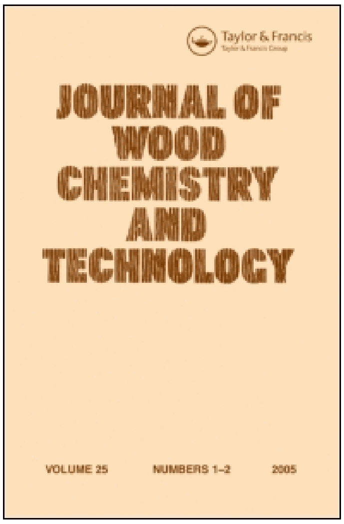

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The Kinetics of Lignin Reactions During Oxygen Bleaching. IV. The Reactivities of Different Lignin Model Compounds and the Influence of Metal Ions on the Rate of Degradation

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THE KINETICS OF LIGNIN REACTIONS DURING OXYGEN BLEACHING, PART 4. THE REACTIVITIES OF DIFFERENT LIGNIN MODEL COMPOUNDS AND THE INFLUENCE OF METAL IONS ON THE RATE OF DEGRADATION

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ABSTRACT

The reactivities of different lignin model compounds with oxygen in alkaline media have been compared. Generally, phenolic structures with a conjugated side chain like stilbene and enol ethers react very rapidly during oxygen bleaching, whereas structures like propylguaiacol and β-aryl ethers are more resistent. Some of the reaction mechanisms involved are probably of a radical type because new crosslinked structures can be formed with even lower reactivity.

The influence of metal ions on the reactivity has also been studied. We have found that Mg^{2+} and transition metal ions like Mn^{2+}, Cu^{2+} and Fe^{2+} influence the rate of degradation as well as the rate of dimerization. Most of the metal ions gave a lower rate of degradation as measured at pH 11. The addition of a small amount of hydrogen peroxide to the oxygen alkali system increases the rate of degradation.

INTRODUCTION

Oxygen prebleaching is a commercially used process to decrease the lignin content in the kraft pulp of softwood before the final bleaching. It is possible to reduce the lignin content by up to 50 % before the cellulose degradation becomes significant with a great loss of viscosity of the pulp. A higher rate of delignification would be beneficial, but to achieve this a greater knowledge of the chemistry involved is essential. The chemistry of oxygen delignification is complicated due to the complexity of the lignin structure as well as the number of different oxygen species formed during the bleaching.

During softwood kraft pulping, new phenolic structures are formed from the cleavage of aryl ether bonds in the pulp lignin.[1,2,3] Studies of the phenolic content of the residual lignin after oxygen bleaching show that most of the phenolic groups have been consumed.[4] This indicates that phenolic groups are highly significant for the oxygen oxidation and are important sites of reaction for oxygen in residual lignin.[5]

The oxygen molecule can be reduced to different species, HO_2^- /H_2O_2, $O_2^{\cdot-}$/$HO_2^{\cdot}$ and $HO^{\cdot}$ and the question of which species are significantly involved in the oxygen prebleaching process has not yet been clearified. However, it is probable that the oxygenation process starts with the abstraction of an electron from the phenolate anion, giving a phenoxy radical. It has been suggested that the formation of the phenoxy radical is the rate-determining step for the oxidation.[6,7] This radical can undergo different reactions, Figure 1, reaction with the perhydroxy radical or the superoxide anion radical which results in demethoxylation, ring cleavage and degradation to water-soluble acids or a coupling of two phenoxy radicals to a more complex lignin structure. [8,9,10]

Transition metal ions are frequently present in wood and pulp, and earlier studies have shown that metal ions like manganese, copper, iron and cobolt play an important role during the lignin oxidation process. The metal ions can act as catalysing agents during oxygen pulping.[11,12] The influence of these metal ions on the oxygen pulping of refiner groundwood was studied and it was found that the presence of manganese ions enhanced the rate of pulp delignification and gave a higher pulp viscosity. The presence of copper ions also enhanced the delignification but had also a detrimental effect on the viscosity.

Studies on a model compound, 2-tert.butyl-4-methylphenol, implied that a direct interaction between metal ion and the phenol is possible and that no phenoxy radicals are formed unless transition metal ions are

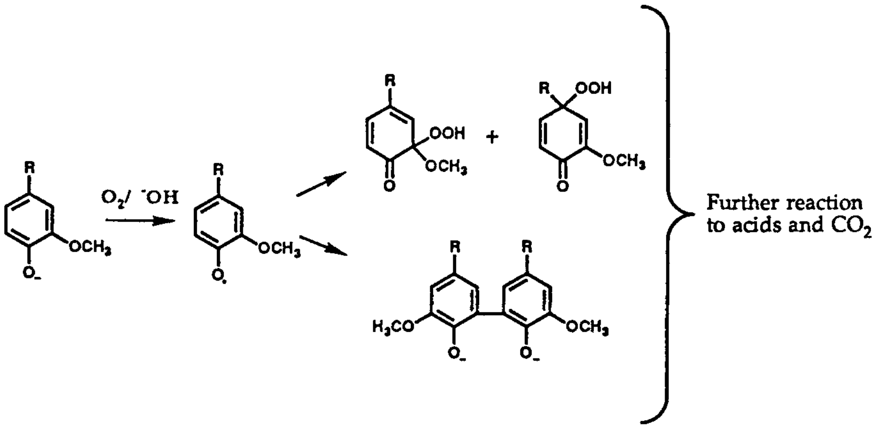

FIGURE 1. Possible Pathways for the Reaction of an Intermediate Phenoxy Radical from Phenolate Anion.[8,9,10]

