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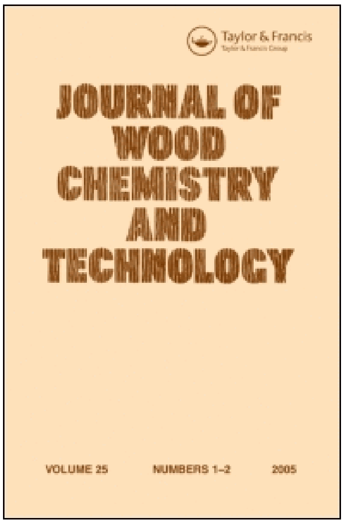

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REDOX CATALYSIS OF ALKALINE PULPING BY ORGANOMETALLIC COMPLEXES

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ABSTRACT

The effectiveness of various metal ion complexes of meso-tetra (p-sulphophenyl)porphyrin (TSPP) and 4, 4', 4", 4''' - tetrasulphophthalocyanine (TSPc) as alternatives to anthraquinone (AQ) as catalysts of alkaline pulping have been evaluated. Using lignin model compounds two of the complexes, Co-TSPP and Fe-TSPc, were found to increase the amount of β-ether cleavage more than AQ. The yield of guaiacol was also increased significantly by increasing the amount of glucose in the controls. Evaluation of the potential of Co-TSPP as a catalyst for the soda pulping of Pinus radiata showed that the complex does promote delignification but not as well as AQ. As with the AQ the pulp yields were higher than the corresponding soda controls. The increased yields, the need for a reducing source, and the formation of vinylguaiacol as a co-product in the model compound studies indicate that the complexes may operate in a similar manner to AQ.

INTRODUCTION

Although anthraquinone (AQ) is effective in remarkably small amounts in enhancing the rate of alkaline pulping, it has still not gained widespread commercial acceptance in other than a few specialised applications. This is mainly because of its cost and is not due to doubts about its performance or environmental

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acceptance. The incentive therefore still exists to find substitutes for AQ which are sufficiently cheaper or more active to make them more cost-effective.

Despite a tremendous research effort in this area on a great variety of compounds, very few have been found which match AQ's performance and none are more cost-effective. Of those compounds which do exhibit catalytic activity, most are structurally very similar to AQ and the ones which are more effective differ only from AQ by having an alkyl substituent in the 2 position.[1,2,3]

One of the fundamental problems in developing substitutes for AQ is that many of the compounds of interest are not stable under pulping conditions and even AQ itself is slowly lost during pulping by condensation with reactive components in the liquor.[4] Because of this problem, the suitability of certain organometallic complexes as pulping catalysts was evaluated since these compounds are known to undergo redox reactions and may be used under alkaline conditions.[5,6] These compounds are quite different structurally from any of the organic compounds previously evaluated and the only previous report of an organometallic complex being used as a pulping catalyst is our own work on the use of the cobalt-Schiff's base complex, salcomine, as a catalyst for oxygen pulping.[7]

This work therefore describes the first detailed study of the use of organometallic complexes as catalysts for alkaline delignification.

RESULTS AND DISCUSSION

Organometallic Compounds

The two series of complexes evaluated as pulping catalysts were the metallo derivatives of meso-tetra (p-sulphophenyl) porphyrin (TSPP) and 4, 4', 4", 4"' - tetrasulphophthalocyanine (TSPc) shown in Figure 1. These compounds, in which the macrocyclic ring is sulphonated, were chosen in order to ensure that the complexes would be soluble in the alkaline pulping liquors.

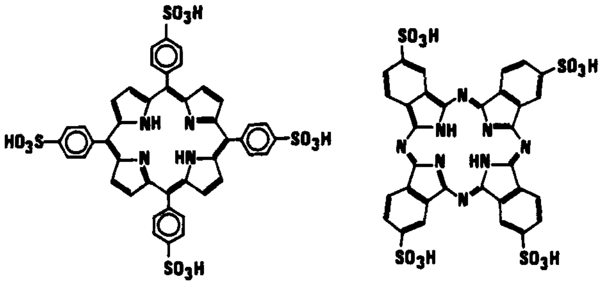
Model Compound Studies

The compounds of interest were initially screened using a model system to find which of the complexes would be the most likely to have catalytic activity. The model system chosen was the classic lignin model compound, guaiacylglycol- β-guaiacyl ether, 1, in which the extent of β-ether cleavage is determined by measuring the yield of guaiacol. This system has been used on numerous occasions and is known to give a good indication of the rate of delignification during pulping.[8]

