Co(salen)-catalysed oxidation of synthetic lignin-like polymer: Co(salen) effects

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Abstract

In this paper, Co(salen) complex, salen = *N,N'*-bis(salicylidene)ethylenediamine, was studied as oxygen activator for the catalytic oxidation of a lignin model polymer using water as the solvent, with molecular oxygen and hydrogen peroxide as the oxidants. The effect of Co(salen) on oxidation was tested by spectroscopic methods (FTIR, ^{13}C-NMR and GC–MS). The reactions catalysed by Co(salen) included C_α-alcohol oxidation, C_α–C_β side chain cleavage, demethoxylation, aromatic ring cleavage, and β-O-4 cleavage. In addition to the mechanistic information obtained, the effect of Co(salen) suggests that Co(salen) can be important for the catalytic oxidation, as it affects the oxidation of lignin model polymer. The reaction performed in the presence of Co(salen) was more efficient than without it. The formation of aldehyde in the catalytic oxidation, as shown by GC–MS, could be identified as the mechanism of oxidative cleavage of the β-O-4 bonds.

Keywords: Co(salen); catalytic oxidation; lignin model polymer; Co(salen) effect; FTIR; ^{13}C-NMR; GC–MS.

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Lignins are polyphenols characterized by a complex network of three main monomeric phenyl propanonic units bonded through an array of different interunit bondings. The main interunit linkages of lignin are called β-O-4, β-β, β-5, β-1, 5-5, 4-O-5, etc., linkages. Among these, the β-O-4 linkage is the most abundant and probably most important substructure in lignin, which greatly affects both the chemical and physical properties of lignins (Figure 1) [1]. Lignin is removed during the pulping process to break down the bulk structure of the fibre source, be it chips, stems or other plant parts, to set free the cellulosic fibrous material. Degradation of lignin (commonly known as delignification) hence constitutes an important step in the manufacturing of paper. Selective removal of lignin from wood is the key operation in paper production [2, 3].

The increasing demand for new and selective catalysts in oxidative transformations had already led to the discovery of the transition metal complexes. As in nature, the most common metals in these enzyme-mi-
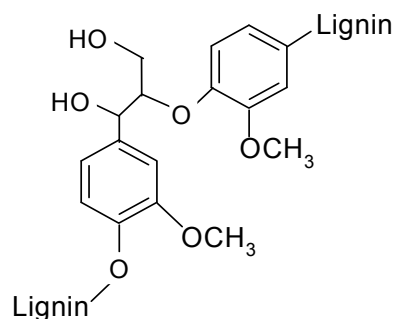

Figure 1. β-O-4 linkage substructure in lignin.

micking synthetic catalysts are cobalt, copper, iron and manganese. Salen-type transition metal complexes are an important class of organometallic compounds, which have been used since 1933 as catalysts for a wide variety of reactions. Many of these reactions are oxidations of organic substrates with oxidants like O_2 and H_2O_2 [4]. The synthesis of water or organic solvent-soluble salen complexes is simple, easy and economical, as reported in by Sipila *et al.* [5]. The oldest and one of the most widely studied combinations of the substrates and metals is the combination of phenolic material and cobalt. Co(salen), salen = *N,N'*-bis(salicylidene)ethylenediamine, is a tetradentate, planar Schiff base complex. Co(salen) complexes usually form either

mononuclear superoxo- or dinuclear peroxo type complexes with dioxygen. In addition to oxygen and nitrogen, donor sites are provided by the salen^{2-}, whereas the metal is typically bound to pyridine (py) to give the complex Co(salen)(py). Such complexes bind O_2 to give derivatives of the type (μ-O_2)[Co(salen)py]$_2$ and [Co(salen)py(O_2)] (Figure 2). There is a delicate energy and/or kinetic balance between the formation of the mononuclear and binuclear complexes, which is affected by solvents, ligands, temperature, pH and several other factors. By choosing the reaction conditions carefully, the equilibrium can be shifted towards the catalytically more active species. However, the chosen substrate can also affect the reaction mechanism [6].

