant:model, 1:1



4. Apocynol remaining after 60 min vs. pH (30°C, 5:5:1 cyanamide:peroxide:model)



5. Apocynol and oxidant remaining after 60 min vs. mole equivalents of cyanamide (30°C, pH 11, 5:1 peroxide:model)

Figure 4 shows that maximum degradation of apocynol with peroxide/cyanamide occurred around pH 11. Oxidant decomposition in these reactions followed a similar pattern to degradation of the model compound, with maximum decomposition occurring around pH 11. This is similar to the pH observed (11.5) for maximum decomposition of lignin models with alkaline hydrogen peroxide alone *(9, 10)*.

Effect of cyanamide:peroxide ratio

The effect of the cyanamide-to-peroxide ratio on the peroxide/cyanamide oxidation was assessed by varying the cyanamide-to-peroxide ratio from 0:1 to 2:1 while maintaining a constant 5:1 mole ratio for peroxide:apocynol. Increasing the cyanamide equivalents increased both the initial rate and the final extent of degradation for the model compound. **Figure 5**, which plots the apocynol remaining after 60 min vs. the equivalents of cyanamide used, shows that below a 1:1 cyanamide: peroxide ratio, the extent of reaction increased linearly with the equivalents of cyanamide used. Above one equivalent of cyanamide, there was no further increase in the extent of apocynol oxidation. The extent of oxidant degradation also increased linearly with the amount of cyanamide below a 1:1 cyanamide: peroxide ratio, with no appreciable increase in the extent of oxidant decomposition above one equivalent. From these results, it is clear that the activation of peroxide is stoichiometric and noncatalytic.

Effect of temperature

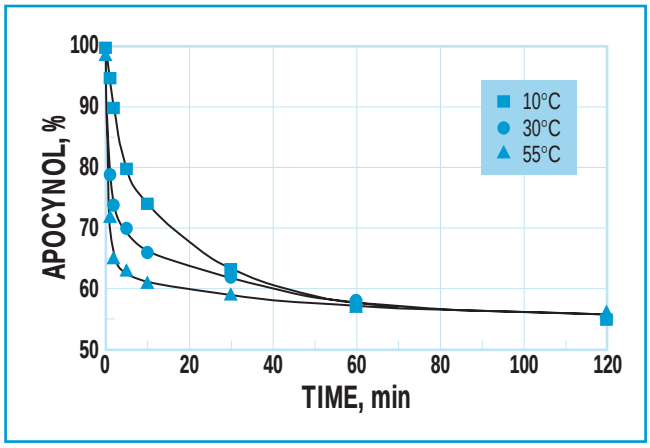
Figure 6 shows the results of peroxide/cyanamide oxidations of apocynol at temperatures of 10, 30, and 55°C. While increasing the reaction temperature increased the initial rate of oxidation, the final extent of model degradation in all three reactions was nearly identical. This was attributed to the fact that increasing the temperature also increased the rate of oxidant decomposition. After 10 min, there was 8% oxidant remaining at 55°C, 34% at 30°C, and 65% at 10°C. However, even at 10°C, the rate of oxidant decomposition during peroxide/cyanamide reactions was indistinguishable in the presence or absence of apocynol.

Effect of oxidant charge

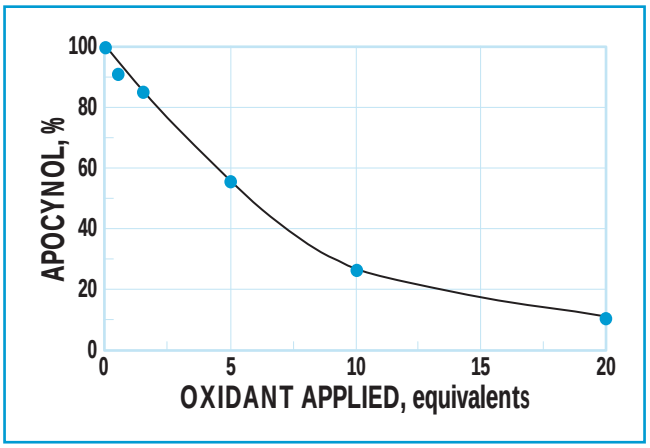
The effect of varying the ratio of oxidant to apocynol while maintaining a 1:1 cyanamide:peroxide ratio is shown in **Fig. 7**. As the oxidant charge increased, both the initial rate and final extent of apocynol oxidation also increased. However, even with 20 equivalents of oxidant, not all of the model compound was consumed. This highlights the importance of oxidant decomposition in limiting the extent of reaction.