present.[13,14] Addition of copper salt to the compound under a nitrogen atmosphere resulted in the formation of phenoxy radicals, measured as a larger amount of formed dimer. The oxidized state of the metal catalyst, M^+, may act as an electron transfer agent between the phenolate anion and oxygen. Under alkaline conditions and in the presence of oxygen, salts of transition metals may catalyse the phenoxy radical formation.

As the main goal is to enhance the degradation of the lignin structure without affecting the degradation of the cellulose, we were interested in finding out how transition metal ions and magnesium ions affected the degradation of some lignin model compounds under oxygen prebleaching conditions. A study of the reactions of model compounds with oxygen in the presence of metal ions might also help to explain better the mechanisms involved in oxygen prebleaching.

The aim of this work was to study the influence of transition metal ions on the degradation of some lignin model compounds during the oxygen prebleaching process in the presence and absence of hydrogen peroxide, and also to establish a comparative scale of reactivities of functional groups in the lignin structure from kinetic data of present and earlier model studies under technical conditions.

RESULTS

1. Comparison of the Reactivity of Lignin Models

The lignin model compounds which were studied for their reactivity with oxygen under alkaline conditions, i.e rate of degradation, were chosen according to their different functional groups, Figure 2.

The reactivities expressed as the rate constant of degradation of the model compounds are shown in Tables 1 and 2. The reactivity has been studied under technical oxygen prebleaching conditions, i.e. at high temperature and at a high oxygen pressure. Some of the compounds, methylcatechol (2), p-hydroxy stilbene (9), diguaiacyl stilbene (10) and enol ether (12) react very rapidly under these conditions and trials with these compounds were therefore performed under milder conditions, 40°C and at atmosphere oxygen pressure, Table 2.

The nonphenolic propylveratrol (8) is almost unreactive under oxygen prebleaching conditions which supports the hypothesis that the presence of a phenolic group is important for the reaction to occur. A hydroxyl or a methoxyl group in the ortho position to the phenolic group increases the degradation rate. For example, the rate of degradation of propylguaiacol (7) containing a methoxyl group is about 12 times faster than that of propylphenol (6), Figure 3.

This increase in degradation rate could also be seen with lignin structures such as diguaiacyl stilbene (10) and p-hydroxy stilbene (9) which react smoothly already at atmospheric oxygen pressure and low temperature.[16] The same phenomenon has earlier been shown with a tertiary butyl group in the ortho position to the phenolic group.[17,18] Two methoxyl groups adjacent to the phenolic group, i.e. syringyl, have been observed to increase the degradation rate even more.[18,19] The presence of a carbonyl or hydroxyl group in the side chain at the α-carbon has a retarding influence on the degradation rate; cf. data for vanillin (4), apocynol (5) and the phenolic β-aryl ether (13), Figure 4. Vanillin, which has a carbonyl at the α-carbon, is even more resistent towards oxygen than structures like apocynol, with a hydroxyl group at the α-carbon. A lignin model for the β-

