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TRANSITION METAL-CATALYSED OXIDATION OF LIGNIN MODEL COMPOUNDS FOR OXYGEN DELIGNIFICATION OF PULP

Väinö Sippola

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ABSTRACT

Molecular oxygen (O₂) is widely used as a delignification agent in pulp bleaching. Unfortunately, carbohydrates are attached to a greater extent during oxygen delignification than during treatment with chlorine-containing chemicals, and the delignification effectiveness of oxygen is limited to about 50% of the residual lignin in kraft pulp. This study was part of a larger project targeted at increasing the use of oxygen in delignification through application of water-soluble transition metal catalysts. The underlying idea of catalytic oxygen delignification is that the oxygen should be fixed reversibly within compounds that are capable of transferring it selectively to lignin under reaction conditions in which carbohydrates remain intact.

In this work, the catalytic performance of a cobalt-Schiff base catalyst, Co-sulphosalen, and complexes generated in situ in the presence of copper and diimine ligands such as *o*-phenanthroline and 2,2'-bipyridine was elucidated with various model compounds. Oxidation experiments were carried out in alkaline water (pH 9–12) with use of oxygen (p(O₂) 1–8 bar) as oxidant. Both Co-sulphosalen and Cu-diimines were active catalysts, increasing the oxidation rate of the phenolic model compounds 4-ethylguaiacol, guaiacol and 2,2'-biphenol. They also catalysed the oxidation of a non-phenolic model compound, veratryl alcohol.

The Co-sulphosalen-catalysed oxidation rate of the lignin model compounds was maximal around pH 11. In studies with a UV-vis spectrometer, Co-sulphosalen was found to form a new complex with an axial ligand, pyridine. Pyridine had almost no effect on the activity of Co-sulphosalen, however, and it was concluded that Co-sulphosalen forms 5-coordinated complexes, Co-sulphosalen(OH⁻) and Co-sulphosalen(pyridine), without and with pyridine, respectively. With a new HPLC method, Co-sulphosalen was shown gradually

to decompose in the alkaline reaction medium. The rate of the decomposition was independent of the catalytic oxidation reaction but increased with pH (9–12).

The concentrations of hydroxide ion (i.e., pH) and ligand also had an effect on the structure and activity of in situ formed Cu-diimines. In active forms of Cu-diimine complexes, the Cu^{2+} ion was coordinated with two ligands and one hydroxide ion. The catalytic activity of Cu-diimines could be enhanced by suitable substitution of the ligand.

Unfortunately, Co-sulphosalen, and still more so the Cu-diimines, also catalysed the oxidative depolymerisation of the carbohydrate model compound dextran. As a result of the depolymerisation, the relative viscosity of the reaction mixture decreased. Irrespective of the transition metal catalyst, both the oxidation of the lignin model compounds and the depolymerisation of dextran generated hydrogen peroxide as by-product. However, the reactions of the generated hydrogen peroxide depended on the catalyst. In the presence of Co-sulphosalen, oxygen was selectively transferred to the lignin model compounds and dextran was depolymerised only by the generated hydrogen peroxide. In the presence of Cu-diimines, the generated hydrogen peroxide was essential for the oxidation of the lignin model compounds, and the depolymerisation of dextran proceeded with oxygen as well as hydrogen peroxide.

The activities of Co-sulphosalen and Cu-diimines in the oxidation of 2,2'-biphenol and veratryl alcohol correlated well with their ability to catalyse the oxygen delignification of softwood pulp. In addition, their strong tendency to increase the depolymerisation rate of dextran was in accordance with the loss in viscosity detected in delignification experiments. The model compound studies were confirmed to be a useful way to obtain information about the reactions occurring during catalytic oxygen delignification.

PREFACE

The work for this thesis was carried out in the Laboratory of Industrial Chemistry, Helsinki University of Technology, between June 1998 and March 2005 and was part of the project "SEKAVA". The funding from the National Technology Agency of Finland (Tekes), M-real Oyj, UPM-Kymmene Oyj, Stora Enso Oyj, Andritz Oy and Kemira Oyj is gratefully acknowledged.

I am most grateful to Professor Outi Krause for her advice and support over the several years of this study. Warm thanks are extended to my co-authors Dr. Tuula-Riitta Viljava, Kati Vilonen, Professor Tapani Vuorinen, Heikki Korpi, Dr. Petro Lahtinen, Professor Markku Leskelä, Dr. Timo Repo, Ilari Filpponen and Dr. Jussi Sipilä. Further, I am grateful to project members within the funding organisations for their valuable comments and to my colleagues and the laboratory staff for creating a pleasant and relaxed working atmosphere. Sami Sauerland, Mari Puoskari, Johanna Lempiäinen and Satu Korhonen provided particularly valuable help in carrying out some of the experiments.

Finally, loving thanks to Mirja and Essi.

Espoo, March 2005

Väinö Sippola

LIST OF PUBLICATIONS

The thesis is based on the following publications (Appendices I–VI), which are referred to in the text by the corresponding Roman numerals:

- I Sippola, V., Viljava, T.-R., Vilonen, K., Krause, O., New method to follow the dimerisation reaction occurring during oxidation of 4-ethylguaiacol, *Holzforschung* **56** (2002) 601–606.
- II Sippola, V.O., Krause, A.O.I., Oxidation activity and stability of homogeneous cobalt-sulphosalen catalyst. Studies with a phenolic and a non-phenolic lignin model compound in aqueous alkaline medium, *J. Mol. Catal. A: Chem.* **194** (2003) 89–97.
- III Sippola, V., Krause, O., Vuorinen, T., Oxidation of lignin model compounds with cobalt-sulphosalen catalyst in the presence and absence of carbohydrate model compound, *J. Wood Chem. Technol.* **24** (2004) 323–340.
- IV Korpi, H., Lahtinen, P., Sippola, V., Krause, O., Leskelä, M., Repo, T., An efficient method to investigate metal–ligand combinations for oxygen bleaching, *Appl. Catal. A* **268** (2004) 199–206.
- V Sippola, V., Krause, O., Bis(*o*-phenanthroline)copper-catalysed oxidation of lignin model compounds for oxygen bleaching of pulp, *Catal. Today* **100** (2005) 237–242.
- VI Korpi, H., Sippola, V., Filpponen, I., Sipilä, J., Krause, O., Leskelä, M., Repo, T., Copper-2,2'-bipyridines: catalytic performance and structures of complexes, *Appl. Catal. A*, in press.

Väinö Sippola's contribution to the appended publications:

- I, III, V The author defined the research plan, carried out or supervised the experiments, interpreted the results and wrote the manuscript.
- II The author defined the research plan, carried out the experiments, interpreted the results and wrote the manuscript.
- IV The author defined the research plan, carried out the measurements and interpreted the results on selectivity experiments. The author defined with the co-authors the research plan on pulp bleaching experiments and wrote the final version of the manuscript with H. Korpi.
- VI The author participated in the definition of the research plan, in the experimental work (he carried out selectivity studies), in the interpretation of the results and in the preparation of the manuscript.

TRANSITION METAL-CATALYSED OXIDATION OF LIGNIN MODEL COMPOUNDS FOR OXYGEN DELIGNIFICATION OF PULP

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1 INTRODUCTION

1.1 Oxygen in the pulp industry

The production of bleached pulp has changed fundamentally during the last few decades. Traditionally, residual lignin of kraft pulp was oxidatively degraded to soluble fragments by chlorine-containing chemicals. Although chlorine and chlorine dioxide are unquestionably effective and selective, they have the serious drawback of forming toxic chlorine-containing compounds during bleaching. In an attempt to avoid the problem, various oxygen-containing chemicals, such as oxygen, ozone and hydrogen peroxide, have been tested as a replacement for chlorine-containing chemicals. Processes based on successive oxygen, ozone and hydrogen peroxide stages are in industrial operation, but they are often compromised between the yield and quality of pulp.

In modern pulp bleaching processes, oxygen delignification (i.e., lignin removal) is applied as an intermediate step between kraft pulping and bleaching. Lignin reacts with molecular oxygen mainly via ionised free phenolic hydroxyl groups. Strongly alkaline reaction medium, elevated temperature (85–115 °C) and oxygen pressure (4–8 bar) are employed to ionise the weakly acidic phenolic hydroxyl groups and achieve appreciable reaction rates. In fact, oxygen delignification is a complex oxidation process with radical chain reactions involving a variety of organic species derived from both lignin and carbohydrates (cellulose and hemicellulose). Carbohydrates are attacked to a greater extent during the course of oxygen delignification than they are during chlorination, with the result that the

delignification effectiveness of oxygen is limited to about 50% of the residual lignin in kraft pulp, after which a severe loss of carbohydrates occurs [1].

The removal of lignin and the degradation of carbohydrates during oxygen delignification have been extensively studied with model compounds representing the structural features of lignin and carbohydrates, respectively [2–5]. Often, the purpose of these model compound studies has been to find ways to increase the use of oxygen in pulp bleaching. The increased use of oxygen is attractive not only for environmental reasons but because of the lower chemical costs.

1.2 Catalytic oxygen delignification of pulp

For catalytic oxygen delignification of pulp to succeed, oxygen should be reversibly fixed in compounds capable of transferring it selectively to lignin under conditions in which carbohydrates remain intact. Another way to achieve the selectivity of oxygen delignification is to add compounds, nickel (Ni^{2+}) in the presence of tartrate, for example, capable of suppressing the degradation of carbohydrates [6–7]. These compounds are sometimes referred to as catalysts, which is misleading.

Polyoxometalates (POMs) are a large class of inorganic clusters primarily composed of early transition metal cations (most commonly W^{6+} , Mo^{6+} and V^{5+}) and oxide anions [8–9]. POM clusters typically contain from six to over 40 transition metal ions and they have a variety of different structures. In recent years, POMs have been used as catalysts in oxidation studies [10–19], since they have extensive and reversible redox chemistry and they are relatively stable and active at high temperatures. In addition, many water-

soluble POMs can be extracted from the aqueous reaction medium with organic solvents.

Selective anaerobic oxidative delignification with POMs has been reported to give good results [10–12]. Under anaerobic conditions, POMs do not, however, behave as catalysts in the usual sense; each POM is capable of extracting only one electron per reaction cycle. Because POMs are massive, an enormous amount of POMs is needed; in the studies of Weinstock *et al.* [12] the POM pulp ratio in the delignification mixture was 170:1 by weight.

The novel aerobic processes are based on the ability of POM to be readily reduced and subsequently re-oxidised [13–19]. Under aerobic conditions, the catalytic performance of POMs strongly depends on the pH. Promising activities have been achieved with use of heptamolybdopentavanadophosphate heteropolyanion $[\text{PMo}_7\text{V}_5\text{O}_{40}]^{8-}$ (HPA-5) at relatively low pH (pH 2–3) [16–18]. Unfortunately, moderate degradation of carbohydrates is unavoidable at low pH [16–18]. The use of HPA-5 at higher pH is unavoidable due to the slow delignification rate at $\text{pH} > 3$ and its partial decomposition at $\text{pH} > 4$ [16–18]. Recently, Gaspar *et al.* [19] described a series of manganese-substituted polyoxometalates $[\text{XW}_{11}\text{Mn}^{\text{III}}(\text{H}_2\text{O})\text{O}_{39}]^{n-}$ (X = B, Si or P) possessing structural stability and reasonable activity in aqueous solutions at pH 3–7. The slow re-oxidation step limited the efficiency of the delignification, however, and their application as such is not feasible.