Due to the complexity of the lignin structure, model compounds resembling the main bonding patterns in native and technical lignins have been widely used in lignin degradation catalysed by Co(salen) type complexes [7–9]. These model compounds are relatively simple and easy to characterize, but they are not able to mimic the polymeric nature of lignin. To overcome these limitations, β-O-4 type oligomers were synthesized [10–12]. Herein, we have used guaiacyl-type (G-type) lignin model polymer that include native β-O-4 linkage to investigate the relationship between lignin structure and Co(salen) catalytic process. In this article the effect of Co(salen) was tested over oxidation by conducting the oxidations in the presence/absence of Co(salen).

EXPERIMENTAL

Co(salen) synthesis

The same procedure was followed to prepare well-known Co(salen). The Schiff base salen (where salen = N,N'-bis(salicylaldehydeethylenediamine) was prepared in 88% yield by condensation reactions of ethylenediamine with salicylaldehyde in methanol. The metal complex were synthesised from the ligand and a slight excess of metal salt from CH_3OH refluxing. $(CH_3COO)_2Co\cdot4H_2O$ was used for the Co(salen) complex (Scheme 1) [13].
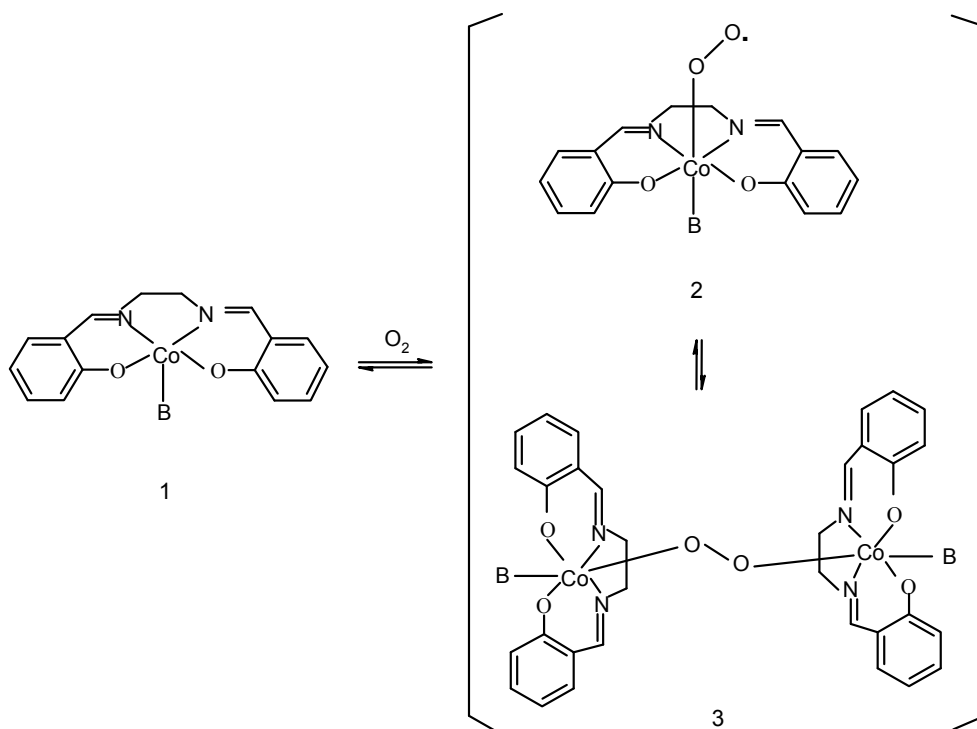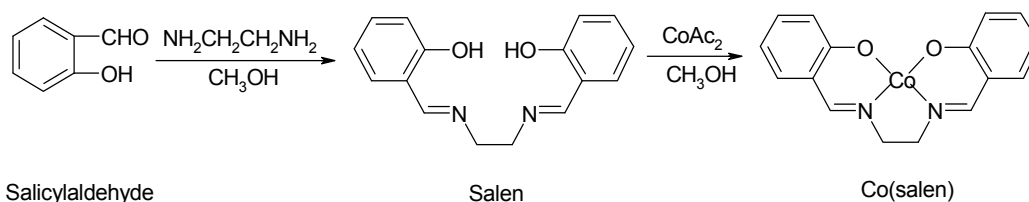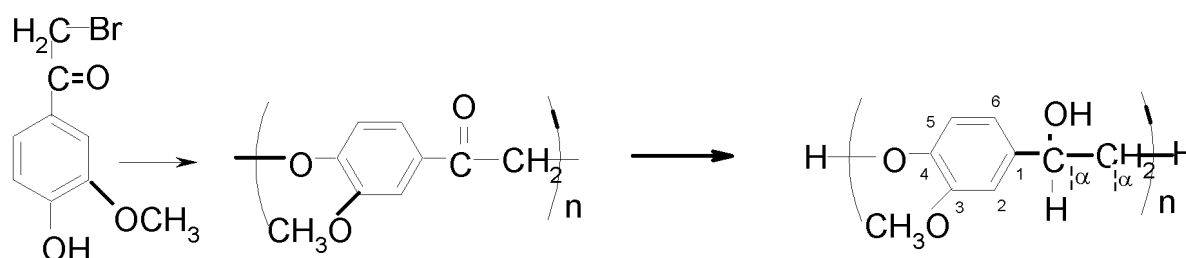