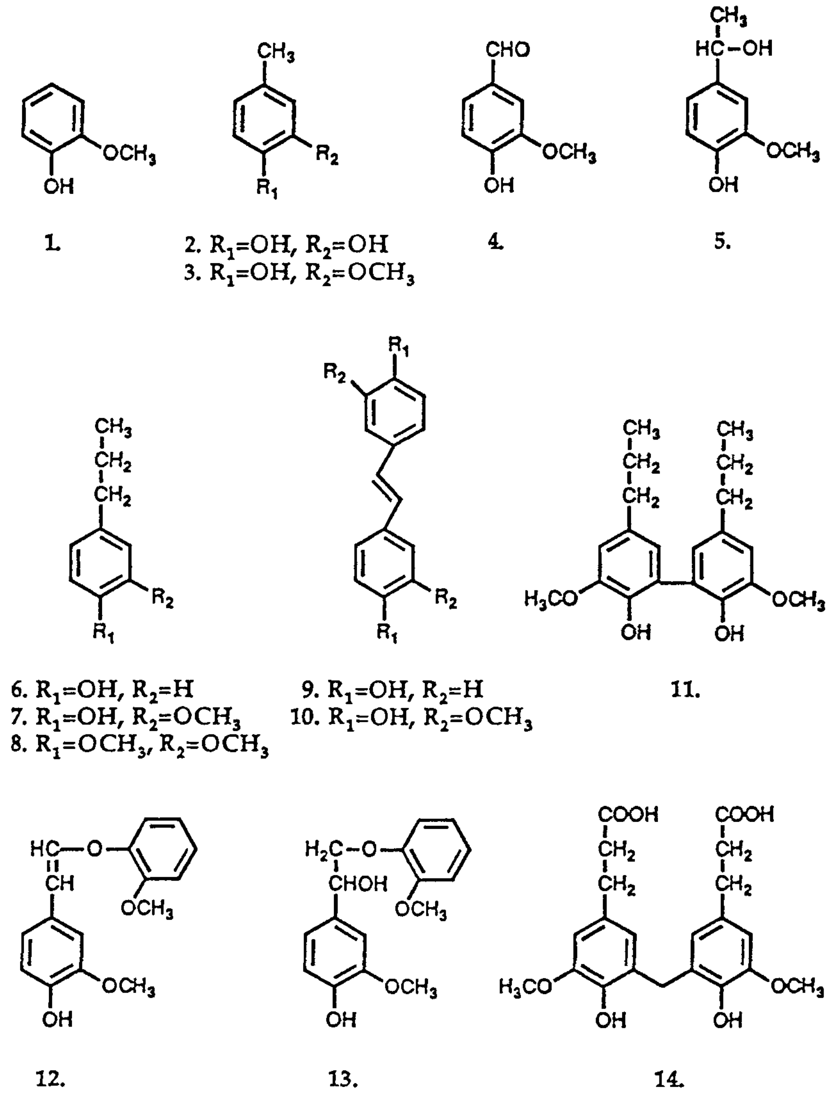

FIGURE 2. Studied Lignin Model Compounds: 1. Guaiacol 2. Methylcatechol 3. Methylguaiacol 4. Vanillin 5. Apocynol 6. Propylphenol 7. Propylguaiacol 8. Propylveratrole 9. p-Hydroxy stilbene 10. Diguaiacyl stilbene 11. Dipropylbiguaiacol 12. Enol ether 13. Phenolic β-aryl ether and 14. Methylenbisdihydroferulic acid.

TABLE I. Observed Pseudo-first-order Rate Constant (k_{obs}) in Different Runs for the Degradation of Lignin Model Compounds and the Corresponding Half-life (time to 50 % degradation) at pH 11, 100°C and 1,1 MPa O_2. For some lignin models data has been obtained earlier.

Lignin models	10^3 k_{obs} min^{-1}	Half-life min
Propylveratrol (8)	3	231
Vanillin (4)	9; 9	77
Propylphenol (6)	16; 15	45
Apocynol (5)	21	33
Dipropylbiguaiacol (11)[10]	38; 47; 38	17
Guaiacol (1)	40	18
Phenolic β-aryl ether (13)[15]	45; 48; 42; 54; 37	17
Methylenbisdihydroferula acid(14)	78	9
Propylguaiacol (7)[10]	119; 177; 192; 164	4
Methylguaiacol (3)	281	2
Enol ether (12)[15]	850	1

10. S. Ljunggren and E. Johansson, Holzforschung, 44, (4) 291 (1990).
15. S. Ljunggren and E. Johansson, Nordic Pulp Paper Res. J. 5, (3) 148 (1990).

TABLE 2. Observed Pseudo-first-order Rate Constant (k_{obs}) in Different Runs for the Degradation of Lignin Model Compounds and the Corresponding Half-life (time to 50 % degradation) at pH 11, 40°C and 0,1 MPa O_2.

Lignin model	10^3 k_{obs} min^{-1}	Half-life min
p-Hydroxy stilbene (9)[20]	121	6
Diguaiacyl stilbene (10)[15]	840	<1
Enol ether (12)[15]	5	139
Methylcatechol (2) at 0°C	180; 265	4

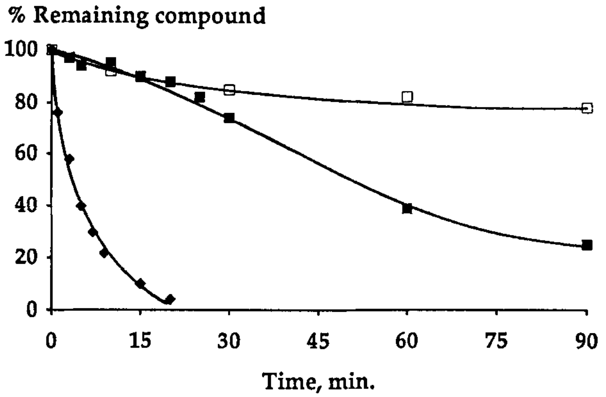

FIGURE 3. Degradation of Propylveratrol (8) □, Propylguaiacol (7) ◆ and Propylphenol (6) ■ during Oxygen Bleaching at pH 11, 100°C and 1,1 MPa O_2.

