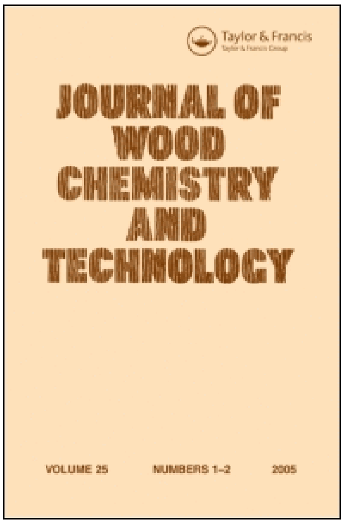

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Oxidation of Lignin Model Compounds with Cobalt-sulphosalen Catalyst in the Presence and Absence of Carbohydrate Model Compound

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ABSTRACT

A method was developed to study the activity and selectivity of potential oxygen delignification catalysts. In the method, phenolic and non-phenolic lignin model compounds (2,2′-biphenol and veratryl alcohol) were oxidised in the presence and absence of carbohydrate model compound (dextran). In this work, useful information was obtained about the catalytic performance of the water-soluble cobalt-Schiff base complex, Co-sulphosalen. Under the reaction conditions typical for industrial oxygen delignification ($T = 90°C$, $pH = 12$, $p(O_2) = 8\,bar$), Co-sulphosalen was an active catalyst in the oxidation of 2,2′-biphenol

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and veratryl alcohol. Unfortunately, it also catalyzed the depolymerization of dextran. The generation of hydrogen peroxide and the reactions of hydrogen peroxide played a central role in the Co-sulphosalen catalyzed oxidation of the lignin compounds and especially in the depolymerization of dextran. The selectivity of the delignification reactions was improved by eliminating the effect of the generated hydrogen peroxide by adding phenylglyoxylic acid to the reaction mixture.

Key Words: Oxidation; Oxygen; Catalyst; Activity, Selectivity; Model compound.

INTRODUCTION

The oxidative degradation of residual lignin of pulp with molecular oxygen (O_2) instead of chlorine-containing chemicals is an attractive alternative, not only because of environmental reasons but also because of the lower chemical costs. The complex oxidation process that occurs in oxygen bleaching includes chain reactions involving a variety of organic species derived from both lignin and carbohydrates. Selectivity, expressed as the ratio of attack on lignin to attack on carbohydrates, is far lower in oxygen bleaching than in bleaching with chlorine chemicals.[1] Attempts have been made to improve the selectivity by adding a catalyst.[2–14] Despite the very promising results achieved in the oxidation of lignin compounds,[3–8] the activity and selectivity of the catalysts proposed for oxygen bleaching of pulp have not been sufficient to encourage to the industrialization of these processes.[4,9–14]

Because the oxidation of lignin compounds gives inadequate and sometimes even misleading information about the applicability of catalysts in bleaching, and because the reactions occurring in the catalytic bleaching of pulp are complex and difficult to follow, we wished to develop a simple yet informative method to evaluate the performance of oxygen bleaching catalysts. In the method proposed, phenolic and non-phenolic lignin model compounds (here 2,2′-biphenol and veratryl alcohol) are oxidized to obtain information about the activity of the catalysts. The selectivities of the catalysts are studied by the method of Heikkilä and Vuorinen[15] in which dextran, a carbohydrate model compound, is added to the reaction mixture. The undesired depolymerization of dextran is followed by determining the changes in the viscosity of the reaction mixture during the oxidation. We assume that our oxidation mixture, containing a carbohydrate as well as lignin model compounds, simulates oxygen bleaching better than a single lignin compound. Moreover, the reactions of model compounds are easier to analyze and understand than the reactions occurring during actual oxygen bleaching. The new method is applied here to test a sulphonated cobalt-Schiff base complex, Co-sulphosalen.

The catalytic performance of Co-Schiff bases has been studied earlier in the oxidation of lignin model compounds[2–4,8,16] and in oxygen bleaching of pulp.[4,9]

EXPERIMENTAL

Procedure

All the experiments were carried out in a semi-batch glass reactor (Büchi Miniclave, 200 mL) equipped with a magnetic stirrer and a mixing baffle. Buffered alkaline water (as solvent) and dextran (if used) were added to the reactor and the reactor was placed gas-tightly in a system containing inlets and outlets both for gases and for liquids. The system was flushed two times with pressurized (8 bar) oxygen in order to remove air from the reactor. After flushing, the system was re-pressurized to 6 bar with oxygen and the reactor was placed in a water bath. After heating of 30 min, the lignin model compounds (or in some experiments just veratryl alcohol), dissolved in 5 mL of the buffer solution, were pumped (PAM syringe pump) to the pressurized and heated (90°C) reactor. The reaction time was started after the catalyst, dissolved in 5 mL of the buffer solution, was pumped to the reactor. To ensure that there was no catalyst in the pistons of the pump, 10 mL of the buffer solution was pumped to the reactor. After reactions of 5, 30, 60, and 180 min, liquid samples were withdrawn from the still pressurized (8 bar) reactor.