Figure 2. Mononuclear cobalt complexes (**1**), mononuclear superoxospecies (**2**) and dinuclear peroxo-bridged species (**3**).

Scheme 1. Synthesis of Co(salen) from salicylaldehyde with ethylenediamine.

Synthesis of lignin model polymer

Referring to the methods of Kishimoto *et al.* [10], the lignin model polymer composed of only the β-O-4 structure were prepared using simple aromatic compounds as starting materials. The commercially available 4-hydroxy-3-methoxy-acetophenone was dissolved in anhydrous 1,4-dioxane-diethyl ether (3:4, v/v), followed by the addition of bromine to the mixture, and then kept at 0 °C for 1 h in order to prepare the bromide. With the addition of K_2CO_3 as the catalyst, the bromide was dissolved in anhydrous DMF, stirred under nitrogen at 50 °C for 3 h, and polymerized to the given polymer. The polymer was reduced with $NaBH_4$ in DMSO to obtain the G-type lignin model polymer composed of the β-O-4 structure. The molecular weight (*Mw*) was determined by gel permeation chromatography (GPC). The *Mw* of the lignin model polymer prepared was 5753. The *Mw* of the polymer was comparable to that of technical lignin (Scheme 2). The chemical structure of the G-type lignin model polymer was characterized by FTIR and ^{13}C-NMR. The FTIR and ^{13}C-NMR showed that the lignin model was a linear polymer. The polymer included the β-O-4 linkage, as in natural lignin. FTIR (Table 1): 1600/1514/1418 cm^{-1} (aromatic ring), 1463 cm^{-1} (CH_3+CH_2), 1260 cm^{-1} (OCH_3), 1226 cm^{-1} (ether–O), 3443/1136 cm^{-1} (–OH). In ^{13}C-NMR (Figure 4), the distinct sharp signals of all carbons indicate that the polymer structure was highly regulated, and that the polymer did actually exist as a mixture of many isomers that have a chiral centre at the α-position. ^{13}C-NMR signal: 74.3 ppm ($C_β$ in β-O-4), 70.7 ppm ($C_α$ in β-O-4), 55.6 ppm (OCH_3).

Catalytic experiments

The reactions and reaction conditions of biological systems were mimicked by carrying out oxidation experiments in aqueous solutions. In these experiments, in which the effect of Co(salen) was evaluated in oxidation of guaiacyl-type lignin model polymer (G) in presence/absence of Co(salen), the standard procedure was to dissolve the lignin model polymer (30 mg), hydrogen peroxide (0.6 mL, 30%), and pyridine (0.96 mL, 0.5 g L^{-1}) in water (10 mL) and adjust the pH with 0.9 mg NaOH (pH ~12). After that, the Co(salen) (4.0 mL, 0.5 g L^{-1}) was added, the reaction flask was evacuated, and the ambient pressure oxygen (≥99.5%) was bubbled constantly through the solution at a rate low enough (2.5 cm^3/min) to avoid evaporation of the solvent. The mixture was then stirred at 90 ºC for 1 h. The reaction was stopped by cooling the solution to ambient temperature, after which the reaction mixture was filtered with fritted glass filter. The final residue was collected for FTIR and ^{13}C-NMR analysis. The pH of the filtrate was adjusted to 12 with 2 M NaOH and soluble organic products were extracted with methylene dichloride. The organic phase was separated. The residual filtrate was adjusted to pH 2 with 2 M HCl and soluble organic products were similarly extracted. The two organic phases were merged and dried with sodium sulphate, filtered, and finally concentrated to 1 mL for reaction product analysis with gas chromatography-mass spectrometry (GC–MS) (Figure 3).