In addition to polyoxometalates, various transition metal complexes with porphyrin, phthalocyanine, Schiff base, diimine and other nitrogen donor ligands have been studied as oxygen delignification catalysts. As in nature, the most usual metals in these enzyme-mimicking synthetic catalysts are cobalt, copper, iron and manganese.

Transition metal porphyrins are important oxygen carriers in several biological units, such as haeme and chlorophyll, and in view of this are seen as potential oxygen delignification catalysts. Zhu and Ford [20] studied the catalytic activities of several water-soluble cobalt, copper, iron and nickel porphyrins and phthalocyanines in aqueous alkaline medium and showed that cobalt phthalocyaninetetra(sodium sulphonate) (CoPcTS) has a unique ability to catalyse the oxidation of a non-phenolic lignin model compound, veratryl alcohol. CoPcTS is also highly active in the oxidation of the phenolic lignin model compound 4-hydroxy-3-methoxytoluene [20]. In the study of Perng et al. [21], manganese meso-tetra(4-sulphonatophenyl)porphyrin was the most active catalyst both in the degradation of several lignin model compounds and in the delignification of pulp. The effectiveness of all the manganese, cobalt and iron porphyrins and phthalocyanines was much less in oxygen delignification than in their model compound studies, however.

Schiff bases are compounds formed by a condensation reaction between an amine and an aldehyde. Schiff bases have an ability to coordinate various metals through imine nitrogen and another group, usually linked to aldehyde. Coordination of metals with Schiff bases stabilises their oxidation state and controls their performance in a wide variety of useful catalytic reactions. A particular class of Schiff bases, salens, are produced by combining two equivalents of salicylaldehyde with a diamine. Salens are very much like porphyrins but easier to prepare. Cobalt complex of the salen, Co-salen, has a well-established ability to reversibly bind oxygen [22]. In the studies of Meguro et al. [23–25], Co-salen was the most active Co-complex in the oxidation of the phenolic lignin model compound guaiacol. Recently, it has been shown to catalyse the oxidation of the non-phenolic model compound veratryl alcohol [26–29]. However, relatively high concentrations (0.5–2.5 wt-% of dry pulp) of Co-salen were needed for oxygen delignification of pulp [30–31]. In addition, Co-salen partly decomposed during the delignification at

120 °C and pH 8.9 and, after the decomposition, uncomplexed cobalt ions caused loss of viscosity of the pulp [31].

A constant challenge in catalyst design is to find active and selective complexes not requiring laborious synthesis. Complexes formed in situ in the presence of copper and certain simple nitrogen-containing ligands such as *o*-phenanthroline and 2,2'-bipyridine have been shown to catalyse the oxidation of a number of alcohols [32–36]. In the studies of Germer [37–39], the transition metals of wood were activated for alkaline oxygen delignification by the addition of *o*-phenanthroline. Later on, Germer found that *o*-phenanthroline and also 2,2'-bipyridine form active compounds with copper and that the addition of excess copper ions improves the delignification efficiency [40–41]. Germer carried out his delignification studies in the presence of pulp of very high lignin content (kappa number about 100) [37–41]. Recently, Argyropoulos et al. [42] showed that the complex formed by Cu^{2+} and *o*-phenanthroline is a highly active catalyst in the oxygen delignification of kraft pulp (initial kappa number 29.9), but it also causes severe loss in viscosity of the pulp.

1.3 Scope of the work

The present study was part of a project targeted at developing water-soluble catalysts for oxygen delignification of pulp. The project began with the synthesis and characterisation of several transition metal complexes, and in the preliminary studies, it was found that salen-type complexes of cobalt have a unique ability to catalyse oxidation reactions in alkaline water [26–28]. On the basis of these studies, sulphonated Co-salen (Co-sulphosalen) was chosen for detailed investigation [I–III]. Since it would be highly advantageous if

delignification catalysts were available without laborious and expensive synthetic procedures, study was also made of in situ generated complexes [IV–VI].

Catalysts suitable for oxygen delignification should be active in the oxidative degradation of lignin under reaction conditions in which the carbohydrates of pulp remain intact. The screening of transition metal complexes in actual oxygen delignification of pulp is an expensive and time-consuming way to find new catalysts, however, and in this work, the activity of potential delignification catalysts was determined as their ability to increase the oxidation rate of phenolic and non-phenolic lignin model compounds [I–VI]. The undesired depolymerisation of carbohydrates was studied using a carbohydrate model compound, dextran [III–VI]. A method was developed to study the oxidation of the lignin model compounds in the presence of the carbohydrate model compound [III]. With this method, the activity and selectivity of a catalyst candidate could be studied simultaneously [III–VI]. Only complexes that showed potential in the model compound studies were selected for catalytic delignification studies [43, IV, VI]. In addition, the model compound studies were used to find optimal process conditions for oxygen delignification and to gain better understanding of the reactions occurring during catalytic oxygen delignification [III, V].

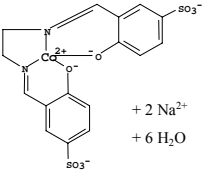
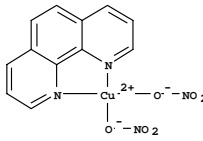

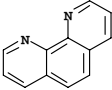
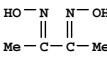
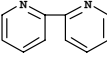
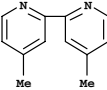
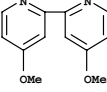
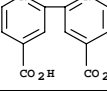
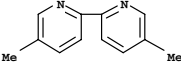
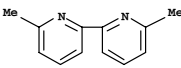
2 EXPERIMENTAL

2.1 Catalysts and chemicals

Cobalt-Schiff base catalyst, Co-sulphosalen (Table 1), was synthesised at the University of Helsinki and used as a catalyst in studies I–III. The ligand was prepared according to Langenbeek and Oehler [44] and Co-sulphosalen was prepared from the ligand and cobalt acetate tetrahydrate by the method of Mukherjee and Rây [45]. The synthesised product was characterised by electrospray ionisation time-of-flight mass spectrometry (Jeol JMS-SX102). An axial ligand, pyridine, was added to the reaction mixture to obtain Co-sulphosalen(pyridine) [II]. The reference catalyst, cobalt acetate tetrahydrate (99%), was purchased from Merck and used as received [II].

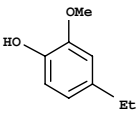
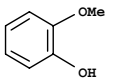
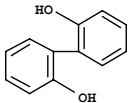
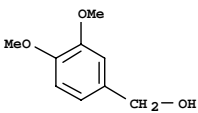
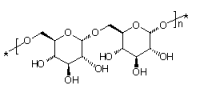
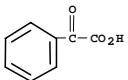
Commercial dinitrato(*o*-phenanthroline)copper (Table 1) was used as Cu-diimine catalyst. Bis(diimine)Cu complexes were generated in situ from copper sulphate (Merck, 99%) and nitrogen-containing ligands [IV, VI], or from dinitrato(*o*-phenanthroline)Cu and *o*-phenanthroline (phen) [V].

Table 1. Catalysts and ligands.

Name (alternative name)	Structure	Producer, purity	Ref.
Catalysts			
cobalt-sulphosalen (cobaltate(2-), [[3,3'-[1,2-ethanediy]bis(nitrilomethylidene)]-bis[4-hydroxybenzenesulphonato]](4-)-N3,N3',O4,O4']-, disodium hexahydrate)		University of Helsinki	I–III
dinitrato(<i>o</i> -phenanthroline)copper (dinitrato(1,10-phenanthroline)copper)		Aldrich, 96%	V
Ligands			
pyridine		Aldrich, 99.5%	II
<i>o</i> -phenanthroline (1,10-phenanthroline)		Aldrich, ≥ 99%	IV–V
dimethylglyoxime		Riedel, ≥ 99%	IV
2,2'-bipyridine		Aldrich, ≥ 99%	IV, VI
4,4'-dimethyl-2,2'-bipyridine		Aldrich, 99.5%	VI
4,4'-dimethoxy-2,2'-bipyridine		Aldrich, 97%	VI
4,4'-dicarboxy-2,2'-bipyridine		Alfa Aesar	VI
5,5'-dimethyl-2,2'-bipyridine		Aldrich, 98%	VI
6,6'-dimethyl-2,2'-bipyridine		Aldrich, 98%	VI

All lignin and carbohydrate model compounds were commercial products and used as received (Table 2). Phenylglyoxylic acid (Table 2) was used to study the role of the generated hydrogen peroxide and it was added to the reaction mixture as an equimolar mixture with sodium hydroxide (J.T. Baker, 99.8%).

Table 2. Model compounds.

Name (alternative name)	Structure	Producer, purity	Ref.
Phenolic lignin model compounds			
4-ethylguaiacol (4-ethyl-2-methoxyphenol)		Lancaster Synthesis Inc, > 98%	I
guaiacol (2-methoxyphenol)		Merck, > 99%	II
2,2'-biphenol		Aldrich, 99%	III–VI
Non-phenolic lignin model compound			
veratryl alcohol, (3,4-dimethoxybenzyl alcohol)		Aldrich, 96%	II–VI
Carbohydrate model compound			
dextran (1,6- α -D-glucan, average molecular weight 73 000 g/mol)		Aldrich	III–VI
Hydrogen peroxide indicator			
phenylglyoxylic acid		Aldrich, 97%	III, V

Buffer solutions (Merck Titrisol™ ampoules) for pH 9, 10, 11 and 12 were used as solvents. The abbreviation pH_{buff.} appearing later in this thesis indicates the pH of the buffer solution. A standard pH meter (Philips PW

9420) was used to measure pH of the reaction mixtures at room temperature. The measured pH values (later $\text{pH}_{\text{meas.}}$) correlated well with $\text{pH}_{\text{buff.}}$ if not otherwise stated. Oxygen (AGA, 99.5%) was used as oxidant.

2.2 Procedures

All the experiments (with model compounds at the Helsinki University of Technology) were carried out in semi-batch glass reactors equipped with magnetic stirrers. The reaction temperature (50–90 °C) was adjusted with water baths and the reaction time was started immediately, when model compounds, oxygen and catalyst were all in the preheated reactor. Liquid samples were withdrawn from the reaction mixture at regular intervals. In studies I–II, the oxygen pressure of the reactor (250 cm³) was one bar and the oxidant, oxygen, was bubbled constantly through the solution at a rate (2.5 cm³/min) low enough to avoid evaporation of the solvent. A Büchi Miniclave reactor (200 cm³) was used to study oxidation reactions under elevated oxygen pressure (8 bar) [III–VI].

The oxidation of the lignin model compounds was followed with use of a Hewlett-Packard 5890 gas chromatograph (GC) [I–II] and an Agilent 1100 Series high performance liquid chromatograph (HPLC) [II–VI]. In the GC and HPLC analyses, 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 components. In study I, a UV-vis spectroscopy method (Varian Cary 50 spectrometer) was developed to determine the amount of 4,4'-diethyl-6,6'-biguaiacol formed in the oxidation of 4-ethylguaiacol. A thermostated (at 25 °C) capillary viscosimeter (Schott Geräte AVS 400) was used to determine the viscosity of reaction mixtures. The structure of active catalyst complexes was studied with

standard UV-vis spectrometers (Varian Cary 50 [II] and Hewlett-Packard 8453 [VI]) and the stability of Co-sulphosalen complex with an HPLC (Agilent 1100 Series) [II]. The main decomposition product of Co-sulphosalen was identified by HPLC–mass spectrometry (Agilent 1100 Series HPLC; Micromass Quattro II triple quadrupole MS equipped with an electrospray interface) at the Technical Research Centre of Finland [II].