The reactions of the lignin model compounds were followed with a high performance liquid chromatograph (Agilent 1100 Series HPLC). The identification of compounds was based on their known retention times, and the quantitative determination was based on the prior analysis of calibration mixtures with known concentration of various components. Samples taken after reactions of 5, 60, and 180 min were cooled to 25°C and they were immediately measured for viscosity with a thermostated (at 25°C) capillary viscometer (Schott Geräte AVS 400) and for pH with a pH meter (Philips PW 9420) equipped with a glass electrode (Hamilton LIQ-glass). The experiments carried out in the absence of dextran were done in the same way as in the presence of dextran, but the viscosity of the samples was not measured.

The role of the generated hydrogen peroxide was studied by adding an equimolar mixture of phenylglyoxylic acid and sodium hydroxide (in buffer solution) to the reactor. In the experiments with added hydrogen peroxide, the hydrogen peroxide (1.5 mmol) was pumped as an aqueous solution to the pressurized reactor during the first 30 min of the reaction.

Materials

2,2′-Biphenol (99%), veratryl alcohol (3,4-dimethoxybenzyl alcohol, 96%), and dextran (1,6-α-D-glucan, average molecular weight 73,000 g/mol), which were used as model compounds, were purchased from Aldrich. Oxygen (AGA, 99.5%) was used as oxidant and the buffer solution (Merck Titrisol™ ampoules) for pH 12 as solvent.

Catalysts

Cobalt-sulphosalen (cobaltate(2-), [[3,3′-[1,2-ethanediyl*bis*(nitrilomethylidyne)]-*bis*[4-hydroxybenzenesulfonato]](4-)-N3,N3′,O4,O4′]-, disodium hexahydrate) was synthesized at the University of Helsinki. The preparation of the ligand was carried out according to Langebeek and Oehler[17] and Co-sulphosalen was prepared from the ligand and $Co(OAc)_2{*}4H_2O$ according to the method of Mukherjee and Rây.[18] The synthesized product was characterized by ESI-TOF mass spectrometry (Jeol JMS-SX102).

Calculations

Conversions of the lignin model compounds were calculated on molar basis. The conversions of veratryl alcohol and 2,2′-biphenol referred to in this study are total conversions of the compounds.

The initial oxidation rates of veratryl alcohol were calculated, following the formation of veratryl aldehyde, from Eq. (1), in which $dc(\text{veratryl aldehyde})/dt$ was calculated by fitting to the data a second-order polynomial equation presenting the concentration of veratryl aldehyde as a function of time and then calculating the derivative of the equation at time zero.

$$-r_{\text{initial,verat.alc.}} = r_{\text{initial,verat.ald.}} = \left(\frac{dc(\text{veratryl aldehyde})}{dt}\right)_{t=0} \tag{1}$$

The reaction order with respect to veratryl alcohol was determined using the method of initial rates.[19] We assume that the rate law can be presented in the form

$$-r_{\text{initial,verat,alc.}} = kc^{a}_{\text{verat.alc.},t=0} \tag{2}$$

The relative viscosity (η_r) was calculated, from the flow times measured with the capillary viscometer, from Eq. (3), in which t is the flow time of the sample and t_0 is the flow time of the solvent.

$$\eta_r = \frac{t}{t_0} \tag{3}$$

RESULTS

Catalytic Oxidation of Veratryl Alcohol

The catalytic activity of Co-sulphosalen was initially studied in the oxidation of one lignin model compound, veratryl alcohol (1–100 mmol/kg). As shown in Fig. 1, Co-sulphosalen was an active catalyst in the oxidation

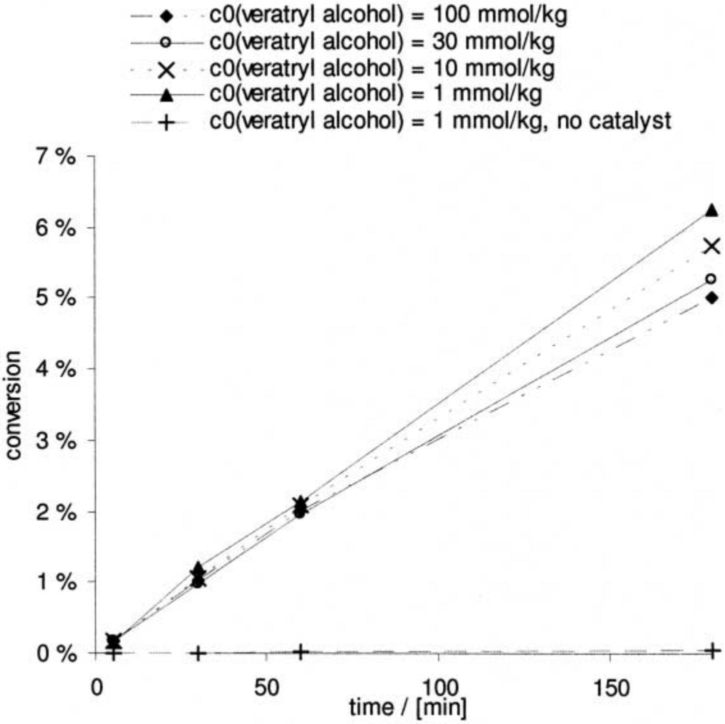


Figure 1. Conversion of veratryl alcohol as a function of time ($c_{cat.} = 0.1$ mmol/kg, $T = 90°C$, pH = 12, $p(O_2) = 8$ bar).

of veratryl alcohol. From the mass balance, it was clear that the only reaction was the oxidation of veratryl alcohol to veratryl aldehyde.