Fourier transform infrared spectroscopy (FTIR)

FTIR spectra of lignin model polymer (G) and residual lignin model polymer ($G_{Co(salen)}$ and G_{water}) obtained

Scheme 2. Synthesis of guaiacyl-type lignin model polymer (G).

Table 1. Relative intensity of different group bands of G, $G_{Co(salen)}$ and G_{water}, by FTIR

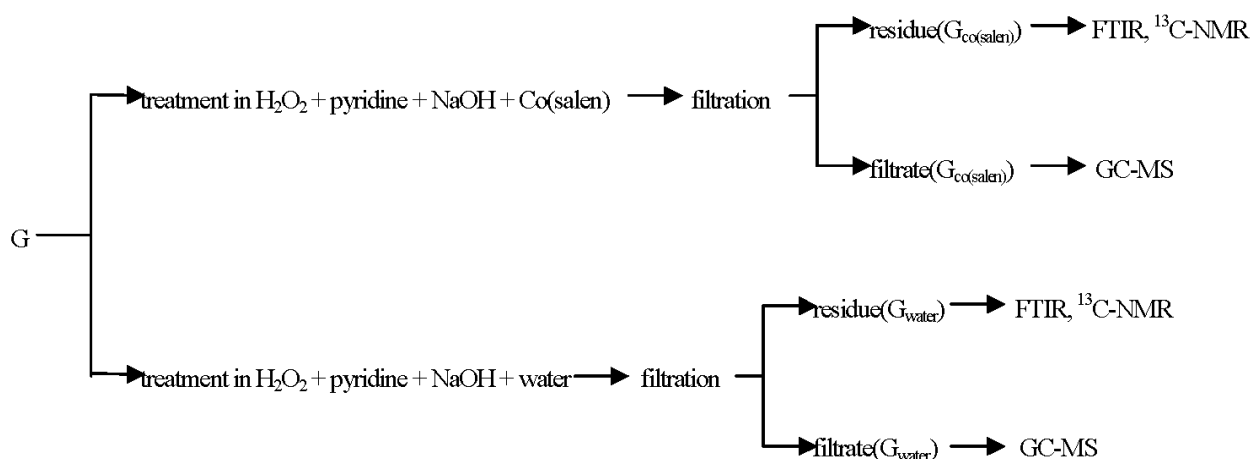| Assignment	Position, cm^{-1}	G	$G_{Co(salen)}$	G_{water}
OH	3443	1.320	1.141	1.185
Aromatic ring	1600	1.000	1.000	1.000
	1514	1.638	1.265	1.322
CH_3 + CH_2	1463	1.258	1.128	1.137
Aromatic ring	1418	1.221	1.119	1.106
Methoxy –OCH_3	1260	1.667	1.283	1.343
Ether –O	1226	1.459	1.220	1.248
Aliphatic OH	1136	1.531	1.248	1.286

Figure 3. Programmable route of experiment.

from catalytic experiments were made on a Bruker Tensor 27 spectrophotometer, between KBr plates with a 0.1 mm thick layer in wavelength bands from 4000 to 400 cm^{-1}. The effect of Co(salen) of catalytic system on substrate was evaluated by FTIR method with corresponding structure.

Relative intensity was measured using OMNIC software, version 7.1, rationed against the aromatic ring (1600 cm^{-1}) to provide relative changes in the structure of lignin model polymer to each other.

^{13}C-NMR Spectrometry

All ^{13}C-NMR spectra were recorded under quan-ti-tative conditions, which were accomplished by using a pulse sequence (inverse-gated) that eliminated the Nuclear Overhauser Effect (NOE) and had a sufficiently long pulse delay, allowing for all nuclei to be fully relaxed before the next pulse. The pulse delay commonly used for lignin, which had been established and verified in the literature, was 10 s [14].

The samples were dissolved in DMSO-d_6 and the spectra were recorded on Bruker DRX 500 apparatus at 318 K with TMS as internal reference (δ 0.00 ppm) in a 5-mm diameter tube. Some of the acquisition parameters used during the recording of the spectra included 9–15 k number of acquisitions, 90° pulse width ($pl = 8$ μs, pl 1 = 1.00 db), 222 ppm sweep width, and a 10-s pulse delay. The total acquisition time for recording each spectrum was typically quite long, ranging from 24 to 36 h. During processing, a line broadening of 10.0 Hz was used to obtain acceptable line widths.