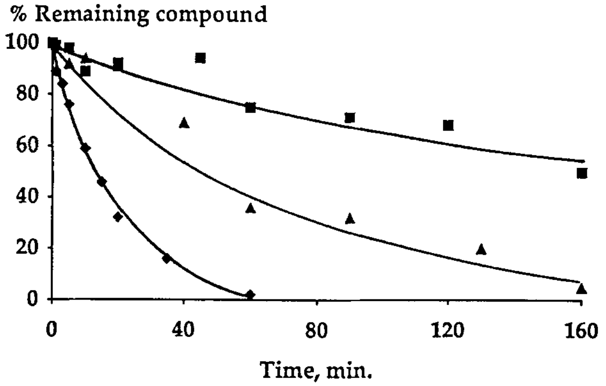

FIGURE 4. Degradation of Vanillin (4) ■, Apocynol (5) ▲ and Phenolic β-aryl ether (13) ◆ at pH 11, 100°C and 1,1 MPa O_2.

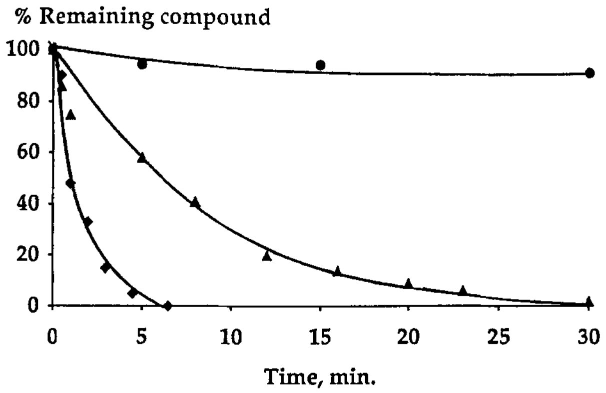

FIGURE 5. Degradation of the Enol ether (12) ●, p-Hydroxy stilbene (9) ▲ and Diguaiacylstilbene (10) ◆ at pH 11, 40°C and 0,1 MPa O_2.

aryl ether structure (with an ether bond at the β-carbon) is surprisingly more reactive than apocynol, but all three structures are still less reactive towards oxygen than a phenol with a saturated side-chain like propylguaiacol.

Unsaturated structures such as stilbenes and enol ethers are more reactive than other phenolic structures, Table 2. They react very rapidly even at atmospheric oxygen pressure, Figure 5.[15,20] The conjugated double bond in these structures is a very reactive site for oxygen species. Vanillin is formed as one main product during the degradation via a dioxetane intermediate from diguaiacyl stilbene.[21] The main degradation products, vanillin from structures like stilbenes, enol ethers and β-aryl ethers, and guaiacol from enol ethers react further only slowly with oxygen.

The presence of two phenolic hydroxyl groups in the aromatic structure also increases the reactivity considerably. Methylcatechol (2) is the most reactive compound of all these studied and the reaction is extremely fast and cannot be followed at room temperature. Only by lowering the temperature to 0°C was it possible to follow the degradation.

The behaviour of all the studied model compounds under oxygen prebleaching conditions may accordingly be summarized in a scale of

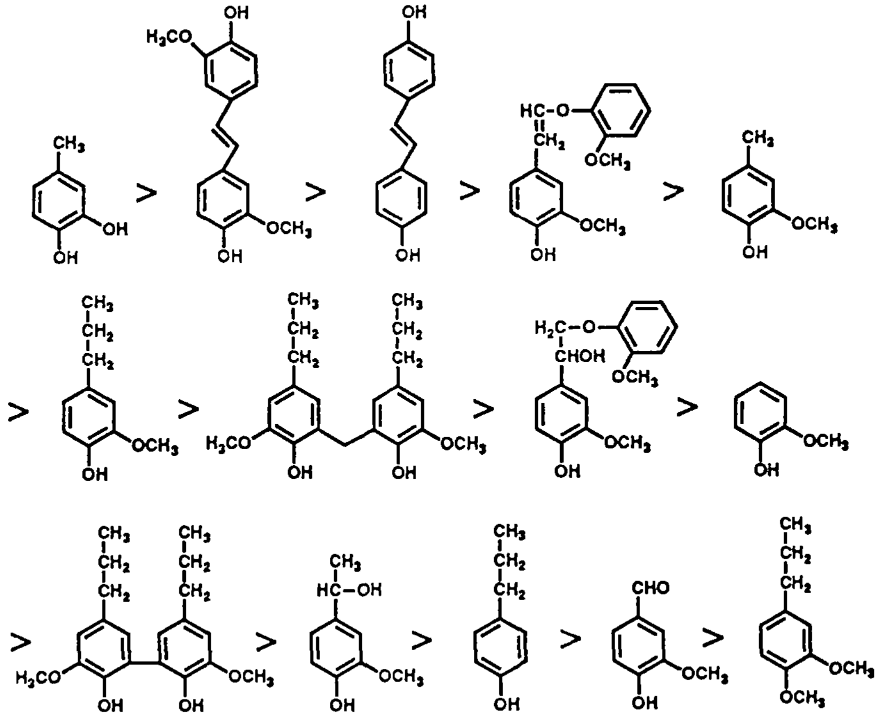

FIGURE 6. The Order of Reactivity of the Studied Lignin Model Compounds under Technical Oxygen Prebleaching Conditions.