To get information about the catalytic oxidation mechanism, the order of reaction with respect to veratryl alcohol was calculated by the method of initial rates. As shown in Fig. 2, the mathematical reaction order (slope, *a*) is 0.99, i.e., the reaction follows pretty well the first-order kinetics with respect to veratryl alcohol.

Simultaneous Oxidation of Veratryl Alcohol and 2,2′-Biphenol

Because lignin is a complex molecule containing both phenolic and non-phenolic aromatic rings, the oxidation of one non-phenolic model compound, veratryl alcohol, probably does not give enough information about the activity

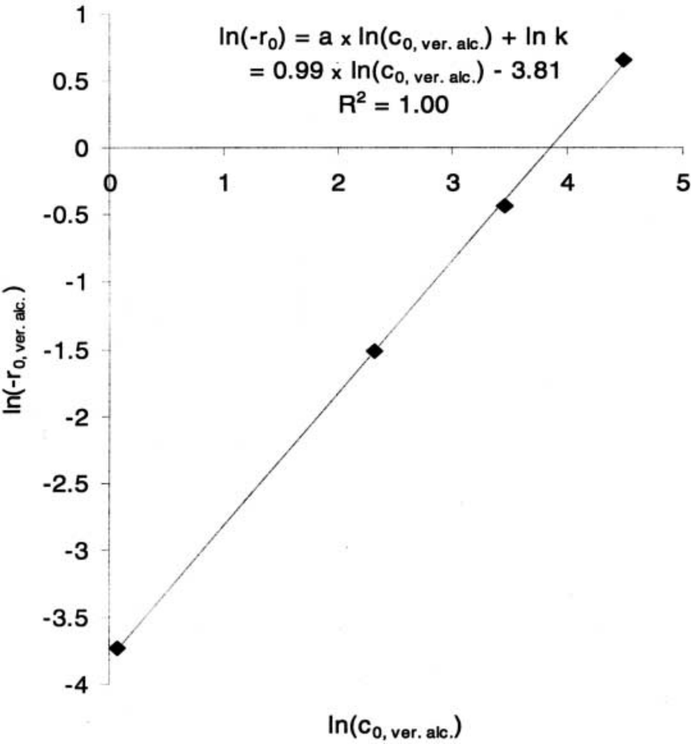


Figure 2. Plot of ln (initial oxidation rate of veratryl alcohol) versus ln (initial concentration of veratryl alcohol).

of a potential bleaching catalyst. As shown in Fig. 3, the addition of a phenolic model compound, 2,2′-biphenol (1 mmol/kg), to the reaction mixture decreases the oxidation rate of veratryl alcohol. The decrease can be explained by the competing catalytic reaction, the oxidation of 2,2′-biphenol. Because of the competing reactions, only a part of the Co-sulphosalen catalyzed the oxidation of veratryl alcohol; the rest took part in the catalytic oxidation of 2,2′-biphenol.

In the simultaneous oxidation, 2,2′-biphenol was a more reactive model compound than veratryl alcohol. The conversion of 2,2′-biphenol after reaction time of 60 min was 6.1% and after 180 min 17.1%, compared with conversions of veratryl alcohol of 1.6% and 4.9%, respectively.