Gas chromatography–mass spectrometry (GC–MS)

Separation and identification of Co(salen) oxidation products were performed using GC-MS with an Agilent Technologies HP 6890/ 5973 system fitted with a fused silica column (HP-INNOWAX, 30 m×0.25 mm i.d., 0.25 μm film thickness). Each sample was injected into a de-

activated glass liner inserted into the GC injection port with He as the carrier gas (~1.0 mL min^{-1}). The GC oven was programmed to work in the range 80 (with a 5 min initial delay) to 290 °C (held 40 min) using a 4 °C min^{-1} temperature ramp. The GC injector and GC–MS interface were maintained at 290 °C. The mass spectrometer was operated in the electron ionization mode (EI, 50 eV). Compound identification was performed using GC retention times and by Mainlib database.

RESULTS AND DISCUSSION

The FTIR and ^{13}C-NMR of lignin model polymer are presented in Figures 4 and 5. The 3443, 1514, 1463, 1260, 1226 and 1136 cm^{-1} peaks decreased in relative intensity as revealed by data in Table 1 obtained from the FTIR spectra. The relative intensity remained decreased upon addition of Co(salen), but these decreases in relative intensity were not significant between $G_{Co(salen)}$ and G_{water}.

The treatment of lignin model polymer (G) in presence/absence of Co(salen) ($G_{Co(salen)}$ and G_{water}) yielded a relevant decrease in aliphatic OH group and ring-opening reaction as a vibration arising at wavenumbers of 3443, 1136 and 1514 cm^{-1}. Moreover, when the reaction was performed in the presence of Co(salen), a weaker vibration was also found, the reaction performed with Co(salen) was more efficient than that with water, thus confirming the role of Co(salen) in the catalytic oxidation of C_{Ar} and C_α. It is worth noting that oxidative cleavage of β-O-4 (1226 cm^{-1}) and methoxy (1260 cm^{-1}) was observed during the treatment of lignin model polymer. According to the relative intensity (Table 1), the number of β-O-4 and methoxy group decreased in the presence of Co(salen). ^{13}C-NMR spectrometry (Figure 5) indicated the changes of β-O-4 and methoxy group in these reactions (C_β in β-O-4 at 74.3 ppm, C_α in β-O-4 at 70.7 ppm, OCH$_3$ at 55.6 ppm).