2.3 Calculations

Conversions and yields were calculated on molar basis. The conversion values reported in this study are the total conversions of the lignin model compounds.

The initial reaction rates (r_0) of phenolic lignin model compounds were calculated from equation (1)

$$-r_{0, \text{model compound}} = -\left(\frac{dc_{\text{model compound}}}{dt}\right)_{t=0} \quad (1)$$

in which $dc_{\text{model compound}}/dt$ was calculated by fitting to the data a second order polynomial equation presenting the concentration (c) of the model compounds as a function of time (t) and then calculating the derivative of the polynomial at time zero.

The initial oxidation rates of veratryl alcohol were calculated, following the formation of veratryl aldehyde, from equation (2):

$$-r_{\text{initial, veratryl alcohol}} = r_{\text{initial, veratryl aldehyde}} = \left(\frac{dc_{\text{veratryl aldehyde}}}{dt}\right)_{t=0} \quad (2)$$

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 polynomial at time zero.

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

$$-r_{\text{initial, veratryl alcohol}} = kc_{\text{veratryl alcohol}, t=0}^a \quad (3)$$

The relative viscosity (η_r) was calculated from the flow times measured with the capillary viscosimeter with use of equation (4),

$$\eta_r = \frac{t}{t_0} \quad (4)$$

where t is the flow time of the sample and t_0 is the flow time of the solvent.

3 ACTIVITY OF CATALYSTS

Lignin is a randomly linked, three-dimensional polymer consisting of diverse aromatic building blocks. In this work, the ability of complexes to catalyse the oxidation of lignin was studied with use of commercially available lignin model compounds. In initial experiments [I–II], monoaromatic phenolic model compounds, 4-ethylguaiacol and guaiacol, were oxidised, with the aim of showing that, in the presence of catalyst, phenolic lignin can be oxidised at a reasonable rate, at lower temperature and under lower oxygen pressure than conventionally are employed in oxygen delignification. A further challenge [III–VI] was to oxidise structures that were almost non-reactive with oxygen in the absence of catalyst. In these studies, non-phenolic veratryl alcohol and carbon-carbon bond-containing diaromatic 2,2'-biphenol were used as model compounds. The pH of the reaction medium was varied to determine optimal reaction conditions for each catalyst tested.

3.1 Activity of Co-sulphosalen

Co-sulphosalen is a synthesised complex of well-defined structure (Table 1). In Co-sulphosalen, electron attracting sulphonyl groups are added to Co-salen to enhance the catalytic activity and water solubility of the complex [26, 45]. The activity of Co-sulphosalen was studied with lignin model compounds 4-ethylguaiacol [I], guaiacol [II], 2,2'-biphenol [III] and veratryl alcohol [II–III].

3.1.1 Oxidation of phenolic model compounds

The reactivity of the phenolic lignin model compounds depended on their structure (Table 2); after non-catalytic oxidation of 330 min, the conversion of 4-ethylguaiacol was 45% at 50 °C and one bar oxygen pressure, the conversion of guaiacol was 33% despite higher (70 °C) temperature, and the conversion of 2,2'-biphenol was only 5% at 90 °C and eight bar oxygen pressure (Figure 1). Co-sulphosalen was an active catalyst, clearly increasing the conversions of these model compounds (Figure 1). A low catalyst concentration (0.01 mM) was sufficient to demonstrate the activity of Co-sulphosalen in the oxidations of 4-ethylguaiacol and guaiacol. In the catalytic oxidation of 2,2'-biphenol, the conversion after reaction of 330 min was only 25% despite a higher concentration (0.1 mM) of Co-sulphosalen.

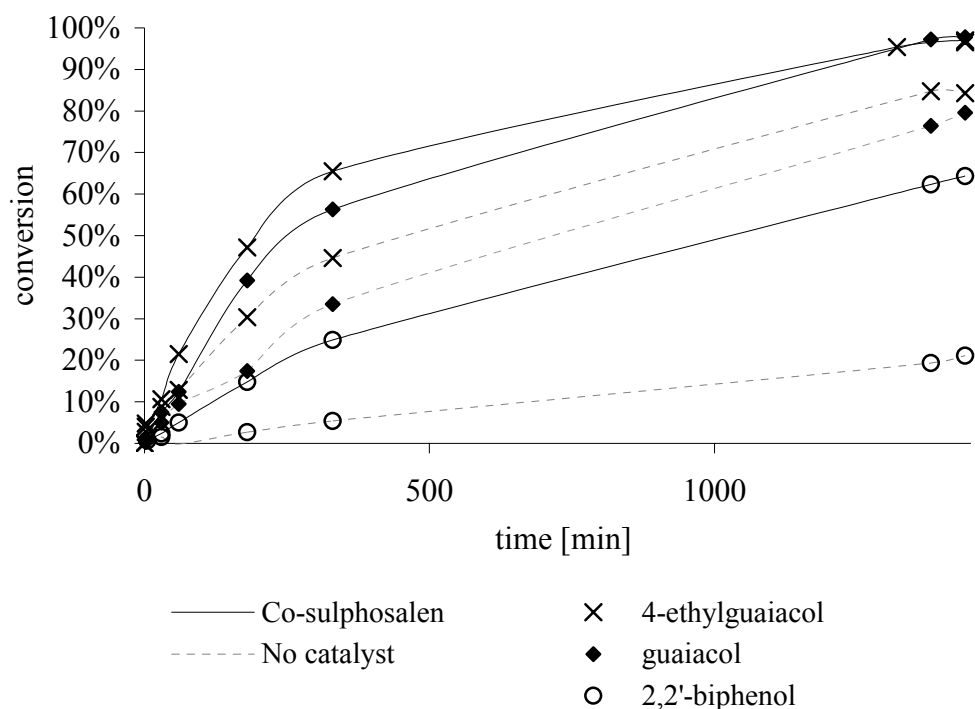


Figure 1. Effect of Co-sulphosalen on oxidation of phenolic model compounds (4-ethylguaiacol 1 mM, 50 °C, $pH_{\text{buff.}}$ 11, $p(O_2)$ 1 bar, Co-sulphosalen 0.01 mM; guaiacol 1 mM, 70 °C, $pH_{\text{buff.}}$ 11, $p(O_2)$ 1 bar, Co-sulphosalen 0.01 mM; 2,2'-biphenol 1 mM, 90 °C, $pH_{\text{buff.}}$ 12, $p(O_2)$ 8 bar, Co-sulphosalen 0.1 mM) .

3.1.2 Oxidation of non-phenolic model compound

The non-phenolic lignin model compound, veratryl alcohol, did not react to any noticeable extent in the absence of catalyst (not even under the reaction conditions typical for industrial oxygen delignification, i.e., 90 °C, $p(O_2)$ 8 bar, $pH_{\text{buff.}}$ 12 [III]). In the presence of Co-sulphosalen, however, the oxidation of veratryl alcohol (1 mM) proceeded even under one bar oxygen pressure (Figure 2). From the mass balance, it was clear that the only reaction was the oxidation of veratryl alcohol to veratryl aldehyde.

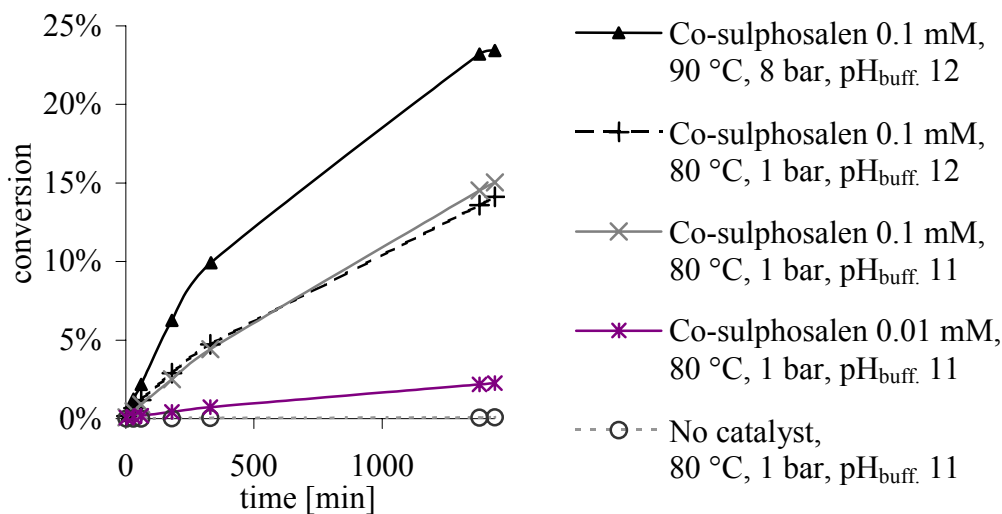


Figure 2. Effect of Co-sulphosalen on the oxidation of the non-phenolic model compound veratryl alcohol.

3.1.3 Effect of pH on activity

The Co-sulphosalen-catalysed reaction rate of the phenolic model compound 4-ethylguaiacol was even more dependent on pH than the rate in the absence of the catalyst (Figure 3a–3b) [I]. At pH_{buff.} 10, the catalytic initial rate was 2.5 times the rate in the absence of the catalyst, but at pH_{buff.} 12 there was hardly any difference between the catalytic and non-catalytic initial rates. Like the rate of the phenolic model compounds, the catalytic oxidation rate of veratryl alcohol was dependent on pH [II]. At 80 °C and one bar oxygen pressure, the initial oxidation rate of veratryl alcohol was maximal at pH 12, and the conversion was maximal after reaction of 1440 min at pH 11 (Figure 3c).

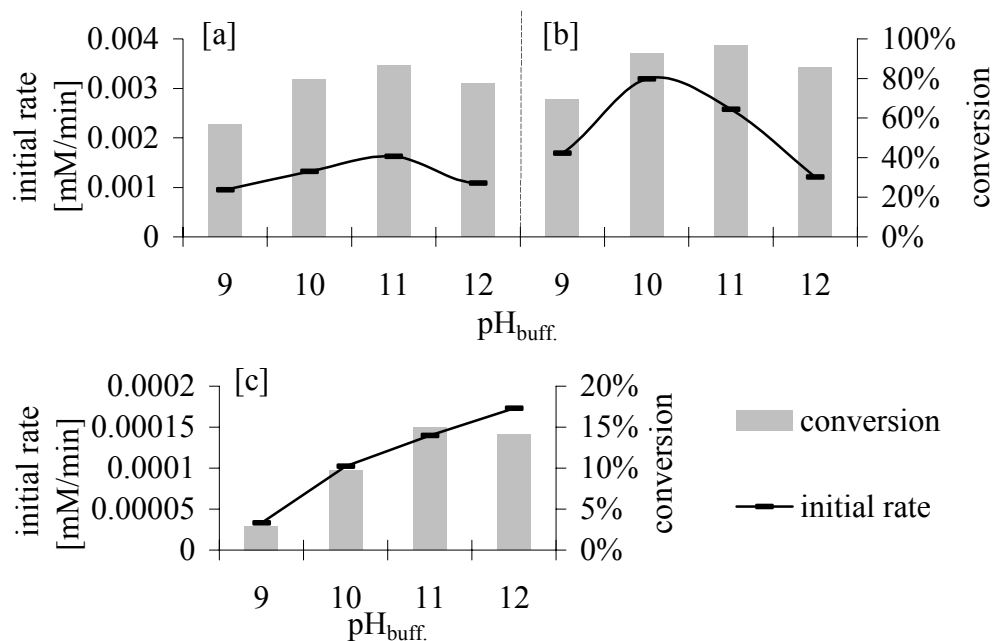


Figure 3. Effect of pH on initial rate and conversion after reaction of 1440 min in the oxidation of 4-ethylguaiaicol (1 mM) without catalyst [a] and with Co-sulphosalen (0.01 mM) [b] ($50\text{ }^{\circ}\text{C}$, $p(\text{O}_2)$ 1 bar) and in the oxidation of veratryl alcohol (1 mM) with Co-sulphosalen (0.1 mM) [c] ($80\text{ }^{\circ}\text{C}$, $p(\text{O}_2)$ 1 bar).