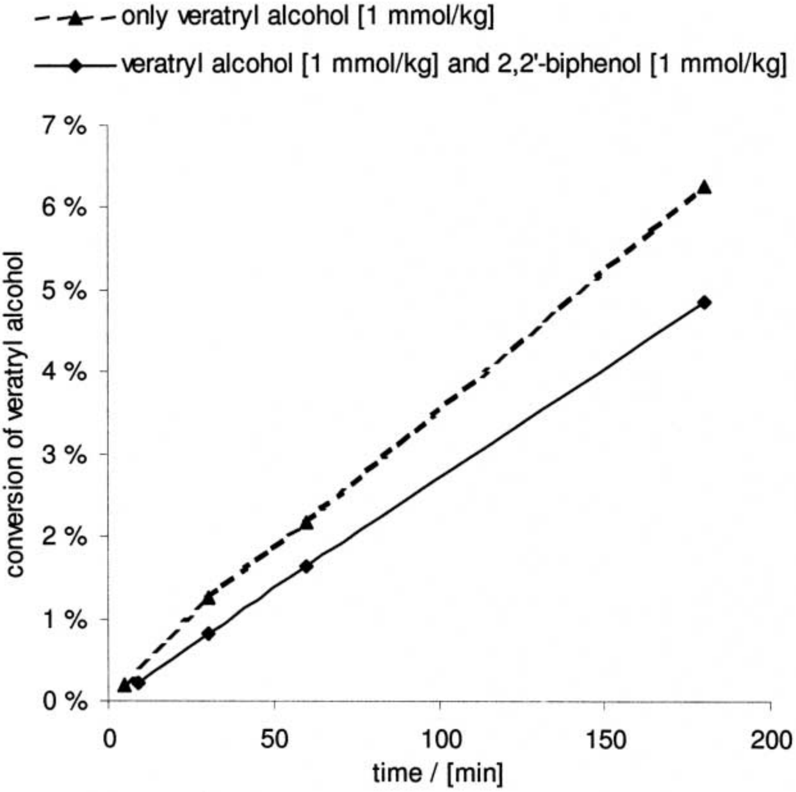


Figure 3. Conversion of veratryl alcohol as a function of time in the presence (1 mmol/kg) and absence of 2,2′-biphenol ($c_{0,\mathrm{ver.alc.}} = 1$ mmol/kg, $c_{\mathrm{cat.}} = 0.1$ mmol/kg, $T = 90°\mathrm{C}$, pH = 12, $p(O_2) = 8$ bar).

Oxidation of Veratryl Alcohol and 2,2′-Biphenol in the Presence of Dextran

The carbohydrate model compound dextran was added to the reaction mixture to study the selectivity of Co-sulphosalen. Unfortunately, the depolymerization rate of dextran increased in the presence of catalyst (Fig. 4). In addition, dextran had virtually no enhancing effect on the conversions of the lignin compounds (Fig. 5).

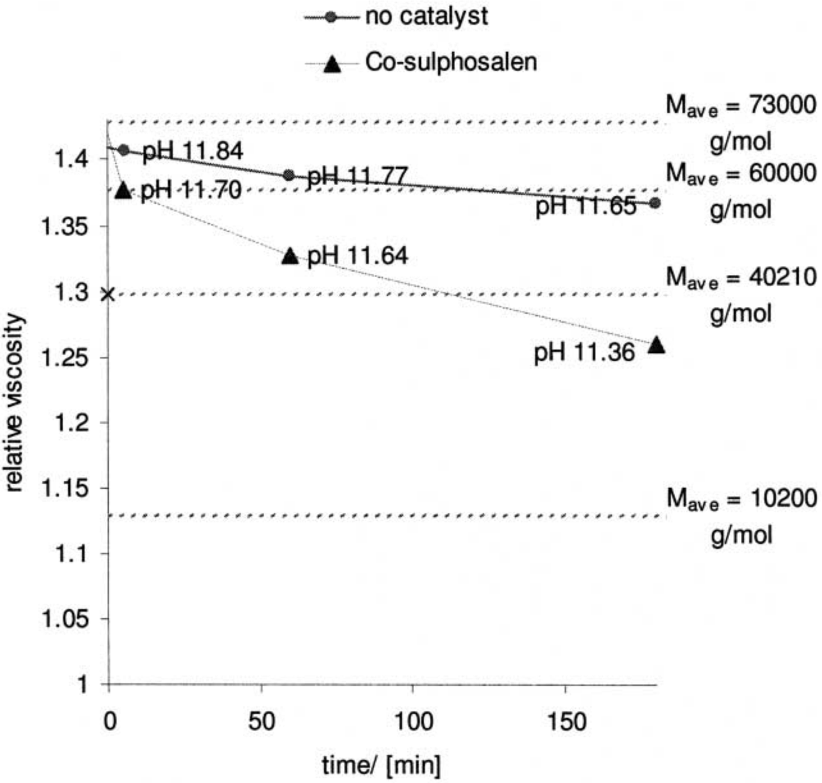


Figure 4. Relative viscosity and pH of the reaction mixture as function of time ($c_{0,\text{ver.alc.}} = 1\,\text{mmol/kg}$, $c_{0,2,2'-\text{biphenol.}} = 1\,\text{mmol/kg}$ $c_{0,\text{dextran}} = 15\,\text{g/kg}$, $c_{\text{cat.}} = 0.1$ mmol/kg, $T = 90°\text{C}$, pH = 12 $p(O_2) = 8\,\text{bar}$). The dotted horizontal lines show the relative viscosity of model samples containing dextran (15 g/kg), together with the given average molar masses.