decreasing reactivity, see Figure 6. Although there is a large difference in reactivity depending on the temperature and oxygen pressure used, it can be concluded that structures like stilbenes and cathecols react extremely rapidly under technical bleaching conditions, since they also react easily under milder conditions.

Based on these reactivity comparisons, a type of "ideal" lignin structure for the highest possible reactivity during oxygen prebleaching can be envisaged: The ideal lignin structure should contain a phenolic group with a hydroxy or a methoxy group in the ortho position and also an α-β unsaturation in the side-chain. Furthermore, this lignin should not contain or be able to form crosslinks. The formation of new crosslinks, e.g. the formation of dipropylbiguaiacol from the radical coupling of propylguaiacol, may result in a more crosslinked phenolic structure in lignin with a higher resistence towards oxygen. A consequence of this is the formation of a lignin which it may be more difficult to oxidize further after the first initial oxidation/degradation has taken place.

2. Effect of Metal Ions

The effect of transition metal ions during hydrogen peroxide bleaching is well known but little is known about their effect in an oxygen alkali system. To study the effects of transition metal ions and magnesium ions on the degradation rate, propylguaiacol (7) was chosen as a suitable lignin model since its kinetic behaviour under oxygen prebleaching conditions has been most studied.[10]

However, according to Table 3, none of the added metal ions increased the rate of degradation of the propylguaiacol. Although the kinetic data is scattered, there is in fact a tendency for the rate to be lowered by the presence of metal ions during oxygen bleaching. Catalytic amounts, 0,1 µM, of the metal salt were added to the buffer solution, Figure 7. Of the added metal ions, the copper ion decreased the rate of degradation least. At higher concentrations of the metal ions, 100 µM, only manganese ions "increased" the rate but it did not exceed the rate of the reference. The magnesium ion is known to protect the degradation of cellulose during oxygen prebleaching but this ion also reduced the rate of degradation of the model compound.

During the oxygen treatment of propylguaiacol, a small amount, 7 to 8 mol%, of dipropylbiguaiacol (11) is formed, see Table 3. The formation of dipropylbiguaiacol was however incresed in the presence of copper and manganese ions, in particular the addition of larger amounts of manganese enhanced the formation of the biphenol (11). This indicates either a higher activity of radical reactions or that more radicals are being formed in the system in the presence of certain metal ions.

A catalytic amount of copper ion, 0,1 µM, changed the pH-dependence of the rate of degradation of propylguaiacol, Figure 8. The

TABLE 3. Observed Pseudo-first-order Rate Constants (k_{obs}) in Different Runs for the Degradation of 1,0 mM Propylguaiacol (7) during Oxygen Bleaching in the Presence of Metal Ions and the Formation of Dipropylbiguaiacol (11). Conditions: pH 11, 100°C and 1,1 MPa O_2.

Metal ions	μM	10^3 k_{obs} min^{-1}	Maximum yield of 11 mol %
Reference (7)	-	x= 163 ± 30	x= 7,5 ± 0,5
Mn^{2+}	0,1	104; 75	12; 13
	10	84; 92	14; 15
	100	131; 129	22; 21
Cu^{2+}	0,1	138; 122	10; 25
	100	136	21
Fe^{2+}	0,1	92; 88	6; 11
	100	63	8
Co^{2+}	0,1	95; 107	7; 6
	1,0	74; 111	7; 7
Mg^{2+}	0,1	91	9
	100	108; 90	8; 4

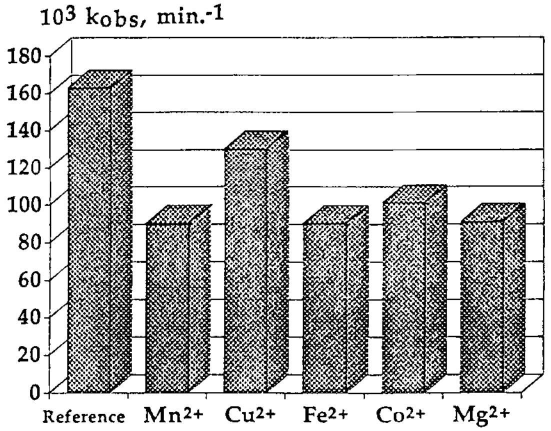

FIGURE 7. Influence of Metal Ions, 0,1 mM on the Reactivity of Propylguaiacol at pH 11, 100°C and 1,1 MPa O_2. Mean value from Table 3.