Moreover, both pH and Co-sulphosalen affected the products of the oxidation reaction; in the oxidation of 4-ethylguaiaicol, the yield of the dimeric product, 4,4'-diethyl-6,6'-biguaiaicol, was maximal in the catalytic experiment carried out at pH_{buff} 10 [I].

3.1.4 Effect of axial ligand on activity

The activity of cobalt Schiff base catalysts has been reported to be strongly dependent on the coordination state of the complex [46]. An attempt was made to improve the activity of Co-sulphosalen through the addition of axial ligand, pyridine [II]. In studies with a UV-vis spectrometer, Co-sulphosalen was

found to form a new complex with pyridine [II]. The activity of the Co-sulphosalen complex was not increased, however, but instead was slightly decreased with the addition of pyridine (Table 3).

Table 3. Effect of pyridine on initial rate and conversion after 1440 min for oxidation of lignin model compounds (guaiacol or veratryl alcohol 1 mM, $p(\text{O}_2)$ 1 bar, $\text{pH}_{\text{buff.}}$ 11) [II].

Model compound	T / [°C]	c(catal.) / [mM]	c(pyridine): c(catalyst)	Initial rate / [mM/min]	Conversion after 1440 min
guaiacol	70	0.01	No pyridine	$2.1 * 10^{-3}$	97%
guaiacol	70	0.01	1:1	$1.8 * 10^{-3}$	97%
guaiacol	70	0.01	10:1	$1.9 * 10^{-3}$	97%
guaiacol	70	0.01	100:1	$1.8 * 10^{-3}$	98%
veratryl alcohol	80	0.01	No pyridine	$0.022 * 10^{-3}$	2.3%
veratryl alcohol	80	0.01	10:1	$0.022 * 10^{-3}$	1.9%
veratryl alcohol	80	0.1	No pyridine	$0.14 * 10^{-3}$	15.1%
veratryl alcohol	80	0.1	10:1	$0.13 * 10^{-3}$	14.0%

In study II, it was reported that, in the absence of pyridine, Co-sulphosalen is a 4-coordinated complex. Recently, in attenuated total reflectance infrared spectroscopy studies, Kervinen et al. [29] showed that hydroxide ion has an ability to attach as axial ligand to unsubstituted Co-salen. Although Co-sulphosalen clearly formed a new complex with pyridine, it is highly likely that the coordination state of Co-sulphosalen is independent of the presence of pyridine and that 5-coordinated complexes, Co-sulphosalen(pyridine) and Co-sulphosalen(OH⁻), are generated both in the presence and in the absence of pyridine. The presence of the 5-coordinated complex in the absence of pyridine could also explain why pyridine had so slight an effect on the activity of Co-sulphosalen.

3.1.5 Effect of stability of complex on activity

The reference catalyst, cobalt acetate, was not at all active in the oxidation of veratryl alcohol and even in the optimal case it increased the oxidation rate of guaiacol only slightly [II]. This poor result shows the enhancing effect of the sulphosalen ligand on the activity of cobalt. A new HPLC method to study the stability of the active Co-sulphosalen complex was developed [II]. According to HPLC analyses, the concentration of Co-sulphosalen catalyst clearly decreased, however, and the concentration of its decomposition product, 2-hydroxy-4-(sodium sulphonate)benzaldehyde, increased with time at 80 °C and one bar oxygen pressure. It was assumed that 2-hydroxy-4-(sodium sulphonate)-benzaldehyde was formed by the alkaline hydrolysis of the imine structures of Co-sulphosalen. The rate of the hydrolysis reaction was independent of the presence of the axial ligand, pyridine, but it increased with pH (9–12). In the catalytic oxidation of veratryl alcohol (at 80°C and pH_{buff.} 11), the concentration of Co-sulphosalen after a reaction time of 1440 min was about 70% of its initial value. However, the decomposition rate of Co-sulphosalen was virtually the same in the reference experiment carried out in the absence of veratryl alcohol, from which it was concluded that the decomposition was independent of the catalytic oxidation reaction. Although inadequate stability is a well-recognised problem with Co-Schiff base complex catalysts [31], this study provided a lot of new information about the kinetics of the decomposition.

3.2 Activity of in situ generated Cu-diimines

Development of new complexes by traditional synthetic methods is laborious, and even then it is likely that the synthesised complex does not possess appropriate catalytic properties, such as adequate activity, selectivity and

stability. New efficient experimental methods, such as combinatorial chemistry, are useful in catalyst development. A simple and efficient parallel screening method was recently developed at the University of Helsinki to study the catalytic activities of in situ generated complexes [47]. The method was applied to evaluate the activity of 189 metal–ligand combinations in the presence of metal and ligand in molar ratio of 1:2 [IV]. Alkaline water-soluble nitrogen-containing mono- and heterocycles emerged as leading ligand structures. The series was supplemented with some non-cyclic nitrogen-containing and cyclic oxygen- or sulphur-containing ligands that were able to form metal complexes in situ. In this preliminary study, all combinations containing manganese, iron, cobalt, zinc, magnesium, aluminium or calcium as metal centre were inactive in the oxidation of veratryl alcohol, while the copper complex of *o*-phenanthroline (phen) was the most active in situ generated catalyst, followed by the copper complexes of 2,2'-bipyridine (bipy) and dimethylglyoxime [IV].

The in situ generation of these active complexes was confirmed in subsequent studies [IV–V]. As shown in Figure 4, dinitrato(*o*-phenanthroline)Cu (Table 1) and the complex generated in situ from copper sulphate and phen in molar ratio of 1:1 are equally active in the oxidation of veratryl alcohol to veratryl aldehyde. Likewise, there was no difference in activities between complexes generated in situ from dinitrato(*o*-phenanthroline)Cu and phen in molar ratio of 1:1 and from copper sulphate and phen in molar ratio of 1:2. However, the complexes generated in the presence of Cu²⁺ and phen in molar ratio 1:2 were considerably more active than those generated in the presence of Cu²⁺ and phen in molar ratio 1:1 (Figure 4). The in situ generated Cu²⁺ complexes of phen, bipy and dimethylglyoxime were also shown to catalyse the oxidation of the phenolic model compound 2,2'-biphenol.

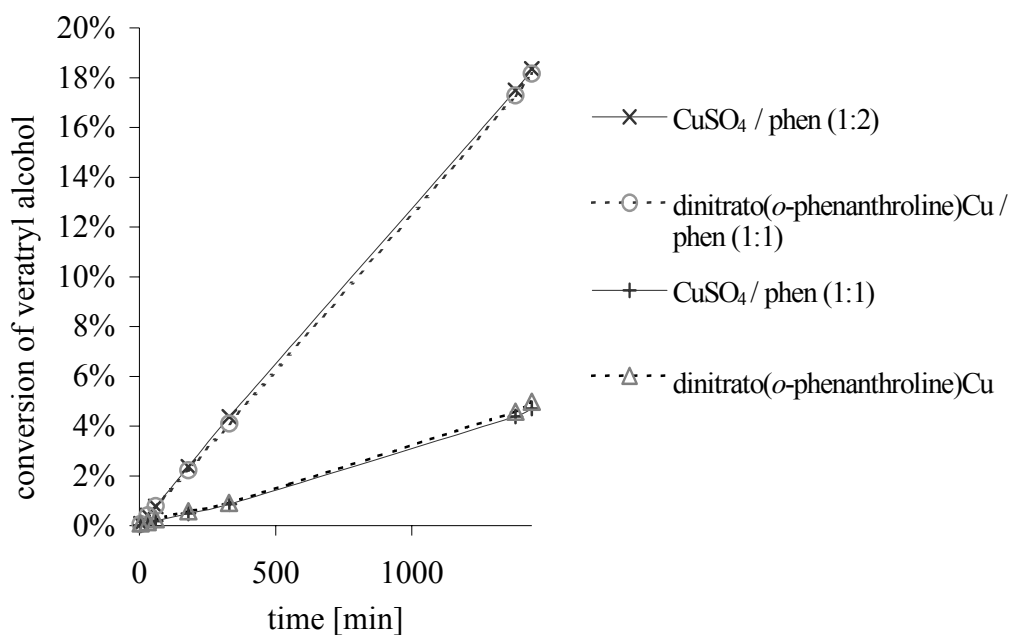


Figure 4. Oxidation activity of complexes formed in the presence of copper (0.1 mM) and phen (90 °C, $p(\text{O}_2)$ 8 bar, $\text{pH}_{\text{buff.}}$ 12).

3.2.1 Structure of active Cu-diimine complexes

In situ generation of Cu-diimine complexes is fast and reversible [48–49]. We used UV-vis spectroscopy to study the generation of various species from Cu^{2+} , bipy and hydroxide ion in water and calculated their distributions using the stability constants (Figure 5) determined by Fábíán [48]. The results of UV-vis spectroscopy and veratryl alcohol oxidation studies, together with the calculated distributions of the species, allowed us to solve the structure of the in situ generated active complex [VI]. In the oxidation of veratryl alcohol with simultaneously varying pH and concentration of bipy, the maximum conversion (67%) was obtained at initial pH 12 (non-buffered) in the presence of Cu^{2+} and bipy in molar ratio of 1:8. The calculated percentage of copper as $\text{Cu}(\text{bipy})_2\text{OH}^+$ had a maximum (70%) at pH 11 in the presence of Cu^{2+} and bipy again in molar ratio of 1:8. From these results (taking into account that

pH decreases during the oxidation), it was concluded that $\text{Cu}(\text{bipy})_2\text{OH}^+$ is the active complex in the oxidation [VI]. On the basis of the oxidation and UV-vis studies, the corresponding $\text{Cu}(\text{phen})_2\text{OH}^+$ species was assumed to be the active complex that forms in situ in the presence of Cu^{2+} , phen and hydroxide ion [50].