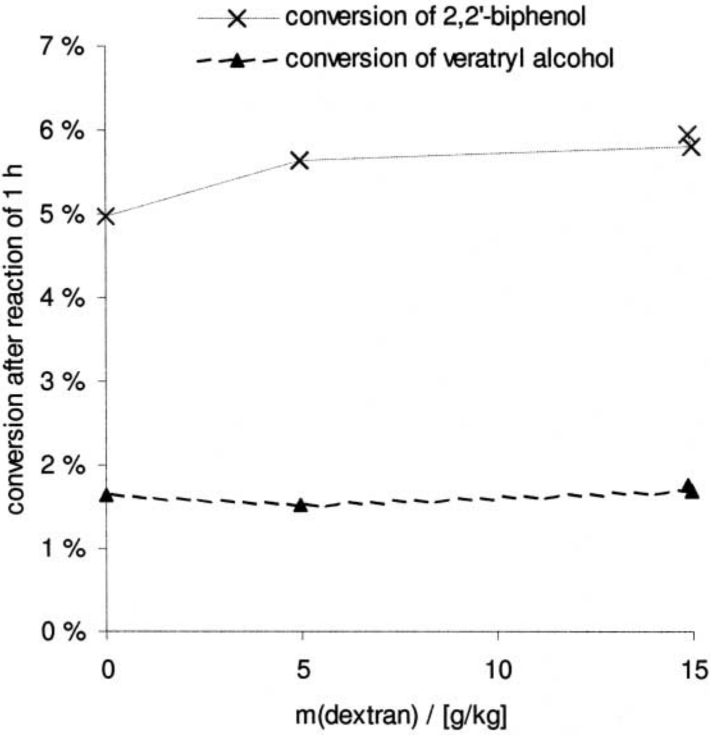


Figure 5. Conversions of veratryl alcohol and 2, 2′–biphenol after reaction of 60 min as a function of the concentration of dextran ($c_{0,\text{ver.alc.}} = 1$ mmol/kg, c_0, biphenol = 1 mmol/kg, $c_{\text{cat.}} = 0.1$ mmol/kg, $T = 90°C$, pH = 12, p(O_2) = 8 bar).

Role of Hydrogen Peroxide

In several non-catalytic studies it has been shown that hydrogen peroxide is generated during the oxidation of the model compounds with oxygen and that the generated hydrogen peroxide considerably affects the oxidation rate of these compounds.[20–22] Considering that hydrogen peroxide probably was generated in our catalytic oxidation, we repeated some of the experiments in the presence of phenylglyoxylic acid, a reagent reported to react immediately with hydrogen peroxide forming a highly unreactive product, benzoic acid.[23,24] As shown in Table 1, benzoic acid did not form in the presence of phenylglyoxylic acid and Co-sulphosalen, but it did form when veratryl alcohol was present as well. This indicates that hydrogen peroxide was

Table 1. Formation of veratryl aldehyde and benzoic acid ($c_{cat.} = 0.1\,mmol/kg$, $T = 90°C$, pH = 12, $p(O_2) = 8\,bar$).

Catalyst	$c_{0,veratryl\ alc.}$ (mmol/kg)	$c_{0,phen.glyox.acid}$ (mmol/kg)	$c_{60\ min,\ ver.ald.}$ $\Delta c_{60\ min,ver.alc.}$ (mmol/kg)	$c_{60\ min,\ benz.\ acid} =$ $-\Delta c_{60\ min,phen.glyox.acid}$ (mmol/kg)
Co-sulphosalen	0	10	—	0.01
Co-sulphosalen	10	10	0.15	0.17
Co-sulphosalen	10	0	0.21	—

generated in the catalytic oxidation of veratryl alcohol. Furthermore, it was hydrogen peroxide that was active in the oxidation of veratryl alcohol to veratryl aldehyde because the concentration of veratryl aldehyde after reaction of 60 min was lower in the presence of phenylglyoxylic acid than in its absence (Table 1). Supporting evidence for the role of hydrogen peroxide in the Co-sulphosalen catalyzed oxidation of veratryl alcohol is presented in Table 2, where addition of hydrogen peroxide is seen to significantly increase the formation of veratryl aldehyde.

Effect of Generated Hydrogen Peroxide on the Selectivity

The formation of benzoic acid in the presence of dextran and phenylglyoxylic acid without the lignin model compounds indicated that hydrogen peroxide was also generated in the catalytic interaction of Co-sulphosalen with dextran. As presented in Table 3, however, the concentration of benzoic acid (0.19 mmol/kg) after the reaction of 60 min was relatively low. Addition of the lignin model compounds in very low concentration ($c_{0,\ veratryl\ alcohol} = 0.17\,g/kg$, $c_{0,\,2,2'\text{-}biphenol} = 0.19\,g/kg$) to the reaction

Table 2. Effect of added hydrogen peroxide on the oxidation of veratryl alcohol ($c_{cat} = 0.1\,mmol/kg$, $T = 90°C$, pH = 12, $p(O_2) = 8\,bar$).

Catalyst	$c_{0.veratryl\ alc.}$ (mmol/kg)	$c_{H_2O_2}$ (mmol/kg)	$c_{60\ min,ver.ald.} =$ $-\Delta c_{60\ min,ver.alc.}$ (mmol/kg)
Co-sulphosalen	10	0	0.21
Co-sulphosalen	10	15	1.02
No catalyst	10	15	0.09

Table 3. Formation of benzoic acid in the presence of dextran and/or veratryl alcohol ($c_{\text{cat.}} = 0.1$ mmol/kg, $T = 90°\text{C}$, pH = 12, $p(O_2) = 8$ bar).

Catalyst	$m_{0.\text{dextran.}}$ (g/kg)	$m_{0,\text{ver.alc.}}$ (g/kg)	$c_{0.\text{phen.glyox.acid}}$ (mmol/kg)	$c_{60\,\text{min,benz. acid}} = \Delta c_{60\,\text{min, phen.glyox.acid.}}$ (mmol/kg)
Co-sulphosalen	15	0	10	0.19
Co-sulphosalen[a]	15	0.17[b]	10	0.36
Co-sulphosalen	0	15	10	1.27

[a] $m_{0,\,2,2'\text{-biphenol}} = 0.19$ g/kg (= 1 mmol/kg).
[b] Equals 1 mmol/kg.

mixture almost doubled the formation of benzoic acid (0.36 mmol/kg). If veratryl alcohol (15 g/kg) was present in the reaction mixture instead of the same concentration of dextran, about seven times more benzoic acid was formed (1.27 vs. 0.19 mmol/kg).