The procedure adopted consisted of heating the organometallic compound with the lignin model compound, 1 in 1 M NaOH in the presence of 2 equivalents of glucose as a reducing source at 135°C under nitrogen in a sealed glass tube for 1 hour. The tubes were then cooled and the contents acidified, extracted, and analysed for guaiacol by g.l.c.[9]

The series of TSPP and TSPc complexes evaluated and their relative β-ether cleavage efficiencies are listed in Table 1, together with those of a control, a cobalt- dimethylglyoxime complex, a cobalt-Schiff's base complex, and AQ.

A number of the complexes gave increased amounts of β-aryl ether cleavage relative to the control and at least two of the organometallic complexes were more effective than AQ. On this basis the model compound system was then modified to determine



TSPPH$_2$ **TSPcH$_2$**

FIGURE 1: Tetrasulphonated phenylporhyrin and phthalocyanine.

TABLE 1
β-Ether Cleavage By Organometallic Complexes

Compound	% Guaiacol	Relative Efficiency[a]
Control	26	1.0
$Na_3[Fe^{III}(TSPP)].2H_2O$	25	0.96
$Cl(DMG)_2py\ Co^{III}$ [b]	27	1.04
$Na_4[Cu^{II}(TSPP)]$	27	1.04
$Na_3[Mn^{III}(TSPP)]$	28	1.08
4-OH salcomine[c]	34	1.31
$Na_3[Cr^{III}(TSPP)]$	35	1.35
$Na_4[Co^{II}(TSPc)]$	41	1.58
$Na_4[Mn^{II}(TSPc)]$	43	1.65
$Na_4[Cu^{II}(TSPc)]$	56	2.15
AQ	56	2.15
$(Na_3[Fe^{III}(TSPc)])_2O$	59	2.27
$Na_3[Co^{III}(TSPP)]$	72	2.77

[a] Ratio of catalysed guaiacol yield to control
[b] chlorobis (dimethylglyoximato) pyridine cobalt (III)
[c] N,N'-ethylenebis (4-hydroxysalicylideneiminato) cobalt (II)

the optimum catalyst concentration and the amount of glucose necessary for maximum activity of the two most active compounds, namely the Fe-TSPc and Co-TSPP complexes.

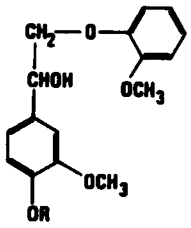
As shown in Fig. 3 the yield of guaiacol (expressed as the mole % of starting material) increases rapidly up to 10% catalyst addition and then levels off with only a slight further increase with larger amounts.

In order to determine the optimum ratio of reducing sugar to organometallic complex, the effect of increasing the amount of glucose on the efficiency of β-ether cleavage with the two complexes was determined. For completeness a series of controls with just glucose and the β-aryl ether were included. As shown in Figure 4 both of the complexes needed slightly more than two equivalents of glucose for maximum performance.

A surprising feature of these results is the large increase in the yield of guaiacol with increasing glucose in the absence of the complexes. This ability of sugars to promote β-ether cleavage appears to have been totally overlooked in the past and may have a number of implications for studies done on the chemistry of various pulping processes using lignin model compounds in isolation.

The low activity of the Co-TSPP complex in the absence of glucose is analogous to AQ in that it is only the reduced form of the complex which is active, whereas the Fe-TSPc complex appears to have considerable activity in the form in which it is added.

As expected, the Co-TSPP complex did not enhance the amount of β-ether cleavage of the methylated β-aryl ether, 2, in which quinone methide formation is blocked.



1 R = H
2 R = CH_3

FIGURE 2: Lignin model compounds.

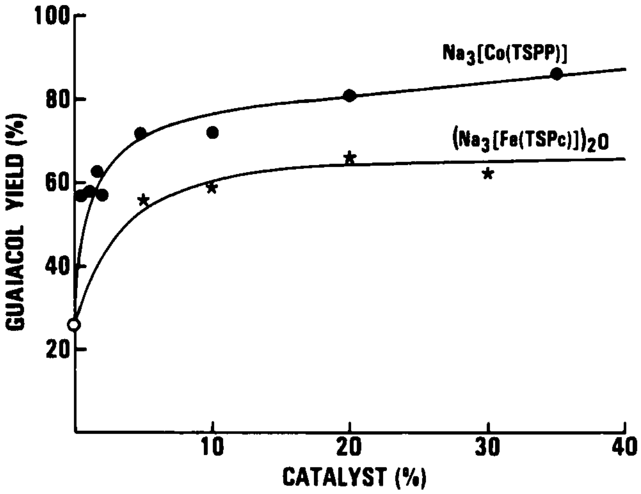


FIGURE 3: Effect of catalyst concentration on the efficiency of β-ether cleavage.