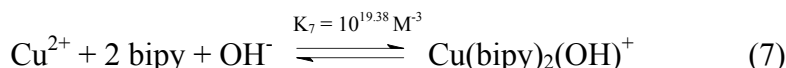
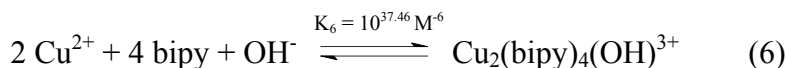
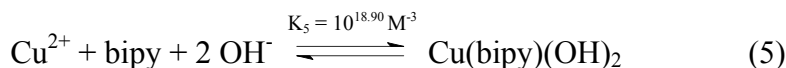
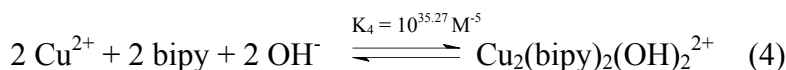
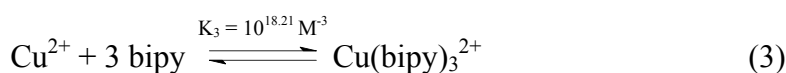
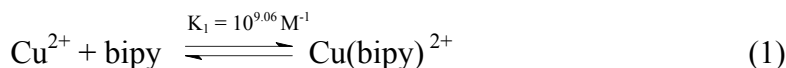


Figure 5. Generation of species in the presence of Cu^{2+} and bipy in aqueous alkaline reaction medium. Stability constants (K_1 – K_7) were determined by Fábán [48].

3.2.2 Activity enhancement by substitution of the diimine ligand

The catalytic properties of transition metal catalysts can be modified by adding substituents to the ligand structure [51–53]. In study VI, 2,2'-bipyridine ligand was modified in an attempt to improve the activity of the in situ generated Cu^{2+} complexes. In the oxidation of veratryl alcohol, the in situ generated Cu^{2+} complexes of 4,4'- and 5,5'-dimethyl- and 4,4'-dimethoxy-2,2'-bipyridine (Table 1) were more active catalysts than the Cu^{2+} complexes of the unsubstituted bipy. Changing the pH and the copper-to-ligand molar ratio had a similar effect on the catalytic activities of Cu^{2+} complexes of unsubstituted bipy and 4,4'- or 5,5'-disubstituted 2,2'-bipyridines. In addition, UV-vis

studies in the presence of 4,4'-dimethoxy-2,2'-bipyridine (dOMebipy) indicated that the chelation of this substituted ligand with Cu^{2+} is closely similar to the chelation of bipy. Evidently, in the presence of dOMebipy and Cu^{2+} , the active complex has the structure $\text{Cu}(\text{dOMebipy})_2\text{OH}^+$. This complex was the most active of the substituted catalysts [VI].

3.3 Comparison of activities

The complex generated in situ in the presence of copper and *o*-phenanthroline in molar ratio of 1:2 (later bis(phen)Cu) was the most active complex in the primary screening of the metal–ligand combinations [IV], and it was chosen together with Co-sulphosalen for the detailed study of activity (Figure 6). In the presence of low initial concentration of veratryl alcohol (1 mM), Co-sulphosalen was a more active catalyst than bis(phen)Cu (Figure 6) [III, V]. However, in the presence of bis(phen)Cu, the conversions increased dramatically with the initial concentration of veratryl alcohol, and in the presence of high initial concentration (100 mM), the bis(phen)Cu-catalysed reaction rate was more than seven times the Co-sulphosalen-catalysed reaction rate.

From the mass balance, it was deduced that, independent of the catalyst, the oxidation of veratryl alcohol to veratryl aldehyde was virtually the only reaction. In the presence of bis(phen)Cu and the highest concentration (100 mM) of the alcohol, however, a trace amount of veratric acid was detected after reaction of 180 min. A possible mechanism for the formation of veratric acid is a base-catalysed Cannizzaro reaction of two veratryl aldehyde molecules to form veratric acid and the original veratryl alcohol [54–55].

Information about the mechanisms of the catalytic veratryl alcohol oxidation was obtained by determining reaction orders by the method of initial rates. Figure 6b shows that Co-sulphosalen-catalysed oxidation followed fairly well the first-order kinetics with respect to veratryl alcohol [III]. In the bis(phen)Cu-catalysed oxidation the order of the reaction was 1.7 (Figure 6b) [V]. This order is close to the reaction order determined by Vieth [56] for the oxidation of veratryl alcohol with the complex generated in situ in the presence of Cu^{2+} and bipy in molar ratio 1:2. In his study, the order was 1.6 at $\text{pH}_{\text{buff.}} 10$ and 1.5 at $\text{pH}_{\text{buff.}} 11$.

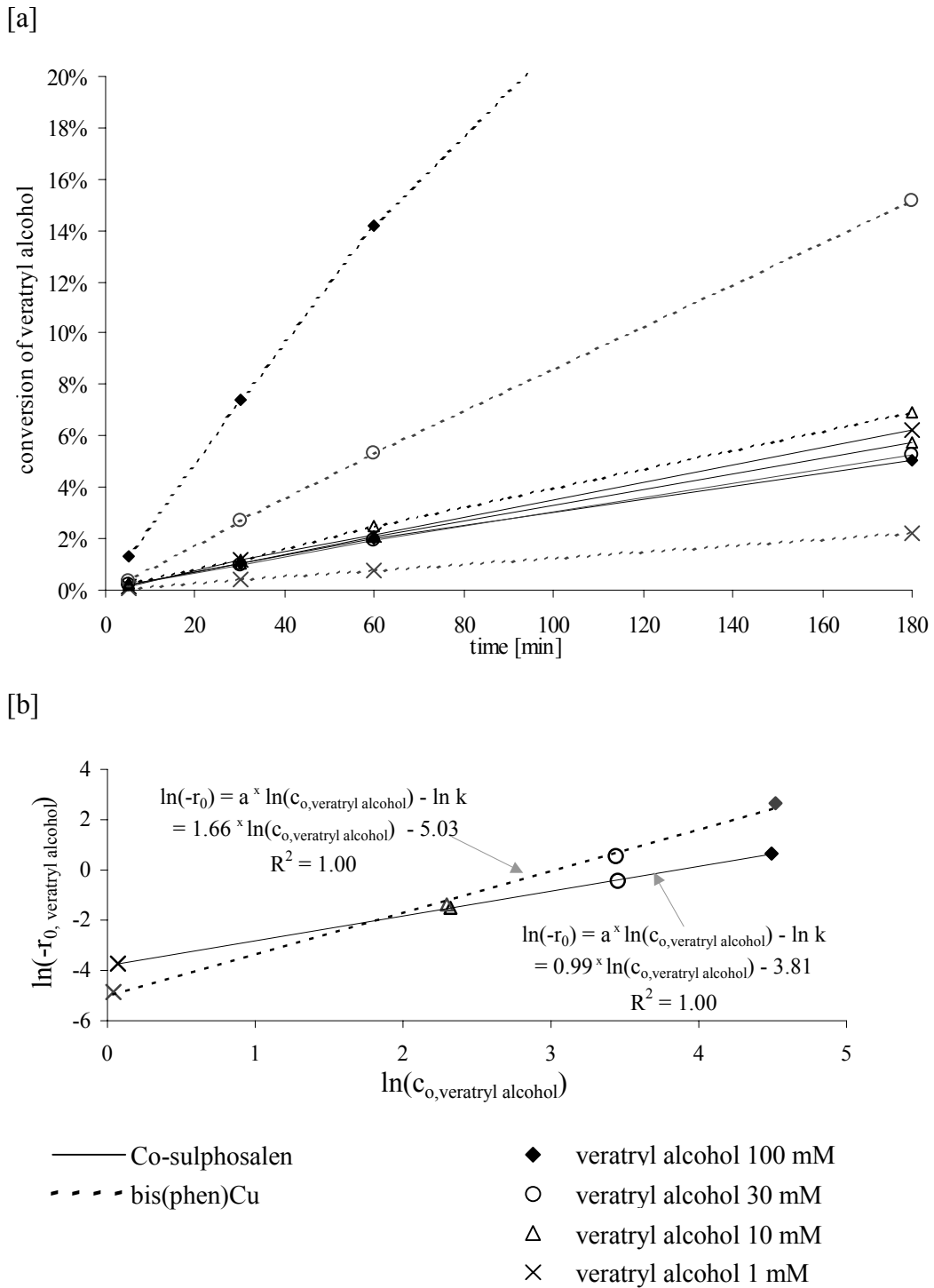


Figure 6. Effect of the initial concentration of veratryl alcohol on its conversion [a] and plots of $\ln(\text{initial oxidation rate of veratryl alcohol})$ versus $\ln(\text{initial concentration of veratryl alcohol})$ [b] (90 °C, $p(\text{O}_2)$ 8 bar, $\text{pH}_{\text{buff.}}$ 12).

3.4 Mechanistic considerations

We have shown that pH has a marked effect on the oxidation rate of the lignin model compounds in both the presence and the absence of catalyst [I, II, IV, VI]. As indicated above (sections 3.1–3.2), the generation of active catalyst complexes such as Co-sulphosalen(OH⁻), Cu(2,2'-bipyridine)₂OH⁺ and Cu(*o*-phenanthroline)₂OH⁺ is dependent on the concentration of hydroxide ions (i.e., pH).

In the non-catalytic oxidation of the lignin model compounds with oxygen, hydrogen peroxide (H₂O₂) and its ionised form, hydroperoxide anion (HO₂⁻), are generated in appreciable amounts [1, 4–5, 57–62]. On the assumption that hydrogen peroxide would also be generated in the presence of catalyst, the catalytic oxidation of the lignin model compounds was studied in the presence of phenylglyoxylic acid (phenylglyoxylic acid reacts immediately with the generated hydrogen peroxide forming a highly unreactive product, benzoic acid [63]). According to the results, scarcely any benzoic acid was generated in the presence of phenylglyoxylic acid and the catalyst (Co-sulphosalen or bis(phen)Cu) alone, but it formed when the lignin model compound was present as well (Table 4) [III, V]. This indicates that hydrogen peroxide was generated as by-product in the catalytic oxidation of the model compound. As expected, the reaction of phenylglyoxylic acid with the generated hydrogen peroxide gave benzoic acid as sole reaction product.

Table 4. Concentration of benzoic acid after reaction of 5, 60 and 180 min (phenylglyoxylic acid 10 mM, catalyst 0.1 mM, 90 °C, p(O₂) 8 bar, pH_{buff.} 12).

Model compound [initial concentration]	Catalyst	Concentration of benzoic acid after 5 min / 60 min / 180 min [mM]
-	bis(phen)Cu	0.00 / 0.00 / 0.01
-	Co-sulphosalen	0.00 / 0.01 / 0.02
veratryl alcohol [10 mM]	bis(phen)Cu	0.02 / 0.05 / 0.15
veratryl alcohol [10 mM]	Co-sulphosalen	0.01 / 0.17 / 0.39
veratryl alcohol [90 mM]	bis(phen)Cu	0.40 / 3.94 / 6.69
veratryl alcohol [90 mM]	Co-sulphosalen	0.12 / 1.27 / 2.74
2,2'-biphenol [10 mM]	bis(phen)Cu	0.01 / 0.13 / 0.35

Figure 7 demonstrates the effect of hydrogen peroxide on the catalytic oxidation of the lignin compounds. Irrespective of the catalyst, the oxidation rate was clearly lowered by the elimination of the generated hydrogen peroxide with phenylglyoxylic acid and enhanced by the addition of hydrogen peroxide [III, V]. In a non-catalytic experiment with added hydrogen peroxide (15 mM), the conversion of veratryl alcohol after reaction of 60 min was only 0.9%. In other words, a catalyst, Co-sulphosalen or bis(phen)Cu, is required to activate the hydrogen peroxide for the oxidation [III, V].