Proposed reaction scheme

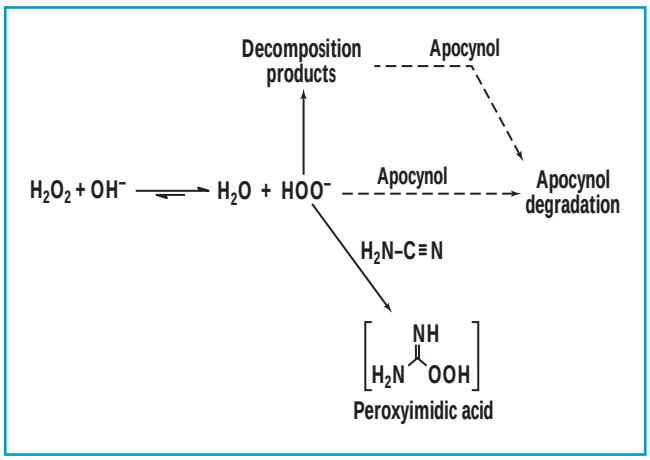
In the absence of cyanamide, peroxide reacts with apocynol either via direct reaction with the hydroperoxide anion *(10)* or by reaction with peroxide decomposition products *(9, 11)*. Figure 3 showed that hydrogen peroxide was largely stable under the conditions used in this study in the absence of apocynol, and that adding the



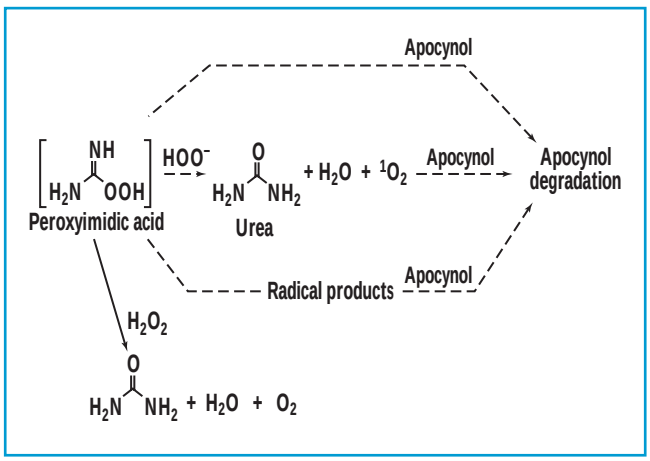
6. Effect of temperature on apocynol degradation (pH 11, 5:5:1 cyanamide:peroxide:model)



7. Apocynol remaining after 120 min at different oxidant charges (30°C, pH 11, 1:1 cyanamide:peroxide)



8. Reactions of hydrogen peroxide



9. Possible reactions of the intermediate peroxyimidic acid with apocynol and hydrogen peroxide

model increased the extent of oxidant degradation. This would suggest that apocynol was degraded either by a direct reaction of the hydroperoxide ion with the model, or possibly by peroxide decomposition products, assuming that the model or its degradation products promote peroxide decomposition.

Hydrogen peroxide is believed to react with nitriles to form peroxyimidic acids *(12–14)*. Such intermediates are highly reactive and have not, to our knowledge, been isolated. The peroxyimidic acid is believed to be formed via addition of the hydroperoxy anion (HOO^-) to the nitrile, as seen in **Fig. 8** *(12)*, explaining why the rate of oxidation with peroxide/cyanamide increases up to pH ≈ 11.

Once formed, such peroxyimidic acids are much more efficient oxidants than hydrogen peroxide. They react with olefins to produce the epoxide plus the corresponding amide *(13, 15–17)*, which in the case of cyanamide is urea. Such direct reactions may also contribute to lignin model compound degradation in the peroxide/cyanamide reactions, as seen in **Fig. 9**.