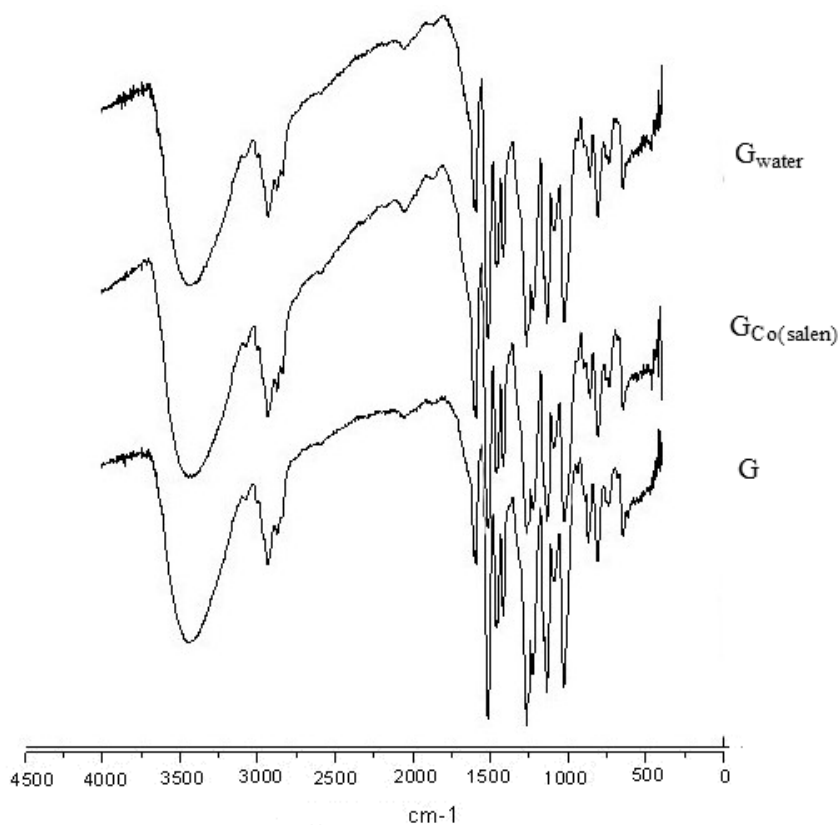*Figure 4. FTIR Spectra of G, $G_{Co(salen)}$ and G_{water}; G: guaiacyl-type lignin model polymer, $G_{Co(salen)}$: residual polymer of treatment in H_2O_2 + pyridine + NaOH + Co(salen), G_{water}: residual polymer of treatment in H_2O_2 + pyridine + NaOH + water.*
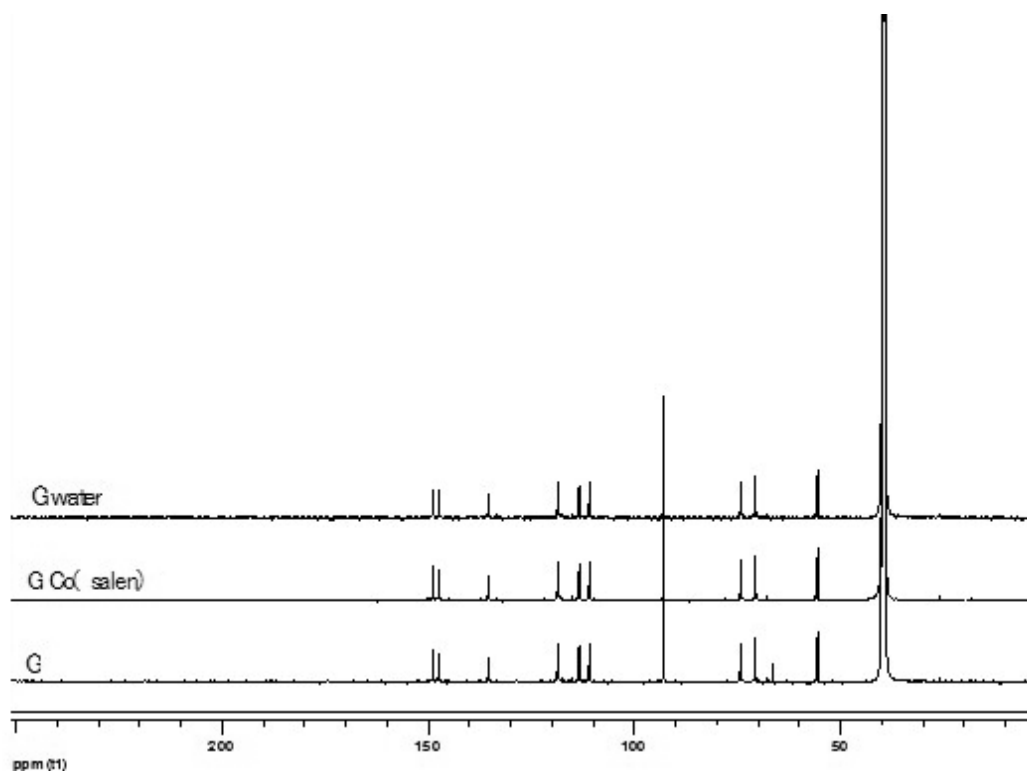

Figure 5. ^{13}C-NMR Spectra of G, $G_{Co(salen)}$ and G_{water}; G: guaiacyl-type lignin model polymer, $G_{Co(salen)}$: residual polymer of treatment in H_2O_2 + pyridine + NaOH + Co(salen), G_{water}: residual polymer of treatment in H_2O_2 + pyridine + NaOH + water.

Similar results were observed during the oxidation of residual lignin [15], suggesting that the Co(salen)/ /oxidant represents one step in the development of technology based green chemistry useful for extensive lignin modification and functionalization.

