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# LIGNIN CHEMISTRY

The Use of (Co(salen))

Salen complexes have been used since 1933 to catalyze a wide variety of reactions. In particular in the field of lignin chemistry, they can be proposed as biomimicks of laccase for both bleaching and the radicalization of lignocellulosic fibers, since they can generate phenoxy radicals on lignin. This paper reports an overview on the use of (Co(salen)) for the radicalization of lignocellulosic fibers. The absolute amount of phenoxy radicals formed on fibers, evaluated by ESR spectroscopy, reaches values 10 times higher than those obtained by enzymatic radicalization.

Salen complexes are an important class of coordination compounds, which have been used since 1933 to catalyze a wide variety of reactions [1], as oxidations of organic substrates with oxidants like oxygen and hydrogen peroxide. Such reactions are interesting in several industrial fields, as that of pulp and paper. In particular, in this field bleaching agents alternative to chlorine-containing reagents are required in order to remove lignin from pulps [2, 3]. At this regard, oxidation catalysts such as laccase [4] and polyoxometallates [5] have shown a good activity in pulp bleaching by oxygen, ozone and hydrogen peroxide, however these enzymes can be conveniently mimicked by different salen compounds. In particular, the N,N'-ethylenebis(salicylideneiminato) cobalt(II), [Co(salen)], can be proposed as laccase biomimick since it has low toxicity and, when cobalt is coordinated in fifth position by a base, it can reversibly coordinate oxygen and generate phenoxy radicals on lignin in the same way as laccase does. Moreover the small size of [Co(salen)], with respect to laccase, allows the interaction also with the sub-surface phenolic groups of lignin. We recently reported that monomeric and dimeric lignin model compounds were oxidized in homogeneous phase with oxygen, using [Co(salen)] as catalyst (Schemes 1 and 2, respectively), giving high amounts of commercially interesting products, as vanillin [6-9].
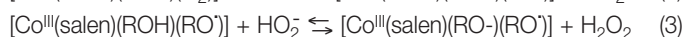
Another field in which the catalytic activity of [Co(salen)] is of great interest is the preparation of new packaging materials by activation of lignocellulosic fibers. As a matter of fact the increase in environmental awareness has raised the interest in the development of new materials from renewable resources [10]. Among the most important renewable resources, lignocellulosic fibers can replace the currently used synthetic or semi-synthetic fibers [11] for packaging applications, since they have biodegradability and thermal recyclability. Lignocellulosic fibers are a product of pulp and paper industry; they are composite materials containing lignin, cellulose, hemicellulose and various extractive components, being lignin and hemicellulose situated as fillers between the highly ordered cellulose microfibrils [12]. In the field of packaging applications, materials

with high barrier and mechanical properties are generally required. Lignocellulosic fibers can achieve these properties, after proper modification. As an example, the treatment of wood fibers from thermomechanical pulp (TMP) with oxygen and laccase as catalyst [13] allowed to obtain glue-less fiberboards with contemporary improvement of the wet strength of paper [14]. The reaction was demonstrated to proceed through radical formation on lignin at the fiber surface: mechanism studies on the laccase-catalyzed oxidation showed that one mole of oxygen reacts with four moles of phenols giving phenoxy radicals [15], which were the intermediate species in modifying the lignin structure:
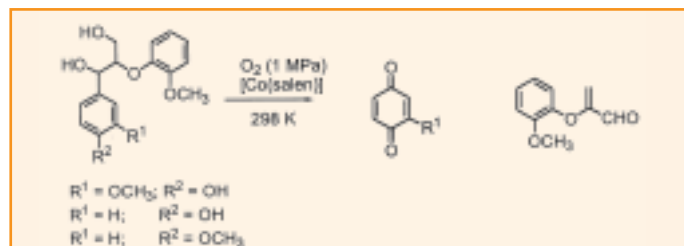
$$4 \text{ PhOH} + O_2 \xrightarrow{\text{laccase}} 4 \text{ PhO}^\bullet + 2 \text{ H}_2O$$
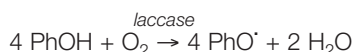
The same radical species were found to be active in the oxidation of lignin model compounds by O_2, in the presence of transition metal complexes as catalysts [16].