In the absence of added organic substrate, peroxyimidic acids can oxidize hydrogen peroxide to oxygen plus the corresponding amide *(12)*. This can explain why addition of cyanamide also leads to rapid decomposition of hydrogen peroxide in the absence of apocynol (Fig. 3). If the rate of reaction of the peroxyimidic acid—either with the lignin model or peroxide—is much faster than the rate at which it is formed, then this would explain why the rate of oxidant degradation is essentially independent of the presence or the structure (discussed later) of the added model (Fig. 3).

There is conflicting evidence suggesting that singlet oxygen ($^1O_2$) may be produced during the reaction of nitriles with hydrogen peroxide *(13, 18)*. Because $^1O_2$ is known to degrade lignin model compounds *(19)*, any formation of this species could contribute to lignin model degradation. However, this would not appear to be the main route by which apocynol is degraded by peroxide/cyanamide, since if the model were being degraded totally via $^1O_2$ formation, then one mole of

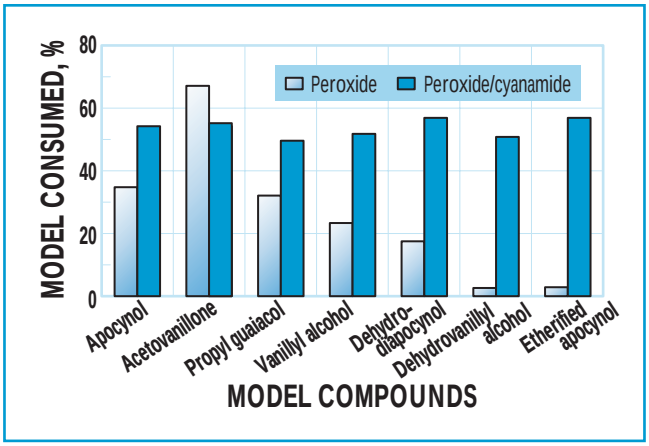
cyanamide would react with two moles of hydrogen peroxide. Rather, it was shown in Fig. 5 that maximum enhancement of apocynol degradation occurred at a 1:1 peroxide: cyanamide mole ratio.

Decomposition of the intermediate peroxyimidic acid to radical species could also be involved in the degradation of the lignin models. Sawaki and Ogata *(13)* presented a range of evidence suggesting that, particularly at higher pH, the peroxyimidate ion decomposed with production of radical species. The hydroxyl radical ($HO^{\bullet}$) and superoxide radical anion ($O_2^{\bullet-}$) are known to be involved in the degradation of lignin during delignification with oxygen and hydrogen peroxide, with the former attacking both phenolic and nonphenolic units in lignin *(20)*. More recently, electron spin resonance (ESR) spectroscopy has been used to show the presence of radical species in the reactions of hydrogen peroxide with lignin models in the presence of cyanamide *(21)* and in the reactions of cyanamide with hydrogen peroxide in the absence of added organic substrate *(14)*. Such radical-induced decomposition could explain why the rate of oxidant decomposition was indistinguishable in the presence or absence of apocynol and why both phenolic and nonphenolic compounds are degraded. However, it has been found that in the presence of cyanamide, delignification of softwood kraft pulps is more selective, with less loss in pulp viscosity for the same loss of lignin *(22)*. This would tend to suggest that high levels of hydroxyl radicals are not formed in the presence of cyanamide plus hydrogen peroxide, since such radical species are well known to promote carbohydrate degradation, leading to losses in pulp viscosity.

Selectivity of peroxide/cyanamide

Several other lignin models were studied to determine what effect addition of cyanamide had on peroxide oxidation of model compounds other than apocynol. The models examined (Fig. 1) included vanillyl alcohol, propyl guaiacol, and acetovanillone, which contain α-hydroxy-, α-methylene-, and α-carbonyl-substituted side chains, respectively, as well as two 5,5′-biphenyl models (dehydrodiapocynol and dehydrodivanillyl alcohol) and the soluble nonphenolic model (etherified apocynol). All oxidations were performed with 5 mole equivalents of peroxide per aromatic ring. The temperatures were 60°C for the reactions with peroxide alone and 30°C for the peroxide/cyanamide reactions.