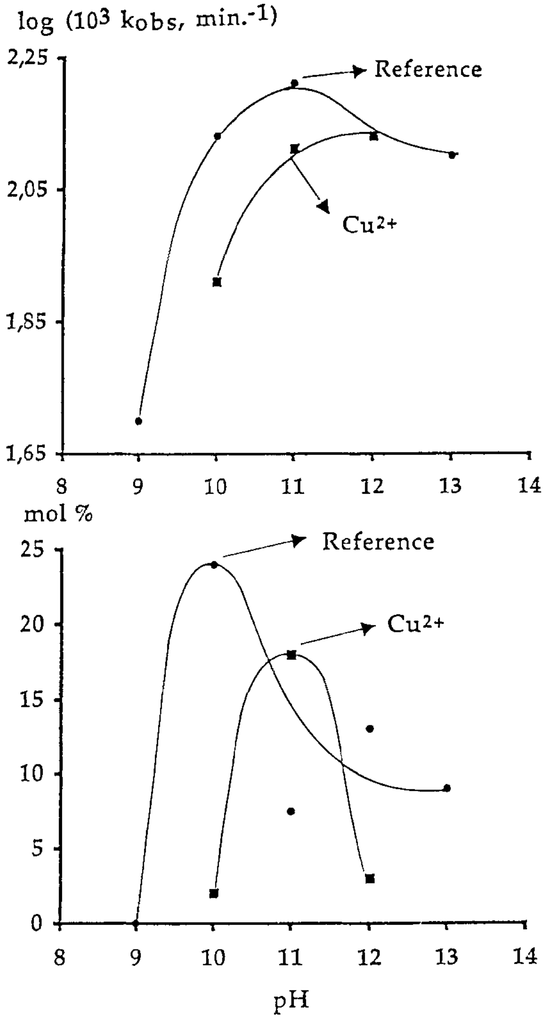

FIGURE 8. Influence of a Catalytic Amount of Cu^{2+}, 0,1 mM, on the Rate of Degradation of Propylguaiacol (upper diagram) and Formation of Dipropylbiguaiacol (lower diagram) as a function of pH. Reference Curve from reference 10.

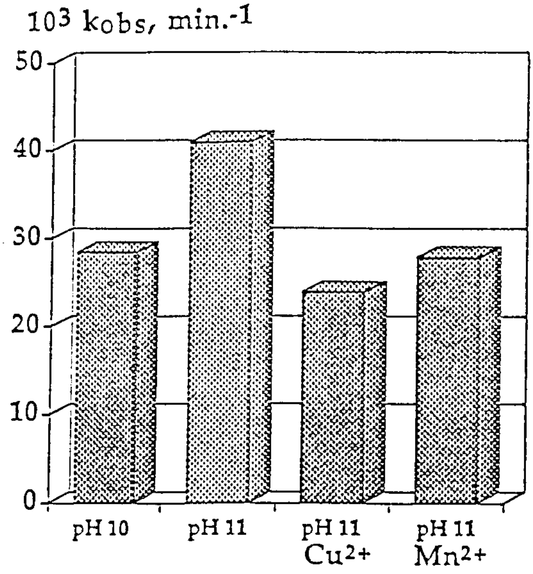

FIGURE 9. Influence of Manganese and Copper ion on the Rate of Degradation of Dipropylbiguaiacol at pH 11.

amount of dimer formed at the pH investigated was also altered. In the presence of copper ions the maximum in the degradation rate for propylguaiacol was shifted from pH 11 to pH 12, and the maximum for the formation of dipropylbiguaiacol from pH 10 to pH 11. As is clear from Figure 8 (left-hand diagram), the rate of degradation of propylguaiacol at pH 10 is the same as the rate at pH 11 and 12 in the presence of copper ions.

The degradation of dipropylbiguaiacol in the presence of manganese or copper ions present was examined and the same result was observed, a lower degradation rate than that of the reference at the same pH, Figure 9. It has earlier been shown that the rate of degradation of dipropylbiguaiacol is also very dependent on pH, the highest rate being observed in the vicinity of pH 11.[10] This results in a lower observable amount of the dimer at pH 11 as the dimer is not only formed but also degraded during the reaction. Therefore, at a given pH, the determination of the dimer is not relevant as a tool to measure the amount of phenoxy radicals formed in the presence of a transition metal, i.e. copper ions.