For the oxidation of lignin model compounds with oxygen, catalyzed by [Co(salen)], the reactivity and the characterization of radical intermediates by electron paramagnetic resonance (EPR) spectroscopy suggested that such oxidation occurs through the following three steps [8, 9, 17]:

$$[Co^{II}(salen)] + ROH + O_2 \leftrightarrows [Co^{III}(salen)(ROH)(O_2^-)] \quad (1)$$

$$[Co^{III}(salen)(ROH)(O_2^-)] + ROH \leftrightarrows [Co^{III}(salen)(ROH)(RO^\bullet)] + HO_2^- \quad (2)$$

$$[Co^{III}(salen)(ROH)(RO^\bullet)] + HO_2^- \leftrightarrows [Co^{III}(salen)(RO\text{-})(RO^\bullet)] + H_2O_2 \quad (3)$$

where ROH is the phenol unit and RO$^\bullet$ the corresponding radical. For the single reaction steps:

1) a superoxocobalt derivative, $[Co^{III}(salen)(ROH)(O_2^-)]$, forms by electron transfer from $[Co^{II}(salen)]$ to O_2;

2) further reduction of O_2^- to HO_2^- occurs, together with the cobalt coordination of a second ROH molecule as RO$^\bullet$, giving the phenoxy cobalt radical $[Co^{III}(salen)(ROH)(RO^\bullet)]$;

3) one ROH ligand loses H$^+$, leading to the formation of the phenoxy-phenate cobalt radical $[Co^{III}(salen)(RO^\bullet)(RO^\bullet)]$.

After the third step, RO$^\bullet$ probably dissociates from the cobalt center, then further reacts with O_2 giving oxidized molecular products. It was expected that lignocellulosic fibers might undergo radical formation under similar oxidative conditions and that, in such a way, they can be activated towards interesting morphological and structural modifications.

With this aim, we identified and quantified by EPR spectroscopy the radicals formed on unbleached fibers obtained from thermomechanical (TMP) and chemothermomechanical (CTMP) pulps after reaction with oxygen, using [Co(salen)] as catalyst. Both materials are rich in lignin and are widely used for industrial purposes. Unbleached CTMP has a slightly higher surface content of lignin than unbleached TMP [18, 19], and some sulphonate groups are grafted to the lignin during manufacture of CTMP [20, 21].

In order to maximize radical formation, the influence of solvent, oxygen pressure and time of reaction on the amount of formed radicals was also investigated.

Results and Discussion

Before studying the changes undergone by fibers after treatment in the presence of oxygen and [Co(salen)], unreacted CTMP and TMP were characterized by EPR spectroscopy.

In both fibers, the EPR spectra allowed to assess the presence of phenoxy radicals, PhO$^\bullet$, photochemically induced and/or caused by thermal, mechanical, chemical treatments during pulp production (spin concentration 1×10^{16} spin/g) [22].

Then, the radical formation in fibers, under reaction with oxygen at 298 K in the presence of [Co(salen)], was studied with the aim of maximizing the radical amount, while preserving the fiber integrity. The optimal conditions were determined by varying i) the reaction medium, ii) the oxygen pressure and iii) the time of reaction.