Relative viscosity did not significantly decrease in the presence of phenylglyoxylic acid (Fig. 6). This means that the depolymerization of dextran was mainly caused by the generated hydrogen peroxide. In the presence of phenylglyoxylic acid, not only the depolymerization of dextran but also the oxidation of the lignin compounds slowed down. The relative viscosities as a function of the conversions of the lignin compounds remained much higher in the presence than in the absence of phenylglyoxylic acid (Figs. 7, 8). From this we can conclude that the addition of phenylglyoxylic acid clearly improved the selectivity of the delignification reactions.

DISCUSSION

Auto-oxidation of organic substances generates hydrogen peroxide.[20–24] In this study, we showed, using the reaction of phenylglyoxylic acid to benzoic acid, that hydrogen peroxide is generated also in Co-sulphosalen catalyzed oxidation. We observed that benzoic acid forms in the presence of the model compound and Co-sulphosalen together. Figure 9 shows that in the Co-sulphosalen catalyzed oxidation of veratryl alcohol to veratryl aldehyde, benzoic acid is formed in molar ratio 1 : 1 with respect to the formation of veratryl aldehyde. From this we assume that the catalytic oxidation of veratryl alcohol to veratryl aldehyde generates hydrogen peroxide in stoichiometric ratio 1 : 1 (reaction 1) and that in the presence of phenylglyoxylic acid all

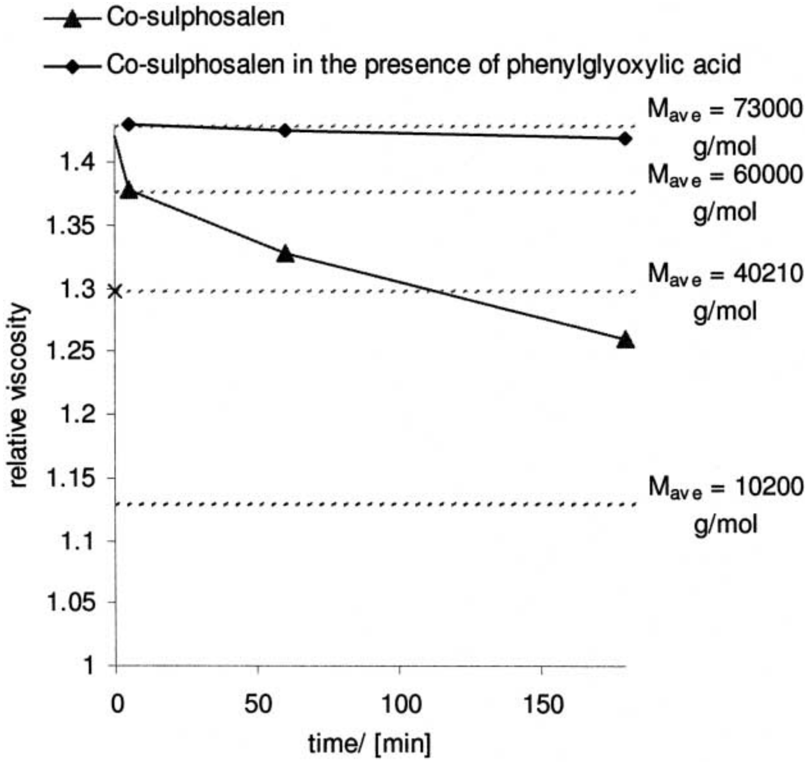


Figure 6. Relative Viscosity as a function of time in the presence and absence of phenylglyoxylic acid ($c_{0,\text{ver.alc.}} = 1$ mmol/kg, $c_{0,\text{biphenol.}} = 1$ mmol/kg, $c_{\text{cat.}} = 0.01$ mmol/kg, $T = 90°$C, pH = 12, p(O_2) = 8 bar).

the generated hydrogen peroxide is consumed by the formation of benzoic acid (reaction 2).

In a previous publication,[8] we reported that the Co-sulphosalen catalyzed oxidation of veratryl alcohol is most probably initiated by reaction steps similar to 1a–1c in Sch. 1. On the basis of the present experimental data, it seems that the oxidation and the generation of hydrogen peroxide proceed through the reaction steps 2 and 3 (Sch. 2). Similar steps to 2 and 3 were reported earlier by Drago and co-workers[25] for the oxidation of primary alcohol solvents in the presence of Co-Schiff base catalyst. A recent in situ ATR-IR spectroscopy study of Kervinen et al.[26] agrees with the oxidation mechanism proposed. In their study, the formation and the catalytic activity of Co(III)Ln–O2 · species as well as the generation of hydrogen