Examination was also made of the products produced in the catalytic oxidation. As was the case in earlier reports [8,16,17], benzaldehyde was the product formed along with the oxidation as identified at 7.28 min in Figure 6 (RSI/SI 858/832, molecular formula $C_7H_6O_2$). Very low production of benzoquinone was found in the presence of Co(salen) in the GC-MS analysis at 21.52 min (RSI/SI 648/477, molecular formula $C_{14}H_{20}O_2$). It can be considered that reactions proceeded selectively, yielding benzaldehyde as the product, with no sign of the corresponding carboxylic acid in ^{13}C-NMR spectra (Figure 5). The formation of aldehyde was probably the mechanism of oxidative cleavage of the β-O-4 bonds. A radical superoxo complex formed from the oxidation of polymer catalysed β-ether cleavage of lignin model polymer [18].

In addition, it is apparent that the added Co(salen) had an obvious influence on the composition of product. Catalytic oxidations benefit from the addition of Co(salen). Without added Co(salen), the polymer was oxidized to produce only very low amount of benzenedicarboxylic (59.07 min, Figure 6). With added Co(salen), Co(salen) complex catalysed oxidation of the polymer to *p*-benzoquinone. Various mechanisms have been suggested for this reaction. The most accepted one involves a cobalt-superoxo complex [19], which abstracts a hydrogen atom from the phenolic group producing a radical. This radical is attacked by a second superoxo complex or a molecule of oxygen producing the quinone (Scheme 3).

In a similar paper, Canevali *et al.* [20] studied the oxidation of dimeric lignin model compounds of aryl-glycerol-*β*-arylether type using dioxygen pressure of 1 MPa and Co(salen) as catalyst. Products benzoquinone and aldehyde arising from C-C bond cleavage were obtained.
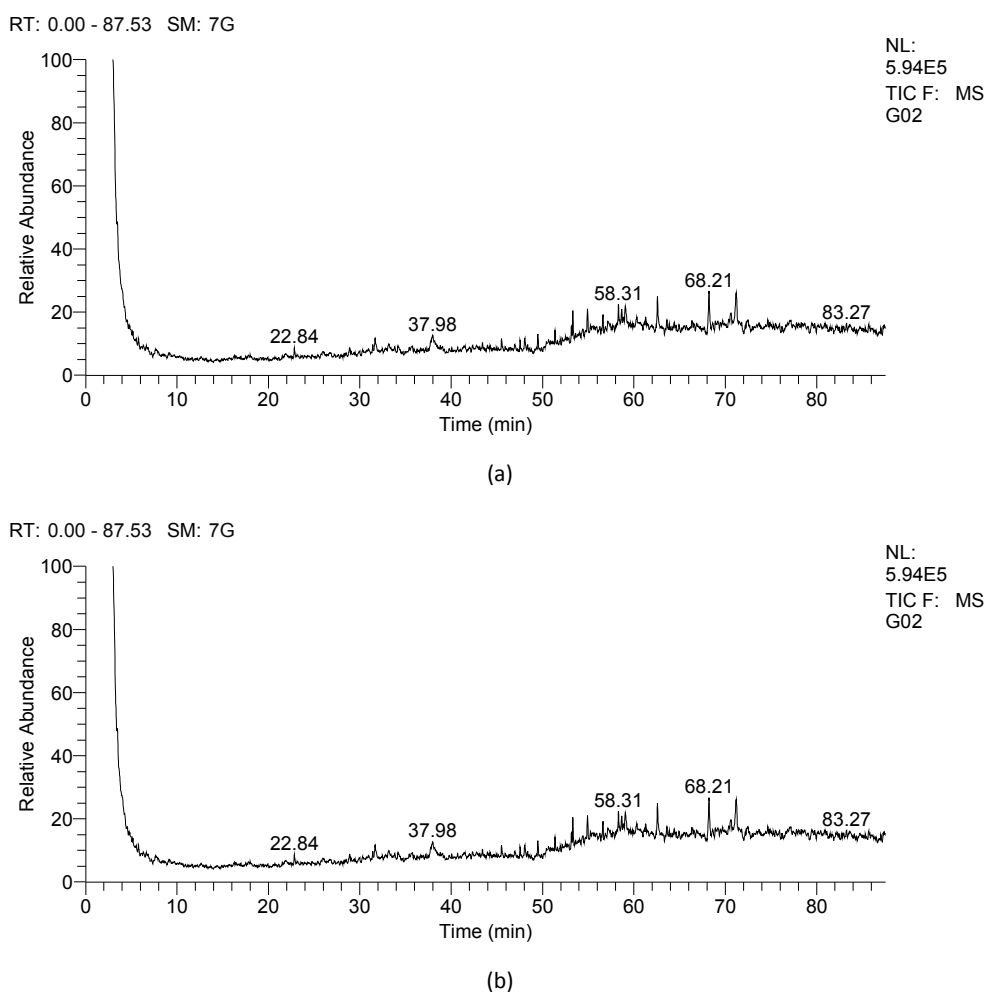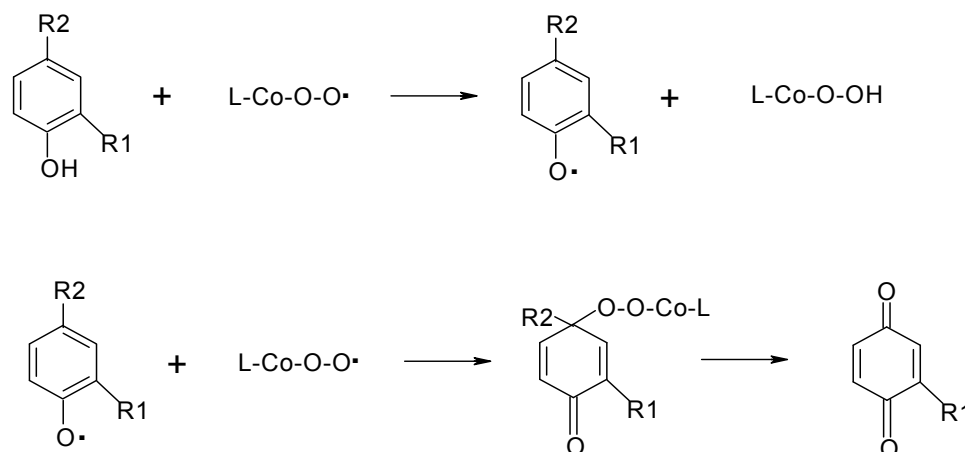