Fiber/[Co(salen)] ratio 10:1 w/w was always used, corresponding to a molar ratio phenol/[Co(salen)] ~0.8. The fiber concentration in the solvent was always 5.0 mg/ml.
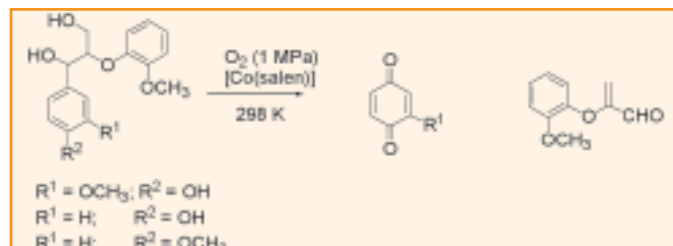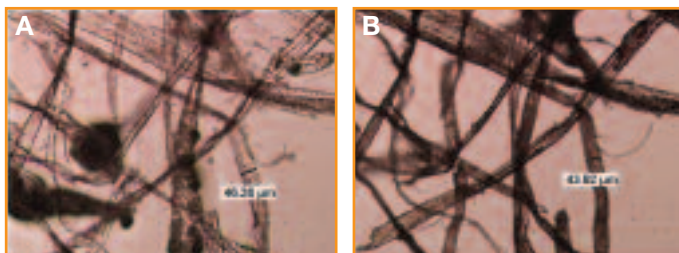

Scheme 1

Scheme 2

Fig. 1 - Optical microscopy images of CTMP fiber a) suspended in methanol and b) after solvent complete evaporation
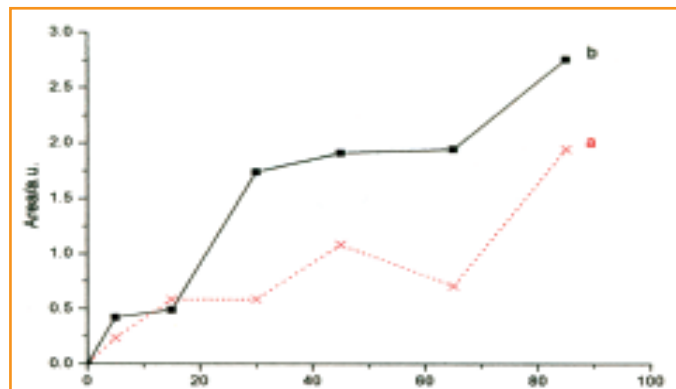

Fig. 2 - Amounts of phenoxy cobalt radicals, reported as area of the EPR resonances, in a) CTMP and b) TMP fibers after oxidation in the presence of [Co(salen)] at 0.1 MPa of oxygen pressure in methanol at different reaction times

i) The formation of radicals in fibers was studied in methanol and in chloroform. The latter was chosen because it was the election solvent for the stabilization of radicals in lignin model compounds [7-9]. CTMP and TMP fibers were suspended in [Co(salen)] solutions in the proper solvent; then the suspension was let react with oxygen (0.1 MPa) for 30 min. At the end, fibers were recovered by filtration, washed, allowed to dry and the EPR spectra recorded at 123 K.

For both fibers, in methanol an eight resonance line signal was detected. Such signal is very similar in shape to the one observed during the oxidative degradation of monomeric and dimeric lignin model compounds [7] and is attributable to the phenoxy cobalt radical [CoIII(salen)(ROH)(RO•)] [9].

Instead, surprisingly, phenoxy cobalt radicals did not form in chloroform, although this solvent stabilized radicals in lignin model compounds. The measure of the distance between the outer walls

of a fibril suspended in a given solvent with that after its complete evaporation, observed by optical microscopy, showed that both fibers are better swelled by methanol than by chloroform. A higher swelling of fibers increases the surface area and favors the fiber interaction with the catalyst, strongly influencing the formation of radicals. The obtained results suggest the choice of methanol as solvent for fiber radicalization (Fig. 1).

ii) The effects of the oxygen pressure both on the amount of phenoxy cobalt radical and on the fiber recovery were investigated by carrying out the radicalization in methanol for 30 min. at different

Bibliografia

[1]   P. Pfeiffer *et al., Liebigs Ann.,* 1933, **503,** 84.

[2]   L. Almberg *et al., Pulp and Paper,* 1980, **54,** 92.

[3]   C.L. Csu, J. Hsieh, *Tappi J.,* 1986, **69,** 125.

[4]   R. Bourbonnais, M.G. Paice, *Tappi J.,* 1996, **79,** 1999.

[5]   I.A. Weinstock *et al., New J. Chem.,* 1996, **20,** 269.