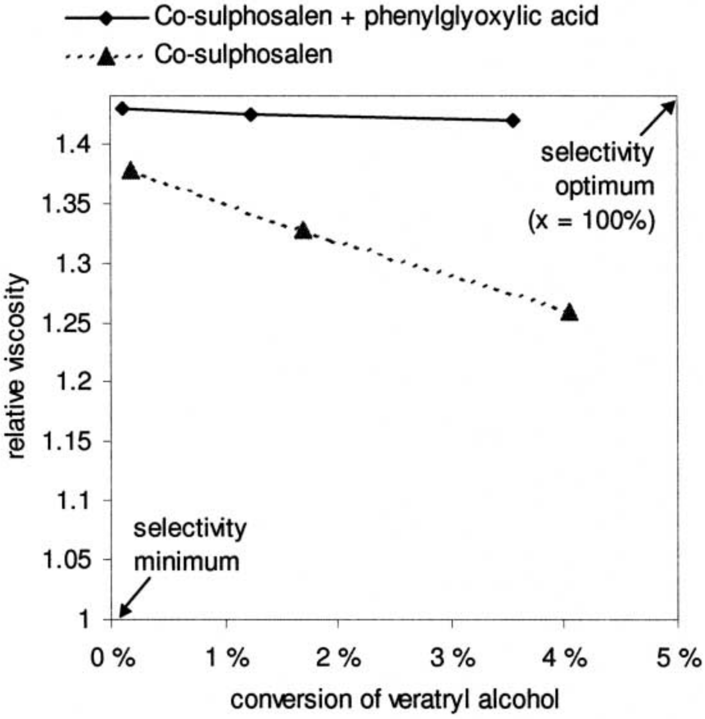


Figure 7. Relative viscosity as a function of the conversion of veratryl alcohol in the presence and absence of phenylglyoxylic acid ($c_{0,\text{ver.alc.}} = 1\,\text{mmol/kg}$, $c_{0,\,2,2'\text{-biphenol}} = 1\,\text{mmol/kg}$, $c_{0,\text{dextran}} = 15\,\text{g/kg}$, $c_{\text{cat.}} = 0.1\,\text{mmol/kg}$, $T = 90°\text{C}$, pH = 12, $p(O_2) = 8\,\text{bar}$).

peroxide were shown in the Co-salen catalyzed oxidation of veratryl alcohol in basic aqueous solution.

According to a kinetic study, the Co-sulphosalen catalyzed oxidation of veratryl alcohol follows first-order kinetics with respect to veratryl alcohol. This agrees with the reaction routes (1–3), in which one veratryl alcohol molecule is oxidized per catalytic reaction cycle.

We showed that hydrogen peroxide was formed as by-product not only in the oxidation of lignin compounds, but also in the catalytic interaction of Co-sulphosalen with dextran. In the presence of Co-sulphosalen, dextran, and phenylglyoxylic acid, the concentration of benzoic acid after reaction time of 180 min was 0.27 mmol/kg (which means that at least the same concentration of hydrogen peroxide was generated). This value is higher than the initial molar concentration of dextran ($\cong$ 0.20 mmol/kg). However, scarcely

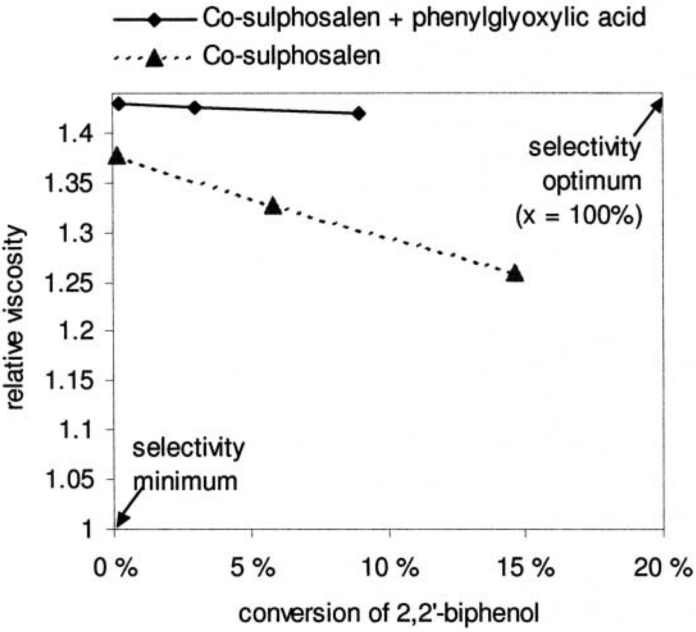


Figure 8. Relative viscosity as a function of the conversion of 2,2′-biphenol in the presence and absence of phenylglyoxylic acid ($c_{0,\text{ver.alc.}} = 1\,\text{mmol/kg}$, $c_{0,\,2,2'\text{-biphenol}} = 1\,\text{mmol/kg}$, $c_{0,\text{dextran}} = 15\,\text{g/kg}$, $c_{\text{cat.}} = 0.1\,\text{mmol/kg}$, $T = 90°\text{C}$, pH = 12, $p(O_2) = 8\,\text{bar}$).

any loss in the viscosity of the reaction mixture was observed (Fig. 6). From this we infer that Co-sulphosalen does not catalyze the depolymerization of dextran with oxygen, instead hydrogen peroxide is generated by the peeling off reaction at the end of the dextran chain. In the absence of phenylglyoxylic acid, a remarked loss of viscosity was observed (Fig. 4). Evidently, the depolymerization of dextran was caused by reaction with the generated hydrogen peroxide.