Figure 10 shows that for oxidations with peroxide alone, the extent of oxidation depended on the structure of the model compound. In accord with previous reports *(23, 24)*, the α-carbonyl model acetovanillone was extensively degraded by peroxide alone. This high reactivity has been attributed to a facile Dakin-like oxidation involving initial attack of the perhydroxyl (HOO^-) anion on

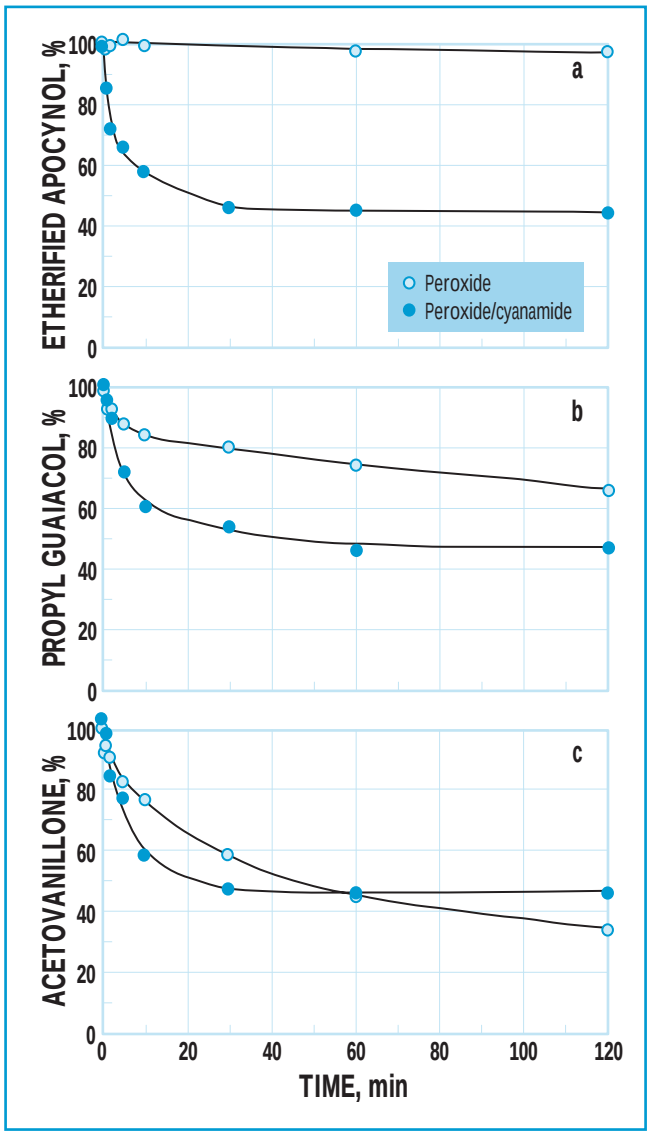


10. Degradation of different models after 120 min in peroxide and peroxide/cyanamide oxidation (pH 11, 5:1 peroxide:aromatic ring, 1:1 cyanamide:peroxide, 60°C for peroxide or 30°C for peroxide/cyanamide)

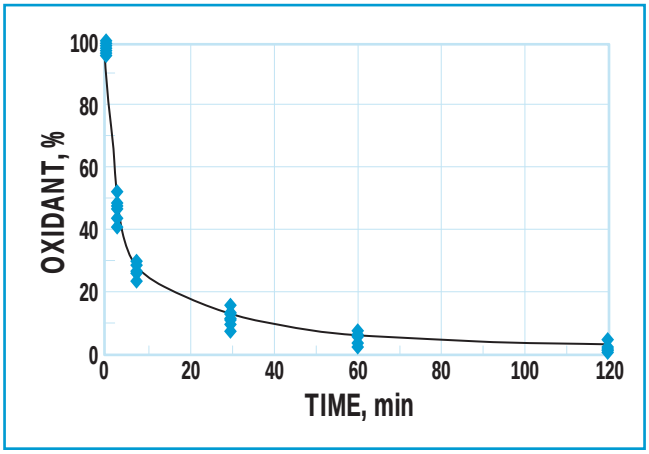
the electron-deficient carbon of the carbonyl group. At the other extreme, the etherified apocynol was virtually unreactive under these conditions (2% consumed). Nonphenolic lignin models have previously been reported to be unreactive toward alkaline hydrogen peroxide *(23)* unless they also contain an α-carbonyl β-aryl ether unit *(24, 25)* or high temperatures are used *(10)*. The results in Fig. 10 also indicate that, for both apocynol and vanillyl alcohol, the monomeric model was more extensively degraded than the corresponding biphenyl model, and that for both the monomeric and dimeric models, the apocynol was more reactive than the vanillyl alcohol. Bailey and Dence *(26)* have earlier reported that creosol (4-hydroxy-3-methoxytoluene) was more extensively degraded by alkaline hydrogen peroxide than the corresponding biphenyl. Apocynol has been reported to be more readily oxidized with alkaline hydrogen peroxide than vanillyl alcohol *(10, 25)*. This was attributed to greater stabilization of the quinone methide intermediate of apocynol due to hyperconjugation *(25)*. In agreement with results reported by Bailey and Dence *(26)* with creosol, propyl guaiacol, containing a saturated side chain, was also significantly degraded by peroxide under these conditions.