[6]   E. Bolzacchini *et al., Journal of Molecular Catalysis,* 1996, **112,** 347.

[7]   E. Bolzacchini *et al., J. Chem. Soc. Dalton Trans.,* 1997, 4695.

[8]   C. Canevali *et al.,* ACS Symposium Series 785 (Oxidative Delignification Chemistry: Fundamentals and Catalysis), 2001, 197.

[9]   C. Canevali *et al., J. Chem. Soc. Dalton Transactions,* 2002, **15,** 3007.

[10] P.L. Nayak, *Macrom.Chem. Phys.,* 1999, **C 39**(3), 481.

[11] D. Feldman, D. Banu, *J. Appl. Polym. Sci.,* 1997, **66,** 1731.

[12] J. Allen, Structure and Chemical Composition of Wood, in

Forest Product Chemistry, P. Stenius (Ed.), Fapet Oy, Jyväskylä, 2000, 12.

[13] M. Lund, C. Felby, *Enzmyme Microb. Technol.,* 2001, **28,** 760.

[14] C. Felby *et al., Holzforschung,* 1997, **51,** 281.

[15] M. Lund *et al., Holzforschung,* 2003, **57,** 21.

[16] R.S. Drago *et al., J. Am. Chem. Soc.,* 1986, **108,** 2453.

[17] C. Canevali *et al., Biomacromolecules,* 2005, **6(3),** 1592.

[18] H. Kangaz *et al.,* Proc. of 7th European Workshop of Lignocellulosic and Pulp, Turku, 2002, 115.

[19] K. Koljonen *et al., Colloids and Surface A: Physicochem. Eng. Aspects,* 2003, **228,** 143.

[20] R.P. Beatson *et al., Tappi J.,* 1984, **67,** 83.

[21] F. Peng *et al., Nord Pulp Paper Res J.,* 1992, **7,** 140.

[22] D.N.S. Hon, Mechanochemistry of Lignocellulosic Materials, in Development in Polymer Degradation, Grassie (Ed.) Applied Science Publisher, Essex England, 1987, 229.

[23] C. Felby *et al., Appl. Microbiol. Biotechnol.,* 1997**, 48,** 459.

[24] R. Ferm *et al., Sven. Pappestidn.,* 1972, **75**(21), 859.

oxygen pressures (0.1, 0.5 and 1 MPa).

For TMP the amount of phenoxy cobalt radicals reaches the maximum value at 0.1 MPa of oxygen pressure, while for CTMP the maximum amount was obtained at 1 MPa.

Since for both the fibers, the recovery at 0.1 MPa (87% for TMP and 90% for CTMP, w/w) was higher than working at 1 MPa (55% for TMP and 60% for CTMP, w/w) [14], the lower pressure value was chosen for fiber radicalization.

iii) The role of the reaction time was investigated by suspending fibers in methanol and by evaluating the intensities of the phenoxy cobalt radi-
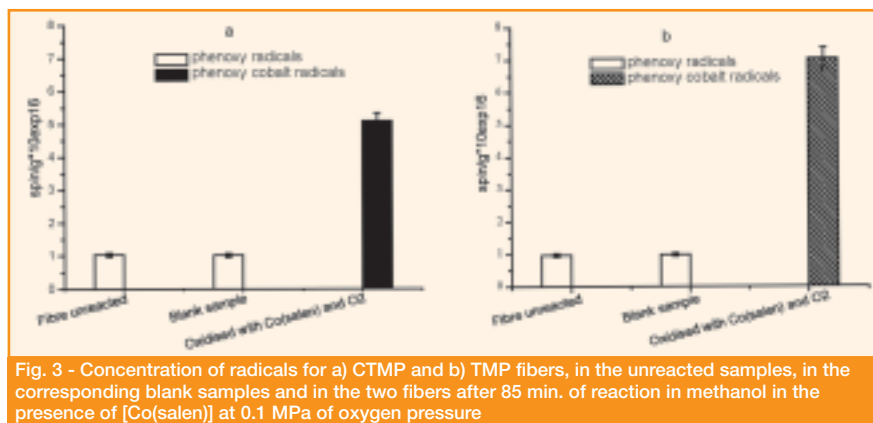