3. Influence of Hydrogen Peroxide

Studies of the rate of degradation of lignin model compounds during oxidation with hydrogen peroxide have shown that the rate was incresed in the presence of transition metal ions. Metal ions have been found to initiate the decomposition of hydrogen peroxide to more active species.[22]

In an oxygen alkali system it has been shown that a small amount of hydrogen peroxide (0,3 % as calculated from the initial model concentrations) is formed.[23] However, this amount does not seem to be influenced by the addition of transition metal ions, as no rate increse was observed in these studies. However, when a small amount, 9 mM, of hydrogen peroxide was added to the copper ion/buffer system under an oxygen pressure, the degradation rate was increased and no dimer could be found, Table 4. The rate was further enhanced by adding the copper salt together with hydrogen peroxide. This results in a decomposition of hydrogen peroxide to give more reactive species such as $HO\cdot$ and $O_2\cdot^-$. The addition of hydrogen peroxide to the model system without metal ions added had the opposite effect, resulting in a decreased rate of degradation but still no observable dimer. The formation of the dimer is probably suppressed by a faster reaction of the lignin model with H_2O_2. Higher amounts of added H_2O_2 had an even more pronounced effect on the degradation. A tenfold increase to 90 mM, increased the observed rate of degradation to ca. 600 x 10^{-3} min^{-1}. The addition of 0,1 μM copper to the higher amount of H_2O_2 gave a dramatic increase in the rate of degradation, >1000 x 10^{-3} min^{-1}.

The influence of hydrogen peroxide during oxygen treatment was also studied with the phenolic β–aryl ether (13). A small amount of H_2O_2 retarded the rate, but higher amounts had a positive effect on the observed rate of degradation, Figure 10. About 7 % guaiacol was formed as a degradation product, in the hydrogen peroxide system but none in the oxygen system without H_2O_2.

TABLE 4. Influence of 0,1 µM Cu^{2+} and 9 mM H_2O_2 on the Rate of Degradation of Propylguaiacol (7) and Formation of Dipropylguaiacol (11) in Different Runs at pH 11, 100°C and 1,1 MPa O_2.

Additative	10^3 k_{obs} min^{-1}	Maximum yield of 11 mol %
Reference (7)	x= 163 ± 30	x= 7,5 ± 0,5
Cu^{2+}	138; 122	10; 25
Cu^{2+}, H_2O_2[1]	438; 392	0; 0
Cu^{2+}, H_2O_2[2]	250;207	0; 0
H_2O_2[3]	92	0

1/ H_2O_2, Cu^{2+} added with sample.
2/ Cu^{2+} in buffer solution, H_2O_2 added with sample.
3/ H_2O_2 added with sample.

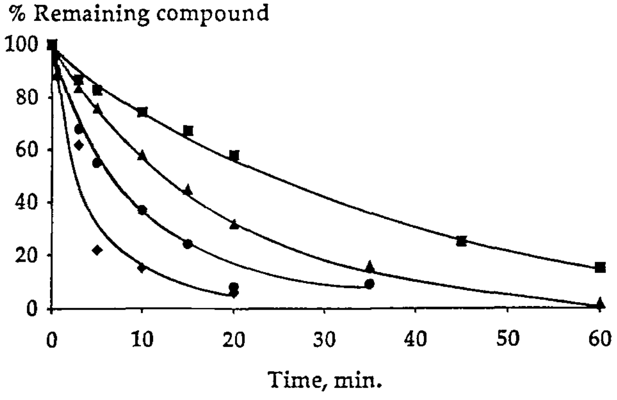

FIGURE 10. Influence of H_2O_2 on Phenolic β-aryl ether (13) at pH 11, 100°C and 1,1 MPa O_2. Reference ◆, 1,32 mM H_2O_2 ■, 13,2 mM H_2O_2 ▲, 90mM H_2O_2 X.

REMARKS AND CONCLUSION

Studies of the kinetics of softwood kraft pulp delignification during oxygen prebleaching have shown that delignification proceeds in two different phases, a fast initial phase followed by a slower final phase.[24] The heterogeneous system during pulp bleaching differs greatly from the homogeneous conditions of the present study and the lignin polymer is in general less reactive than the lignin model compounds here used.[5] Therefore it can only be assumed that structures such as stilbenes, enol ethers and catechols react during the initial phase. Structures like vanillin, guaiacol and biphenols which are formed during the oxygen prebleaching are probably not affected until the slow final phase of the bleaching is reached.

The addition of transition metal ions such as manganese and copper during oxygen bleaching results in a lower rate of degradation of propylguaiacol at pH 11, and the maximum rate of degradation is shifted to a higher pH, i.e. pH 12. One explanation of this behaviour might be the formation of a complex formed between the phenolate anion and the metal ion, which would make the oxygenation process less effective. This hypothesis of complex formation is being examined in continuing studies.

The addition of a small amount of hydrogen peroxide increases the rate of degradation of lignin model compounds such as propylguaiacol and phenolic β-aryl ethers. The addition of hydrogen peroxide accelerates the rate of degradation especially in the presence of metal ions such as copper. The decomposition products of hydrogen peroxide form more reactive species, as oxygen itself is a poor electron abstractor.

From these studies it can be concluded that the presence of transition metal ions may be of some significance in the oxygen delignification process.