The addition of phenylglyoxylic acid clearly improved the selectivity of the Co-sulphosalen catalyzed delignification reactions (Figs. 7, 8). Relevant to this, Kontturi's[24] study without catalyst showed that the addition of phenylglyoxylic acid has a very positive effect on the selectivity of the oxygen delignification of pulp. Both in our study and Kontturi's, the phenylglyoxylic acid reacted immediately with the generated hydrogen peroxide forming benzoic acid. This prevented the reactions of hydrogen peroxide, which otherwise would have caused the loss of carbohydrates.

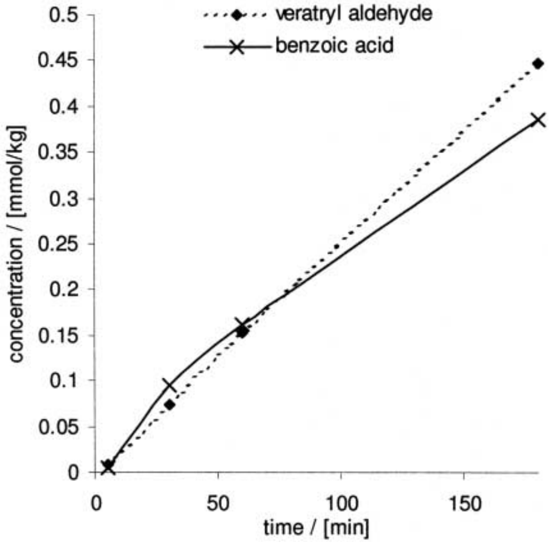
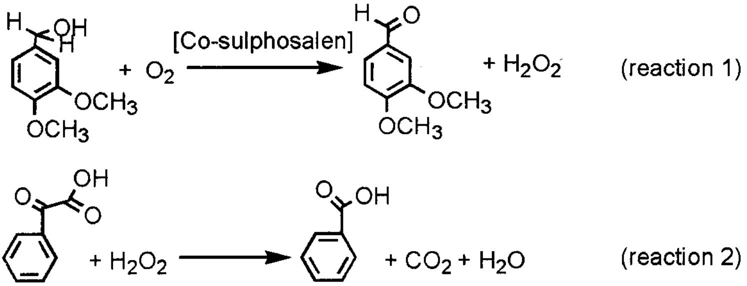


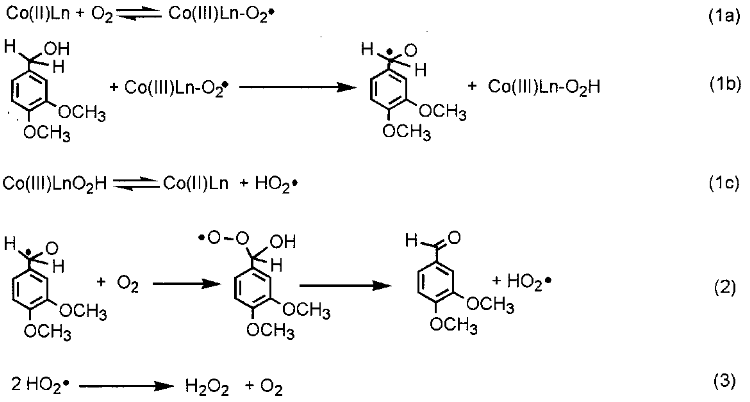
Figure 9. Concentrations of veratryl aldehyde and benzoic acid as a function of time ($c_{0,\text{ver.alc.}} = 10\,\text{mmol/kg}$, $c_{0,\text{phen.glyox.acid}} = 10\,\text{mmol/kg}$, $c_{\text{cat.}} = 0.1\,\text{mmol/kg}$, $T = 90°\text{C}$, pH = 12, $p(O_2) = 8\,\text{bar}$).

CONCLUSIONS

We have shown that the oxidation of lignin model compounds in the presence and absence of carbohydrate model compound gives very useful information about the catalytic performance of Co-sulphosalen. Under reaction conditions typical of industrial oxygen delignification ($T = 90°\text{C}$, pH = 12, $p(O_2) = 8\,\text{bar}$), Co-sulphosalen is an active catalyst in the oxidation of both



Scheme 1.



Scheme 2.

phenolic and non-phenolic model compounds. Unfortunately, it also catalyzes depolymerization of the carbohydrate compound.

The generation of hydrogen peroxide and the reactions of the generated hydrogen peroxide play a central role in the Co-sulphosalen catalyzed oxidation of the lignin compounds, and especially in depolymerization of the carbohydrate compound. The depolymerization of the carbohydrate compound can be inhibited and the selectivity of the Co-sulphosalen catalyzed delignification reactions can be improved by eliminating the effect of the generated hydrogen peroxide, here by adding phenylglyoxylic acid to the reaction mixture.

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