Fig. 3 - Concentration of radicals for a) CTMP and b) TMP fibers, in the unreacted samples, in the corresponding blank samples and in the two fibers after 85 min. of reaction in methanol in the presence of [Co(salen)] at 0.1 MPa of oxygen pressure

cals formed under 0.1 MPa of oxygen pressure at different times of reaction (5, 15, 30, 45, 65, 85 min.).

During the reaction, both fibers show an increase in the amount of phenoxy cobalt radicals, which reaches the maximum value after 85 minutes of reaction (Fig. 2).

Phenoxy cobalt radicals formed in fibers in the best radicalization conditions (in methanol, at 0.1 MPa of oxygen pressure, after 85 min. of reaction) showed a very long life time at room temperature. The inclusion of radicals in fibers is probably responsible for such long life time. A similar behavior was reported for phenoxy radicals generated in fibers, by using laccase as catalyst [23].

In order to accurately compare radicals generated on different fibers, we determined their absolute amount in terms of spins per gram of fiber. The absolute amount was calculated by referring the area under the absorption signal to a calibration curve determined using standard solutions of DPPH in toluene/nujol at a ratio of 2:1 v/v.

The absolute amount of radicals in fibers, expressed as spin/g of fiber, was evaluated for: i) each unreacted fiber, ii) the corresponding blank sample (that is, the fiber reacted for 85 min. in the absence of catalyst) and iii) each fiber radicalized in the presence of [Co(salen)] under the optimized conditions (after 85 min., in methanol, at 0.1 MPa of oxygen pressure). Phenoxy radicals were present in unreacted fibers and in blank samples in similar small amounts (about $1x10^{16}$ spin/g, Figure 3 a, b). In the presence of [Co(salen)], in both fibers, phenoxy radicals dis-

appeared and phenoxy cobalt radicals formed in high amount ($7x10^{16}$ spin /g in TMP, $5x10^{16}$ spin/g in CTMP).

The concentration of radicals in fibers, when using [Co(salen)] catalyst, reaches values 10 times higher than those reported in the literature by Felby [23] and by Ferm [24] for the oxidation of respectively TMP and milled wood lignin by oxygen, in the presence of laccase. It cannot be excluded this was partly due to the smaller molecular dimension of [Co(salen)] with respect to laccase, which allows the catalyst to interact also with subsurface lignin phenol groups.

Conclusions

The oxidation of unbleached CTMP and TMP fibers by oxygen, catalyzed by [Co(salen)], induces the formation of phenoxy cobalt radicals similar in structure to those observed during the oxidation of lignin model compounds.

The best radicalization conditions, assessed by EPR spectroscopy, depend on the reaction medium, the oxygen pressure and the time of reaction. In particular, the swelling of fiber in the reaction medium favors the formation of radicals.

The concentration of radicals formed in the best radicalization conditions reaches values 10 times higher than those reported in the literature by Felby [23] and by Ferm [24] for the oxidation of respectively TMP and milled wood lignin by oxygen, in the presence of laccase. Thus, it can be concluded that such radicals can represent the key point for fiber modifications.

L'uso di complessi di salen nella chimica della lignina

ABSTRACT 🇮🇹

I complessi del salen sono usati fin dal 1933 per catalizzare un'ampia varietà di reazioni. In particolare, nel campo della chimica della lignina rappresentano una valida alternativa agli enzimi sia nel campo del bleaching sia per la radicalizzazione delle fibre. In questo articolo viene descritto l'utilizzo del [Co(salen)] per la radicalizzazione di fibre lignocellulosiche. La quantità assoluta di radicali generata dal trattamento delle fibre, valutata tramite spettroscopia ESR, risulta 10 volte maggiore dei valori che si ottengono tramite radicalizzazione enzimatica.