In contrast to the results obtained with peroxide alone, all seven models were consumed to a similar extent (49–56%) when cyanamide was added. With one exception, the extent of model oxidation increased in the presence of cyanamide. The benefit of cyanamide was most evident with the models that reacted only to a minor extent with peroxide alone. For example, the etherified apocynol and dehydrodivanillyl alcohol reacted to a minor extent with peroxide alone, but they were consumed to the extent of 56% and 50%, respectively, in the presence of cyanamide.

Figure 11 shows the degradation of three of these model compounds as a function of time. The degrada-



11. Remaining model vs. time for peroxide and peroxide/cyanamide oxidation of (a) etherified apocynol, (b) propyl guaiacol, and (c) acetovanillone (conditions as in Fig. 10)



12. Remaining oxidant vs. time for peroxide/cyanamide reactions without added model and in the presence of the seven models used in this study

tion profiles for each of the three model compounds with peroxide/cyanamide were essentially identical, exhibiting a high initial rate of oxidation followed by little further degradation after 30 min.

Figure 12 shows that oxidant degradation during peroxide/cyanamide oxidation of the seven model compounds was very similar and also indistinguishable from the degradation that occurred in the absence of added model compound. In the initial stages of the reaction, degradation of the oxidant was very high, with about 50% being consumed in the first 3 min. The low levels of oxidant remaining after 30 min can explain why model degradation in these reactions was minimal after this time (Fig. 11). The greater degradation of acetovanillone observed after 120 min in the absence of cyanamide (Fig. 11c), even though the initial rate of degradation was significantly slower, can also be readily explained in terms of the effect of cyanamide on oxidant degradation. In the peroxide/cyanamide reaction, model degradation is limited by degradation of the oxidant, whereas in the absence of cyanamide, oxidation continues throughout the reaction period, albeit at a slower rate, resulting in greater model degradation.

In the peroxide/cyanamide system, the extent of model degradation is determined by the relative rate of reaction of the peroxyimidic acid intermediate, or its subsequent degradation products, with the model vs. its reaction with remaining hydrogen peroxide. The fact that all the different models, including the nonphenolic model (etherified apocynol), were degraded by peroxide/cyanamide to a comparable extent suggests that the reactive intermediate formed in these reactions is of sufficiently high reactivity that it reacts with all the models at an indistinguishable rate. On the other hand, the reactive species (such as the perhydroxyl anion) that are present during reaction with peroxide alone are considerably less reactive, requiring a higher reaction temperature and reacting preferentially with those models that are most easily degraded.

CONCLUSIONS

Addition of cyanamide to peroxide oxidations significantly increased both the rate and extent of degradation of lignin model compounds. However, the addition of cyanamide also significantly increased the rate of oxidant decomposition, limiting the eventual extent of degradation for the model compounds. The laboratory results were consistent with formation of a peroxyimidic acid intermediate. The increased oxidation rate of model compounds was attributed to this intermediate itself (or its decomposition products) reacting with the model compounds at a rate higher than peroxide alone. Significantly, cyanamide-activated peroxide reacted with different model compounds at the same rate and to the same

extent, regardless of their structure. Because of this lack of selectivity, peroxide/cyanamide was particularly beneficial for oxidizing structures showing a low reactivity toward peroxide alone. Thus cyanamide-activated peroxide may be particularly useful for oxidizing residual lignin in pulp. TJ

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