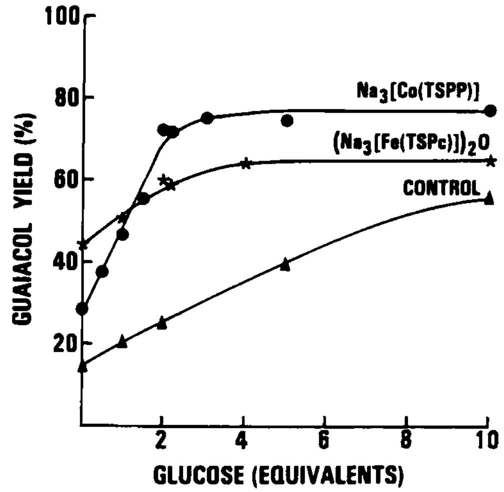


FIGURE 4: Effect of glucose concentration on the efficiency of β-ether cleavage.

Vinylguaiacol

As with AQ, cleavage of the β-aryl ether with the organometallic complexes also gave vinylguaiacol as a co-product of the reaction indicating that a fragmentation type reaction may be involved.[10] As shown in Figure 5 the amount of vinylguaiacol formed in the presence of Co-TSPP increases with increasing glucose up to 2.5 equivalents and then decreases slightly. Vinylguaiacol is also formed, but to a lesser extent, in the glucose control cooks.

Pulping Studies

The effectiveness of the most active complex, Co-TSPP, as a pulping catalyst was evaluated using a standard set of pulping conditions in which the amount of organometallic complex was varied. All pulping was done under nitrogen in a 6-unit rotary

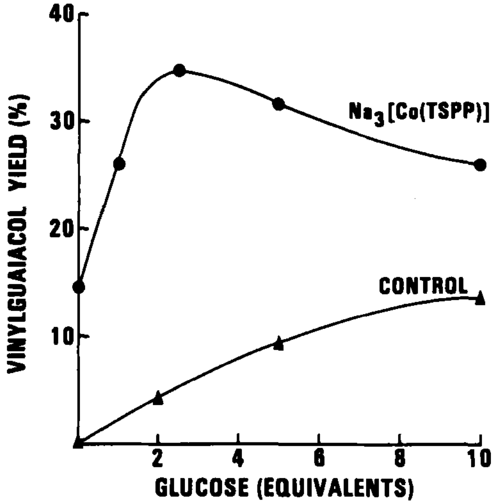


FIGURE 5: Effect of glucose concentration on the yield of vinylguaiacol.

bomb digester using Pinus radiata wood chips and a normal liquor-to-wood ratio of four to one. The quantities of complex used were calculated to be equivalent to the same number of moles of AQ where the AQ is expressed as a percentage of the weight of oven-dry wood. As with previous AQ studies, the results were expressed as the percentage reduction in Kappa number relative to the control and plotted versus the percent catalyst added on a logarithmic scale (figure 6). For comparative purposes the corresponding plot for AQ[11] is also shown. Although it is clear that the complex does enhance the rate of alkaline pulping, it is not as effective as AQ.

In contrast to the excellent reproducibility in the model compound and AQ studies, there is considerable scatter in the Co-TSPP data. This variability is highlighted by the two bracketed points in the figure with substantially better than average catalytic activity. If this variability could be

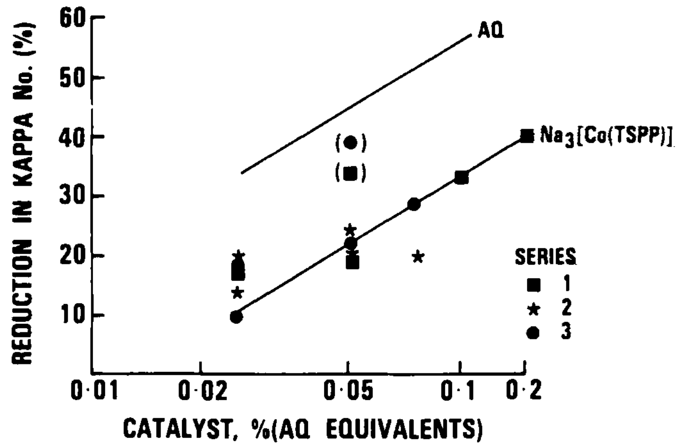


FIGURE 6: Relative effectiveness of $Na_3[Co(TSPP)]$ and AQ as pulping catalysts.