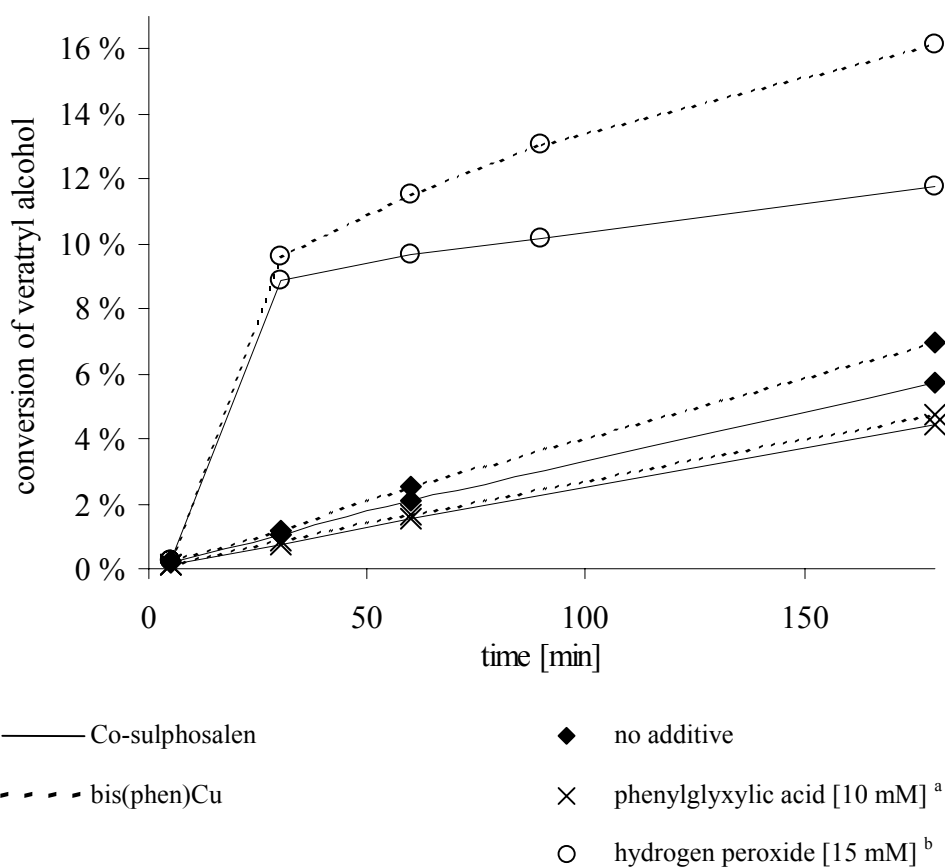


Figure 7. Effect of hydrogen peroxide on the conversion of veratryl alcohol (veratryl alcohol 10 mM, catalyst 0.1 mM, 90 °C, $p(\text{O}_2)$ 8 bar, $\text{pH}_{\text{buff.}}$ 12).

^a An equimolar mixture of phenylglyoxylic acid and sodium hydroxide (in buffer solution) was pumped to the pressurised reactor before the start of the reaction time.

^b 3 mL of an aqueous solution of H_2O_2 (0.5 M) was pumped to the pressurised reactor at the rate 0.1 mL/min during the first 30 min of the reaction.

The reaction steps for the different model compounds catalysed by Co-sulphosalen were discussed in studies I–III, and the mechanism of the Co-Schiff base (Co-salen) and Cu-diimine (bis(phen)Cu) catalysed oxidation of veratryl alcohol was studied in detail by Leskelä's group [29, 50]. The derived mechanisms support the generation of hydrogen peroxide. However, they fail to describe the catalytic reactions of the model compounds with the generated

hydrogen peroxide, which I have shown to have an important role in the catalytic oxidation (Figure 7).

In our study [1], and also that of San Clemente et al. [57], the non-catalytic oxidation rate of the phenolic model compound 4-ethylguaiacol was maximal at pH 11 (Figure 2a). In fact, pH around 11 has been shown to be optimal in the oxidation of many phenolic lignin model compounds [58–61]. This value is reasonable given the maximal formation of reactive hydroxyl ($\text{HO}\cdot$) and superoxide radicals ($\text{O}_2^-\cdot$) from generated hydrogen peroxide and hydroperoxide anions at pH 11.5 [58]. Moreover, pH 11 is high enough to ionise the phenolic model compounds of this study [57, 64–65]. As indicated earlier, ionisation is a prerequisite for effective oxidation in the absence of catalyst [1].

To summarise, the pH of the reaction medium has an effect on the concentration of the active form of the catalyst, the concentrations of reactive hydroxyl and superoxide radicals and the concentration of ionised hydroxyl groups of phenolic model compounds. All these need to be considered when deriving the oxidation mechanisms for the lignin model compounds.

4 SELECTIVITY OF CATALYSTS

A catalyst suitable for delignification of pulp should be active in oxidation of the various lignin substructures, but it should not catalyse the depolymerisation of carbohydrates. The depolymerisation of carbohydrates was studied with a carbohydrate model compound, dextran [III–VI] following the changes in viscosity of the reaction mixture [66].

4.1 Catalytic reactions of carbohydrate model compound

In addition to oxidation of the lignin model compounds, Co-sulphosalen, and even more so bis(phen)Cu, catalysed the oxidative depolymerisation of the carbohydrate model compound dextran [III–V]. As a result of the depolymerisation, the relative viscosity of the reaction mixture decreased as a function of the reaction time (Figure 8). After 180 min, the relative viscosity of the reaction mixture in the presence of Co-sulphosalen was almost as low as the relative viscosity of the model sample with average molar mass of 40120 g/mol, and in the presence of bis(phen)Cu it was almost as low as the relative viscosity of the model sample with average molar mass of 10200 g/mol. With Co-sulphosalen (in an experiment without the lignin model compounds), pH_{meas} after the reaction of 180 min was 11.6, but with bis(phen)Cu only 8.3. These results indicate that at least some of the depolymerisation products of dextran were acidic and that the concentration of the generated acidic products was in accordance with the depolymerisation level.

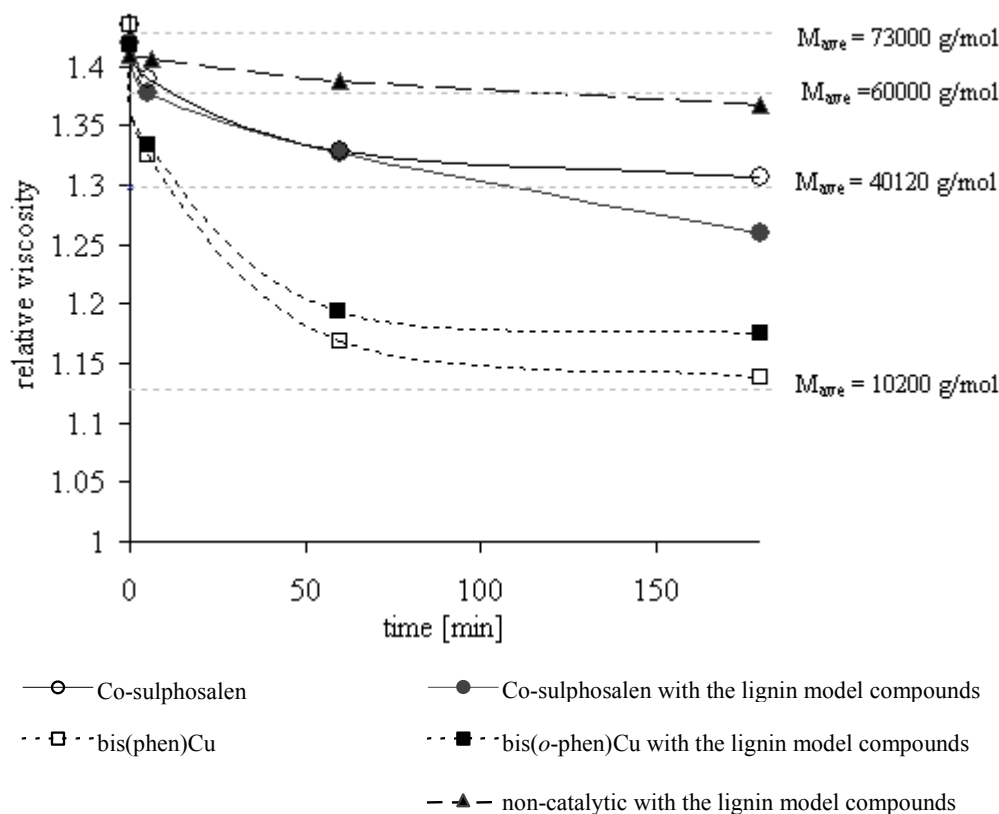


Figure 8. Relative viscosity as function of time (15 g dextran in 1 L of the reaction mixture, 90 °C, $\text{pH}_{\text{buff.}}$ 12, $\text{p}(\text{O}_2)$ 8 bar; in the experiments with the lignin model compounds veratryl alcohol 1 mM and 2,2'-biphenol 1 mM). The dashed horizontal lines show the relative viscosities of model samples containing dextran (15 g/L) and the given average molar masses.

The formation of benzoic acid from added phenylglyoxylic acid indicated that the reactions of dextran, like those of the lignin model compounds, generated hydrogen peroxide as by-product (Table 5) [III, V]. In the presence of dextran and phenylglyoxylic acid, benzoic acid was formed about 25 times faster with bis(phen)Cu as catalyst than with Co-sulphosalen. The elimination of hydrogen peroxide with phenylglyoxylic acid caused a slight decrease in the bis(phen)Cu-catalysed depolymerisation rate of dextran and totally prevented

the depolymerisation in the presence of Co-sulphosalen (Table 5). From these results, it was concluded that bis(phen)Cu catalyses the depolymerisation of the carbohydrates both with oxygen and with the generated hydrogen peroxide but Co-sulphosalen only with hydrogen peroxide. In study III, the Co-sulphosalen catalysed reaction of dextran with oxygen generating some hydrogen peroxide (detected as benzoic acid) was assumed to be a peeling off reaction at the end of the dextran chain.

Table 5. Concentration of benzoic acid and relative viscosity of the reaction mixture after reactions of 5, 60 and 180 min (15 g dextran in 1 L of the reaction mixture, phenylglyoxylic acid 10 mM, catalyst 0.1 mM, 90 °C, pH_{buff.} 12, p(O₂) 8 bar).

Catalyst	Concentration of benzoic acid after 5 min / 60 min / 180 min [mM]	Relative viscosity after 5 min / 60 min / 180 min
Co-sulphosalen	0.03 / 0.19 / 0.27	1.39 / 1.39 / 1.39
bis(phen)Cu	0.64 / 4.65 / 7.01	1.39 / 1.26 / 1.22

4.2 Catalytic oxidation of lignin model compounds in the presence of carbohydrate model compound

A method was developed to study simultaneously the activity and selectivity of potential delignification catalysts [II]. In the method, a phenolic model compound (2,2'-biphenol) and a non-phenolic model compound (veratryl alcohol) were oxidised in the presence of dextran. Interestingly, the bis(phen)Cu-catalysed oxidation rates of 2,2'-biphenol and veratryl alcohol increased markedly with the concentration of dextran up to 5 g/L (Figure 9) [V]. Meanwhile, the bis(phen)Cu-catalysed depolymerisation rate of dextran was slower in the presence than in the absence of the lignin model compounds (Figure 8). In the presence of Co-sulphosalen, the initial oxidation rates of the

lignin model compounds were virtually independent of the concentration of dextran (Figure 9) and correspondingly the initial depolymerisation rate of dextran was independent of the lignin model compounds (Figure 8) [III].