EXPERIMENTAL

For measurements of the degradation of the lignin model compounds at high oxygen pressure, an autoclave with Teflon lining was used (Berghof Co., Germany). The autoclave was equipped with gas and liquid inlets and a liquid sample outlet. The solution was buffered to maintain a constant pH during the run. Buffer-titrisol (H_3BO_3 and NaOH) diluted with distilled water was used. The buffer solution was preheated and saturated with oxygen before the sample was added to the mixture. $MgSO_4$ and transition metal salts such as $MnSO_4$, $FeSO_4$, $CuSO_4$, $CoCl_2$ and $CoAc_2$ were added to the buffer solution as aqueous solutions. For convenience, the pH was measured at room temperature instead of the more reliable pOH at the actual reaction temperature. The lignin model compound, 0,1 mmol, was dissolved in a small amount of dimethylformamide, 5 % of the total amount (100 ml), to achieve a homogeneous solution with a high reproducibility.[20] At suitable intervals, samples were withdrawn and extracted in the organic solvent, CH_2Cl_2. The samples were silylated with BSTFA containing 1% TMCS prior to analysis by gas chromatography.

The lignin model compounds guaiacol (1), methylcatechol (2), methylguaiacol (3), vanillin (4), propylphenol (6) and p-hydroxy stilbene (9) was purchased from Aldrich Chemie, Germany. The lignin model compounds propylguaiacol (7)[25], guaiacyl stilbene (10)[26], dipropylbiguaiacol (11)[27], enol ether (12)[28], β-aryl ether (13)[29] and methylenbisdihydroferulic acid (14)[30] were prepared according to the literature. Apocynol (5) was prepared by reduction of acetovanillon (from Aldrich) with $NaBH_4$ and propylveratrol (8) was prepared by hydrogenation of 1,2-dimethoxy-4-propenylbenzene (from Aldrich).

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REFERENCES

1. J. Gierer, Sven. Papperstidn. 73, (18) 571 (1970).
2. S. Ljunggren, Sven. Papperstidn. 83, (13) 363 (1980).
3. G. Gellerstedt and E. Lindfors, Sven. Papperstidn. 87, (15) R115 (1984)

4. G. Gellerstedt, K. Gustavsson, E. Lindfors, Nordic Pulp Paper Res. J. 1, (3) 14 (1986)

5. S. Ljunggren, G. Gellerstedt and M. Pettersson, 6th ISWPC, Melbourne, Australia, Appita proc. 1, 229 (1991).

6. M.R. Gersmann and A.F. Bickel, J.Amer.Chem. Soc. 81, 2711 (1959).

7. M.R. Gersmann and A.F. Bickel, J.Amer.Chem. Soc. 84 , 2356 (1962).

8. K. Kratzl, J. Gratzl and P. Claus, Adv. in Chem. 59, 157 . Am. Chem. Soc. Washington D.C. (1966)

9. J. Gierer and F. Imsgard, Sven. Papperstidn. 80, (16) 510 (1977).

10. S. Ljunggren and E. Johansson, Holzforschung, 44, (4) 291 (1990).

11. L.L. Landucci and N. Sanyer, Tappi 57, (10) 97 (1974).

12. L.L. Landucci and N. Sanyer, Tappi 58, (2) 60 (1975).

13. L.L. Landucci, CPPA Trans. Tech. Sect. 4, (1), TR 25 (1978).

14. L.L. Landucci, Tappi 62, (4) 71 (1979).

15. S. Ljunggren and E. Johansson, Nordic Pulp Paper Res. J. 5, (3) 148 (1990).

16. S. Ljunggren, Pulp Paper Sci. 12, (2) J54 (1986).

17. R.C. Eckert, H. Chang and W.P. Tucker, Tappi 56, (6) 134 (1973).

18. J. Gierer and F. Imsgard, Acta Chem. Scand. B31, 546 (1977).

19. V. Sultanov and A. Wallis, 6th ISWPC , Melbourne, Australia, Appita proc. 1, 191 (1991)

20. S. Ljunggren, Nordic Pulp Paper Res. J. 5, (1) 38 (1990).

21. J. Gierer and N. Nilvebrant, Holzforschung 40, 107 (1986).

22. R. Agnemo and G. Gellerstedt, ACTA Chem. Scand. B 33, 337 (1979).

23. J.D. Freiberg, Doctors Dissertation, The Institut of Paper Chemistry, Appleton, Wisconsin (1980)

24. L. Olm and A. Teder, Tappi 62, (12) 43 (1979).

25. I.A.Pearl, J. Org. Chem. 24, 736 (1959)

26. L. Lonsky, W. Lonsky, K. Kratzl and I. Falkehag, Monatshefte für Chemie 107, 685 (1976)

27. J.C. Pew, J. Org. Chem. 28, 1048 (1963)

28. J. Ralph, Doctors Dissertation, University of Wisconsin, Madison, Wisconsin, USA (1982)

29. B. Leopold, Acta Chem. Scand. 4 1523 (1950)

30. P.K. Smith and T. McDonough, Sven. Papperstidn. 88 (12) R106 (1985)