controlled the potential exists for increasing the activity of the cobalt complex. At present the reason for this variation is unknown. The most obvious explanation that it is due to the presence of residual amounts of oxygen in the digesters is unlikely as extensive precautions were taken to remove all air prior to cooking.

In addition to increasing the rate of delignification, another major benefit of using AQ is the increased pulp yield obtained as a consequence of the shorter cooking time required and the oxidative stabilisation of the carbohydrate component of the pulp. It was of particular interest to see if this was also the case with the Co-TSPP complex as a potential problem with the use of organometallic complexes is that if they are not completely stable they can release free metal ions into solution which will promote carbohydrate degradation. This was a major problem with our earlier work using salcomine where the pulps were found to have a high cobalt content and the yields were reduced because of the carbohydrate degradation which occurred.

Figure 7 shows that no such degradation occurred in the present study. All the pulps were obtained in substantially higher yields than the corresponding soda controls at the same kappa number.

The increased stability of these complexes relative to salcomine is also supported by the fact that there was no increase in the amount of cobalt on the Co-TSPP pulps.

Mechanism

On the basis of the results obtained from the model pulping reactions, it appears that β-ether cleavage is significantly promoted by the reaction of a reduced form of Co-TSPP with a quinone methide intermediate. Fragmentation of this adduct then leads to the formation of guaiacol and vinylguaiacol possibly by a mechanism of the type proposed for AQ.[10] Similarly, reaction of sugar degradation products with a quinone methide may proceed by the same reaction pathway.

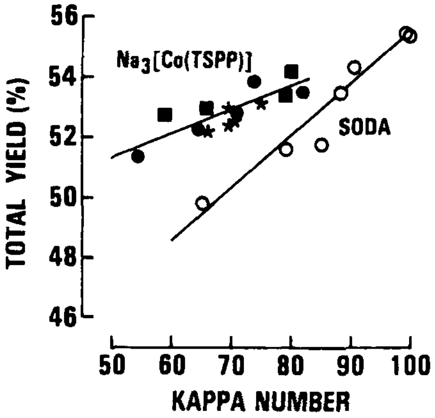


FIGURE 7: Effect of $Na_3[Co(TSPP)]$ catalysis on pulp yield.

CONCLUSIONS

This study has demonstrated that alternative redox systems quite different from AQ can be used to enhance the rate of alkaline delignification of softwoods and that the potential exists for finding organometallic compounds which may outperform AQ. Also the generality of the cleavage of β-ether bonds by reducing sugars is of fundamental significance and work in this area is continuing.

Although less effective than AQ, particularly on a weight basis, at least two of the complexes examined, namely Co-TSPP and Fe-TSPc, do appear to have the necessary prerequisites of a pulping catalyst. They have been shown to efficiently promote β-ether cleavage of lignin-like structures and are stable in alkali at high temperatures with no evidence of any carbohydrate degradation reactions promoted by uncomplexed metal ions occurring.

In many respects the organometallic compounds parallel AQ in that they are effective in small amounts, require a reducing source to generate the active form and increase pulp yields by carbohydrate stabilisation.

EXPERIMENTAL

The lignin model compounds 1-(4'-hydroxy-3'-methoxyphenyl)-1-hydroxy-2-(2-methoxyphenoxy) ethane,[12] 1-(3',4'- dimethoxyphenyl)-1-hydroxy-2-(2-methoxyphenoxy) ethane[13] and the organometallic complexes chlorobis (dimethylglyoximato) pyridine cobalt (III),[14] N,N'-ethylenebis (4-hydroxysalicylideneiminato) cobalt (II),[15] $Na_4[Co(TSPc)]$,[16] $Na_4[Mn(TSPc)]$,[16] $Na_4[Cu(TSPc)]$,[16] $(Na_3[Fe(TSPc)])_2O$,[16] $Na_3[Fe(TSPP)].2H_2O$[17,18] $Na_4[Cu(TSPP)]$,[17,18] $Na_3[Mn(TSPP)]$,[17,18] $Na_3[Cr(TSPP)]$[17,19] and $Na_3[Co(TSPP)]$[17,18] were prepared according to literature methods.