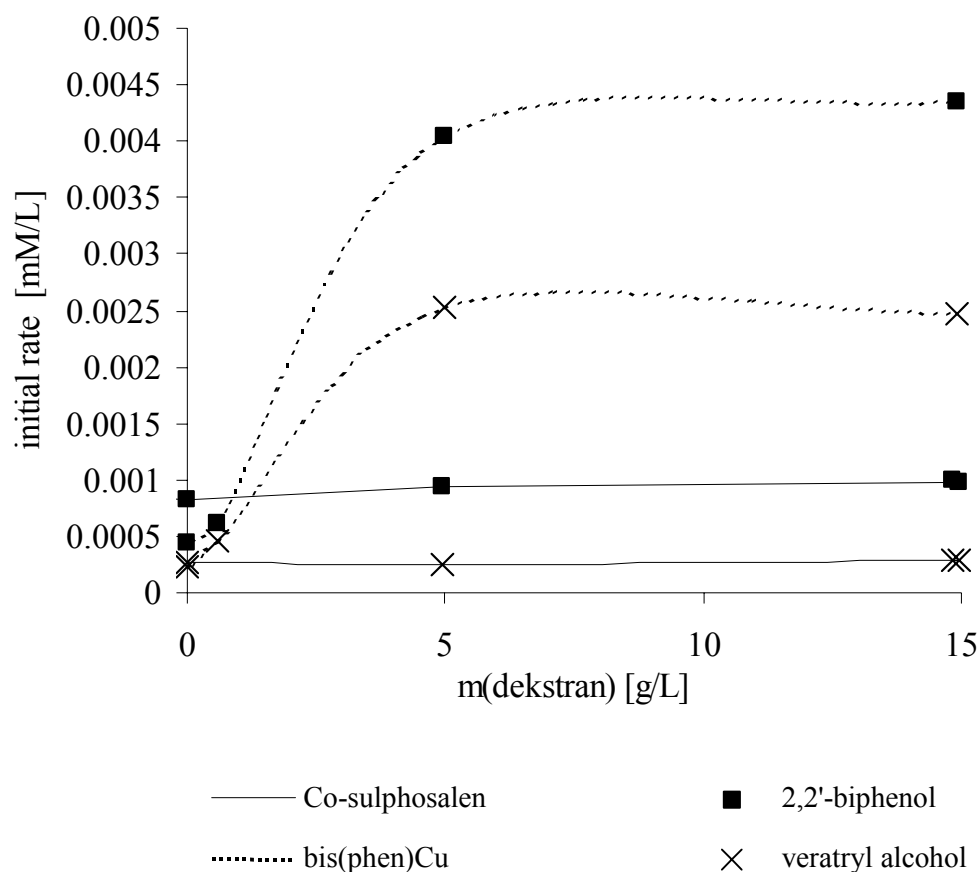


Figure 9. Effect of the concentration of dextran on initial oxidation rates of 2,2'-biphenol and veratryl alcohol (2,2'-biphenol 1 mM, veratryl alcohol 1 mM, 90 °C, $pH_{\text{buff.}}$ 12, $p(O_2)$ 8 bar).

In study V, it was proposed that the more abundant generation of hydrogen peroxide in the presence of dextran with bis(phen)Cu than with Co-sulphosalen as catalyst (Table 5) is the reason why only the bis(phen)Cu-catalysed oxidation rates of the lignin model compounds increased with the concentration of dextran. In addition, I proposed that bis(phen)Cu probably

has a better ability than Co-sulphosalen to catalyse the oxidation of the lignin model compounds with the generated hydrogen peroxide [V].

4.3 Comparison of selectivities

The selectivity of the catalysts was evaluated by plotting the relative viscosities of the reaction mixture as a function of the conversions of 2,2'-biphenol (Figure 10a) and veratryl alcohol (Figure 10b). In the presence of dextran (15 g/L), the initial oxidation rates of the lignin model compounds with bis(phen)Cu were 4.5 to 8.5 times those with Co-sulphosalen (Figure 9), but still the selectivities of the two catalysts were at the same level (Figure 10).

In the presence of either of the catalysts, elimination of the generated hydrogen peroxide through the addition of phenylglyoxylic acid to the reaction mixture suppressed the reaction rates of both the lignin model compounds and dextran. With bis(phen)Cu, the selectivity was worse in the presence than the absence of phenylglyoxylic acid (Figure 10). In a supplementary experiment with bis(phen)Cu and higher concentration (100 mM) of phenylglyoxylic acid, the oxidation of 2,2'-biphenol was totally prevented, but despite that the relative viscosity of the reaction mixture decreased due to the depolymerisation of dextran [V]. This result shows that the generated hydrogen peroxide is essential for the bis(phen)Cu-catalysed oxidation of the lignin structures, but the bis(phen)Cu-catalysed depolymerisation of carbohydrates also proceeds with oxygen. In the presence of phenylglyoxylic acid, the Co-sulphosalen-catalysed oxidation of the lignin model compounds proceeded without the depolymerisation of dextran (Figure 10) [III], which indicates that, although Co-sulphosalen does not catalyse the depolymerisation of dextran with oxygen, it has the ability to transfer oxygen to the lignin model compounds.

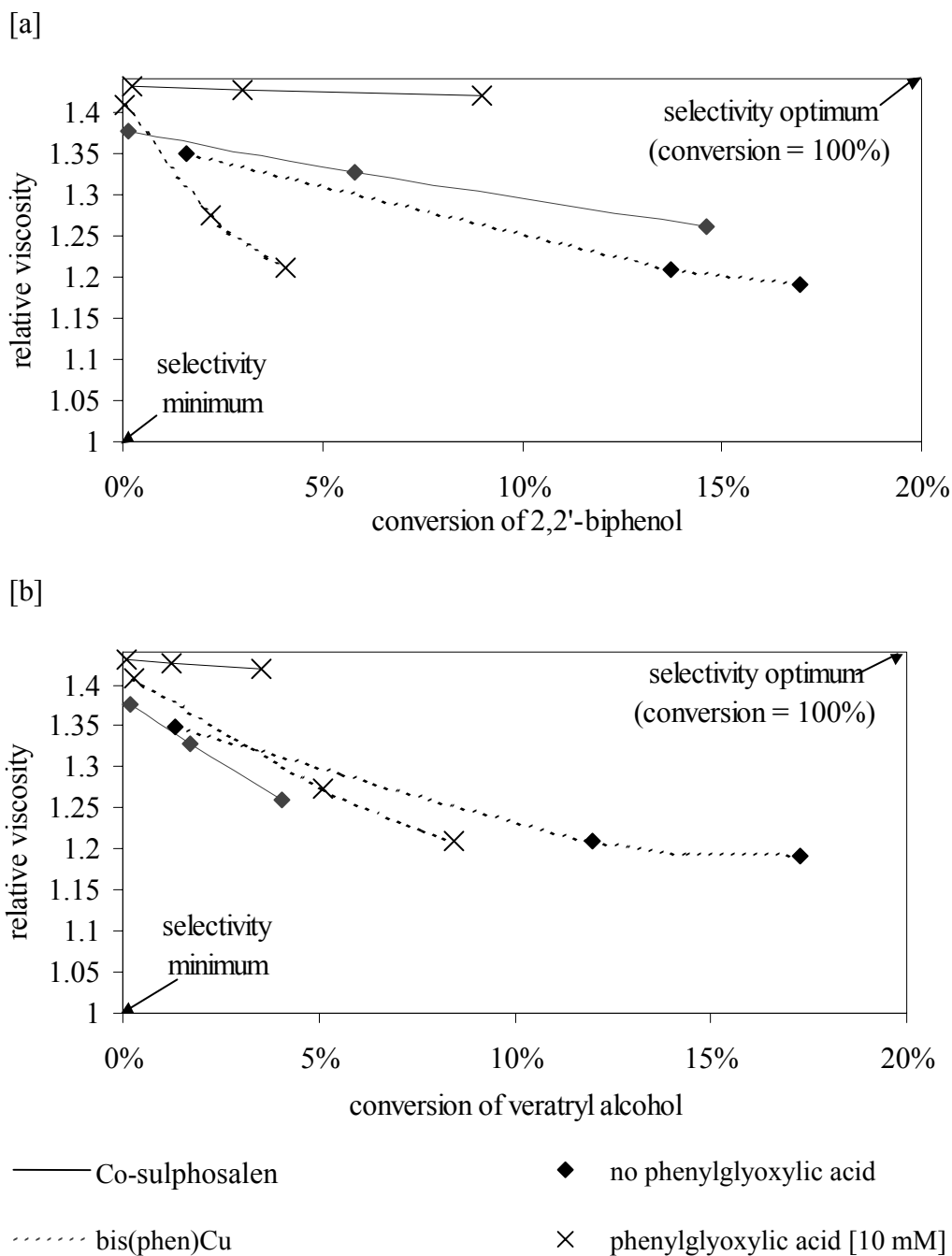


Figure 10. Relative viscosity as a function of the conversion of 2,2'-biphenol [a] and veratryl alcohol [b] in the presence and absence of phenylglyoxylic acid (15 g dextran in 1 L of the reaction mixture, 2,2'-biphenol 1 mM, veratryl alcohol 1 mM, catalyst 0.1 mM, 90 °C, $pH_{\text{buff.}}$ 12, $p(O_2)$ 8 bar).

4.4 Effect of ligand on selectivity of in situ generated Cu-diimines

In work at the University of Helsinki, dimethylglyoxime, *o*-phenanthroline, 2,2'-bipyridine and 4,4'- or 5,5'-disubstituted 2,2'-bipyridines were found to generate in situ active complexes with copper [IV, VI]. My studies showed that all these Cu²⁺ complexes catalyse the simultaneous oxidation of veratryl alcohol and 2,2'-biphenol but also cause fast oxidative depolymerisation of dextran (Table 6). The highest conversion of 2,2'-biphenol was obtained in the presence of 4,4'-dimethoxy-2,2'-bipyridine and the highest conversion of veratryl alcohol in the presence of *o*-phenanthroline. In addition, copper sulphate, in the absence of any ligand, catalysed both the oxidation of the lignin model compounds and the oxidative polymerisation of dextran [VI]. Without ligand, however, the oxidation rates of the lignin model compounds were very low and the depolymerisation rate of dextran still high. For comparison, Table 6 shows the results of an experiment carried out at lower temperature (70 °C) in the presence of Cu²⁺ and 2,2'-bipyridine. In this experiment, both the conversions of the lignin model compounds and the relative viscosity were higher than with copper sulphate at 90 °C.

Table 6. Effect of ligands on conversions of 2,2'-biphenol and veratryl alcohol and on the relative viscosity of the reaction mixture. The structures of the ligands are given in Table 1 (15 g dextran in 1 L of the reaction mixture, 2,2'-biphenol 1 mM, veratryl alcohol 1 mM, 90 °C, CuSO₄ 0.1 mM, ligand 0.2 mM, pH_{buff.} 12, p(O₂) 8 bar).