Figure 6. Total ion current of GC–MS. a) $G_{Co(salen)}$: product of treatment in H_2O_2 + pyridine + NaOH + Co(salen), b) G_{water}: product of treatment in H_2O_2 + pyridine + NaOH + water.

Scheme 3. Postulated oxidation of lignin model polymer to p-benzoquinone over Co(salen).

CONCLUSION

The treatment of lignin model polymer with Co(salen) catalytic system yielded a aliphatic-OH decrease, ring-opening reaction, β-O-4 cleavage and demethoxylation. In addition, it is apparent that the added Co(salen) to the reaction mixture had an obvious influence on the reaction, the reaction performed with Co(salen) was more efficient than that without Co(salen), thus confirming the role of Co(salen) in the catalytic oxidation. Identification of the products produced in the catalytic oxidation by GC–MS supported the proposed degradation mechanism of the lignin model polymer.

Acknowledgement

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IZVOD

UTICAJ Co(SALEN) KOMPLEKSA NA KATALIZOVANU OKSIDACIJU POLIMERA SLIČNIH LIGNINU

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(Naučni rad)

U ovom radu, Co(salen) kompleks, salen = *N*,*N'*-bis(saliciliden)etilendiamin, ispitivan je kao aktivator kiseonika u katalitičkoj oksidaciji model polimera nalik na lignin, korišćenjem vode kao rastvarača sa molekulskim kiseonikom i vodonik-peroksidom kao oksidantima. Uticaj Co(salen) kompleksa na oksidaciju ispitivan je spektroskopskim metodama (FTIR, ^{13}C-NMR i GC–MS). Reakcije katalizovane Co(salen) kompleksom su oksidacija C_α-alkohola, cepanje C_α-C_β bočnih lanaca, demetoksilacija, cepanje aromatičnog prstena, i β-O-4 cepanje. Pored toga, efekat Co(selen) kompleksa ukazuje na to da on može biti bitan za katalitičku oksidaciju, pošto utiče na oksidaciju polimera sličnih ligninu. Reakcija izvođena u prisustvu Co(salen) kompleksa je efikasnija nego bez njegovog prisustva. Obrazovanje aldehida u katalitičkoj oksidaciji, kako je pokazano GC–MS ispitivanjima, može se identifikovati tokom raskidanja β-O-4 veza.

Ključne reči: Co(salen) • Katalitička oksidacija • Polimeri slični ligninu • FTIR • ^{13}C-NMR • GC–MS