Ether Cleavage Studies

A typical model cook was as follows:

The lignin model dimer (30.0 mg), D-glucose (40.0 mg, 2.15 eq) and $Na_3[Co(TSPP)]$ (10.9 mg, 0.1 eq) were placed in a glass tube and 1.0 M NaOH (4 ml) added. The solution was purged with a stream of nitrogen for 2-3 min and then sealed (under nitrogen). The tube (usually one of a batch of ten) was then suspended in an efficiently stirred oil bath at 135°C for 1 hour. The tube was removed and allowed to cool to room temperature, opened and the contents immediately and quantitatively poured into 100 ml of 0.75 M HCl. This solution was extracted with 3 x 15 ml of chloroform. The chloroform extract was dried by filtering through anhydrous sodium sulphate and the filtrate and washings made up to 50 ml. The solution was analysed for guaiacol by g.l.c. as the TMS derivative using p-cresol as the internal standard as previously reported.[9]

Pulping Studies

Pinus radiata chips with an average basic density of 472 kg/m^3 were screened on a Williams classifier and those chips retained on 16 -and 13-mm screens were used in the present study. The chips (100 g o.d. per cook) were heated in a 6-unit polyglycol heated Stalsvets rotary digester using 20% NaOH on o.d. wood, a liquor-to-wood ratio of 4:1, and a cooking time of 90 min to 170°C and 90 min at 170°C. The organometallic complex, $Na_3[Co(TSPP)]$, was added in concentrations equivalent to 0.025 to 0.15% AQ on a mole basis, where the AQ level is expressed as the % weight of o.d. wood. Thus at the 0.1% level 0.527 g of $Na_3[Co(TSPP)]$ are required for 100 g o.d. wood. Prior to each cook the liquor in the bombs was purged with nitrogen and then each bomb sealed, evacuated and flushed with nitrogen twice.

The kappa number of the resultant pulps was determined using a half scale modification of the Tappi Standard method (T236).

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REFERENCES

1. H.H. Holton, Pulp Paper Can., 78 (10), T218 (1977).
2. W.H. Algar, A. Farrington, B. Jessup, P.F. Nelson and N. Vanderhoek, Appita, 33(1), 33 (1979).
3. R.C. Eckert and L.W. Amos, J. Wood Chem. Tech., 2(1), 57 (1982).
4. T.J. Fullerton and B.I. Fleming, Svensk Papperstid., 83 (14) 396 (1980).
5. F.H. Moser and W.H. Rhodes, Kirk Othmer Encylopedia of Chemical Technology, 3rd Ed, 17, 777 (1978).
6. The Porphyrins, Ed. D. Dolphin, Academic Press:New York (1978).
7. T.J. Fullerton and S.P. Ahern, Tappi, 61 (12), 37 (1978).
8. J. Gierer and I. Noren, Holzforschung, 34, 197 (1980).
9. T.J. Fullerton, Svensk Papperstid., 78(6), 224 (1975).
10. L.L. Landucci, Tappi, 63(7), 95 (1980).
11. T.J. Fullerton, Tappi, 62(8), 55 (1979).
12. E. Adler, I. Falkehag, J. Marton and H. Halvarson, Acta Chem. Scand., 18, 1313 (1964).
13. J. Gierer and I. Noren, Acta Chem. Scand., 16, 1713 (1962).
14. G.N. Schrauser, Inorg. Syn. Vol XI, ed. W.L. Jolly, 62 (1968).

15. H. Diehl, L.M. Liggett, G.C. Harrison, C.C. Hach and R. Curtis, Iowa State J. Sci., 22, 91 (1947).

16. J.H. Weber and D.H. Busch, Inorg. Chem., 4, 469 (1965).

17. E.B. Fleischer, J.M. Palmer, T.S. Srivastava and A. Chatterjee, J. Amer. Chem. Soc., 93, 3162 (1971).

18. C.A. Busby, R.K. DiNello and D. Dolphin, Can. J. Chem., 53 1554 (1975).

19. O. Herrmann, S.H. Mehdi and A. Corsini, Can. J. Chem., 56, 108 (1978).