Ligand	Conversion of 2,2-biphenol after 60 min	Conversion of veratryl alcohol after 60 min	Relative viscosity after 60 min
no ligand, no CuSO ₄	1%	0.1%	1.43
no ligand	6%	1.2%	1.27
6,6'-dimethyl-2,2'-bipyridine	10%	2.0%	1.27
dimethylglyoxime	10%	1.3%	1.21
2,2'-bipyridine	32%	5.3%	1.19
4,4'-dimethyl-2,2'-bipyridine	48%	8.2%	1.17
4,4'-dimethoxy-2,2'-bipyridine	51%	7.5%	1.19
4,4'-dicarboxy-2,2'-bipyridine	25%	5.2%	1.19
5,5'-dimethyl-2,2'-bipyridine	35%	8.0%	1.20
<i>o</i> -phenanthroline	17%	9.3%	1.18
2,2'-bipyridine (at 70 °C)	19%	2.7%	1.30

5 COMPARISON OF RESULTS OF MODEL COMPOUND AND OXYGEN DELIGNIFICATION STUDIES

Catalysed oxygen delignification experiments were carried out in laboratory scale at KCL with use of different procedures and various softwood kraft pulps. Tables 7 and 8 summarise the results of these studies, which are reported in detail elsewhere [43, IV, VI]. The activities of Co-sulphosalen and Cu-diimines in delignification were seen as lower kappa numbers (κ) than those obtained in non-catalysed reference experiments (Tables 7–8).

Co-sulphosalen increased the oxidation rate of 4-ethylguaiacol even at 50 °C and pH 10 (Figure 2) [I]. However, it did not increase the delignification at low temperature (50 °C) or low alkalinity (NaOH 0.5 wt.-% of dry wood) (Table 7). In the studies of Haakana [43], the catalytic activity of Co-sulphosalen was seen only in experiments in which the delignification proceeded to relatively low lignin content. In his studies, low lignin content was obtained only at high temperature (90 °C) and high alkalinity (NaOH 2.5 wt.-% of dry wood). I found [II] that Co-sulphosalen decomposes gradually at 80 °C and that the rate of decomposition increases with alkalinity. The maximal delignification activity of Co-sulphosalen under these severe reaction conditions indicates that the decomposition rate of the complex is so low that the decomposition does not disturb the catalytic oxygen delignification (but will hinder the recycling of the catalyst).

The complexes generated in situ in the presence of copper and diimine ligand *o*-phenanthroline (phen), 2,2'-bipyridine (bipy) or 4,4'-dimethoxy-2,2'-bipyridine (dOMebipy) were highly active in the oxidation of 2,2'-biphenol and veratryl alcohol and decreased the kappa number of pulp substantially (Table 8) [IV, VI]. As expected on the basis of the model compound studies, excess

of the ligand and the 4,4'-disubstitution of 2,2'-bipyridine had a positive effect on the kappa reduction [VI].

Unfortunately, the catalysts decreased the kappa number only with simultaneous loss in viscosity (η) of the pulp (Tables 7–8). The strong tendency of Co-sulphosalen and especially the Cu-diimines to catalyse the oxidative depolymerisation of the carbohydrates of the pulp was predictable given the high depolymerisation rate of dextran (Figure 8).

The aim of oxygen delignification is to remove as much lignin from pulp as possible without any deterioration in pulp strength (i.e., to obtain as low kappa number as possible without loss in viscosity). The selectivities of the delignification experiments can thus be evaluated by dividing the loss of kappa number by the loss of intrinsic viscosity [67, IV]. The highest values (from 0.07 to 0.10 dm³/kg) were obtained in the non-catalytic experiments, whereas the corresponding values in the presence of Co-sulphosalen were less than 0.06 dm³/kg, and in the presence of Cu-diimines only 0.03–0.04 dm³/kg. The low selectivity in the presence of Cu-diimines can be explained by our finding that these complexes catalyse the oxidative depolymerisation of the carbohydrates with both oxygen and hydrogen peroxide.

To summarise, the activities of Co-sulphosalen and in situ generated Cu-diimines in the oxidation of 2,2'-biphenol and veratryl alcohol correlated well with their ability to catalyse oxygen delignification. In addition, their strong tendency to increase the depolymerisation rate of dextran was in accordance with loss in viscosity during the oxygen delignification.

Table 7. Effect of Co-sulphosalen on kappa number (κ) and intrinsic viscosity (η) of softwood kraft pulp (consistency 8%, $p(\text{O}_2)_{\text{initial}}$ 8 bar) [43].

Cobalt concentration (wt.-% of pulp)	$\kappa_{\text{no catalyst}} - \kappa_{\text{with catalyst}}$	$\eta_{\text{no catalyst}} - \eta_{\text{with catalyst}}$ [dm ³ / kg]	Procedure
0.1	29.1 - 29.3 = - 0.2	1270 - 1310 = - 40	50 °C, NaOH 0.5 wt.-%, ^{a)}
0.1	25.3 - 25.7 = - 0.4	1280 - 1220 = 60	90 °C, NaOH 0.5 wt.-%, ^{a)}
0.1	27.0 - 26.9 = 0.1	1250 - 1250 = 0	50 °C, NaOH 2.5 wt.-%, ^{a)}
0.1	16.2 - 14.5 = 1.7	1100 - 930 = 170	90 °C, NaOH 2.5 wt.-%, ^{a)}
0.028	15.4 - 14.8 = 0.6	1060 - 930 = 130	90 °C, ^{b)}

^{a)} zirconium-lined autoclave, heating time 30 min, time at reaction temperature 60 min, κ_{initial} 33.8 and η_{initial} 1270 dm³/ kg

^{b)} zirconium-lined autoclave, two-stage oxygen treatment (NaOH 1.7 + 0.8 wt.-%, heating time 2 × 30 min, times at reaction temperature 30 and 60 min), κ_{initial} 35.0 and η_{initial} 1270 dm³/ kg

Table 8. Effect of complexes generated in situ in the presence of CuSO₄ and diimine ligands on kappa number (κ) and intrinsic viscosity (η) of softwood kraft pulp (consistency 8%, 90 °C, $p(\text{O}_2)_{\text{initial}}$ 8 bar).

Copper concentration (wt.-% of pulp)	Ligand / copper–ligand molar ratio	$\kappa_{\text{no catalyst}} - \kappa_{\text{with catalyst}}$	$\eta_{\text{no catalyst}} - \eta_{\text{with catalyst}}$ [dm ³ / kg]	Proc. / [Ref.]
0.071	phen / 1:2	20.1 - 16.1 = 4.0	1070 - 630 = 440	^{a)} , [IV]
0.084	bipy / 1:2	20.1 - 15.0 = 5.1	1070 - 620 = 450	^{a)} , [IV]
0.02	bipy / 1:2	18.1 - 17.9 = 0.2	1040 - 830 = 210	^{b)} , [VI]
0.02	bipy / 1:5	18.1 - 17.1 = 1.0	1040 - 810 = 230	^{b)} , [VI]
0.02	dOMebipy / 1:2	18.1 - 17.6 = 0.5	1040 - 870 = 170	^{b)} , [VI]
0.02	dOMebipy / 1:5	18.1 - 16.1 = 2.0	1040 - 800 = 240	^{b)} , [VI]
0.02	no ligand	18.1 - 18.0 = 0.1	1040 - 870 = 170	^{b)} , [VI]

^{a)} teflon-lined autoclave, heating time 30 min, time at reaction temperature 30 min, NaOH 2.3 wt.-% of dry pulp, κ_{initial} 31.8 and η_{initial} 1230 dm³/ kg

^{b)} zirconium-lined autoclave, heating time 30 min, time at reaction temperature 30 min, NaOH 2.5 wt.-% of dry pulp, κ_{initial} 31.3 and η_{initial} 1200 dm³/ kg

6 CONCLUSIONS

This work was targeted at increasing the use of oxygen in the delignification of pulp through application of transition metal complexes as catalysts. Cobalt-sulphosalen and complexes generated in situ in the presence of copper and diimine ligands such as *o*-phenanthroline or 2,2'-bipyridine were found to be highly active oxidation catalysts. Co-sulphosalen was active only in alkaline reaction medium, however, where the 5-coordinated Co-sulphosalen(OH⁻) complex is generated. Unfortunately, the complex structure of Co-sulphosalen gradually decomposed. The rate of the decomposition increased with alkalinity (pH 9–12). The concentrations of hydroxide ion (i.e., pH) and ligand also influenced the structure and the activity of in situ formed Cu-diimines. In active forms of Cu-diimine complexes, Cu²⁺ ion was found to coordinate with two ligands and one hydroxide ion. In addition to the oxidation of lignin structures, Co-sulphosalen and Cu-diimines also increased the rate of depolymerisation of the carbohydrates, which means that, as such, none of them is feasible for chemical pulping.

This study revealed that the generation of hydrogen peroxide plays a key role in catalytic oxygen delignification. However, the reactions of the generated hydrogen peroxide vary with the catalyst. In the presence of Cu-diimine catalyst, the generated hydrogen peroxide is essential for the oxidation of lignin structures but the depolymerisation of carbohydrates proceeds with oxygen as well as hydrogen peroxide. In the presence of Co-sulphosalen, oxygen is selectively transferred to the lignin model compounds and the carbohydrates are depolymerised solely by the generated hydrogen peroxide.

The transition metal complexes were studied mainly with model compounds. The performance of the catalysts in the model compound studies was in good

accordance with their performance in oxygen delignification of softwood pulp. Studies with the model compounds were confirmed to be a highly convenient method to obtain information about the reactions occurring during actual oxygen delignification.

7 LIST OF ABBREVIATIONS AND SYMBOLS

a	order of reaction
bipy	2,2'-bipyridine
bis(phen)Cu	complex generated in situ in the presence of copper-to- <i>o</i> -phenanthroline with the molar ratio 1:2
c	concentration, mmol/L = mM
c ₀	initial concentration, mmol/L = mM
Co-sulphosalen	cobaltate(2-),[[3,3'-[1,2-ethanediylbis(nitrilomethylidyne)]-bis[4-hydroxybenzenesulphonato]](4-)-N3,N3',O4,O4']-, disodium hexahydrate
CoPcTS	cobalt phthalocyaninetetra(sodium sulphonate)
dOMebipy	4,4'-dimethoxy-2,2'-bipyridine
GC	gas chromatograph
HPA-5	heptamolybdopentavanadophosphate heteropolyanion
HPLC	high performance liquid chromatograph
k	rate constant, mM ^(1-a) /min
K	stability constant, M ⁽⁻ⁿ⁾ (n = 1, 2, 3, 4, 5 or 6 depending on the equation)
MS	mass spectrometry
p	pressure, bar
pH _{buff.}	pH value of buffer solution used as solvent
pH _{meas.}	measured pH value
phen	<i>o</i> -phenanthroline
POM	polyoxometalate
r ₀	initial rate, mM/min
salen	<i>N,N'</i> -bis(salicylidene)ethylenediamine
t	time, min

Greek Letters

κ	kappa number (A technical value that correlates with the lignin content of pulp and that is determined by Scandinavian Pulp, Paper and Board Testing Committee as following: The number of millilitres of 20 mmol/L potassium permanganate (KMnO ₄) solution consumed by one gram of moisture free pulp at 25 °C during 10 minutes. The measured value is converted to correspond to 50 % KMnO ₄ consumption [68].)
η	intrinsic viscosity, dm ³ /kg
η_r	relative viscosity

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