PRACE NAUKOWE – RESEARCH PAPERS

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Co(SALEN)-CATALYSED OXIDATION OF SYNTHETIC LIGNIN-LIKE POLYMER: O$_2$ EFFECTS

Molecular oxygen (O$_2$) is widely used as an oxidant in catalytic oxidation. This study was part of a biomimetic oxidation targeted at increasing the use of lignin in the production of chemicals through the application of salen transition metal catalysts. In this work, the catalytic performance of a cobalt-Schiff base catalyst Co(salen) in the presence of an oxidant and a ligand, such as pyridine, was analysed using two polymeric lignin model compounds. Oxidation experiments were carried out in alkaline water (pH 11-12) with the use of H$_2$O$_2$ and atmospheric oxygen (1atm) as oxidants. Co(salen) was an active catalyst, increasing the oxidation rate of the S- and G- type phenolic model polymers. In studies with FTIR, C-13 NMR, and GC-MS spectroscopy, the Co(salen)--catalysed oxidation rate was found to be high in the presence of O$_2$. O$_2$ had effects on the activity of the Co(salen), and it was concluded that the rate of the decomposition of the polymer was increased with the addition of O$_2$. The structure of the lignin model polymers also had an effect on their decomposition. In the form of two CH$_3$O-group polymers (S-type lignin model polymer), the depolymerisation decreased. Irrespective of the polymer (both S- and G- type lignin model polymers), the depolymerisation generated benzaldehydes as the main observed products. The model polymer studies were confirmed to be a useful way to obtain information about the reactions occurring during catalytic oxidation.

Keywords: Co(salen), catalyst, catalytic oxidation, lignin model polymer, O$_2$ effect, FTIR, C-13 NMR, GC-MS

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Introduction

Co(salen) is a coordination complex derived from the salen ligand and cobalt. The complex reversibly binds O_2 to give the oxygenated product, a $1:1$ ($Co:O_2$) or a $2:1$ ($2Co:O_2$) complex. O_2 accepts one electron from each Co^{2+}, forming a superoxide, O_2^-, bound to Co^{3+}, in the $1:1$ complex; O_2 accepts one electron from both Co^{2+}, forming a peroxide, O_2^{-2}, bound to two Co^{3+}, in the $2:1$ complex (fig. 1). This complex is very much like porphyrin but is relatively easy to prepare, cheap, stable in water and small in size, and a number of its derivatives have been widely used as catalysts in a wide variety of useful catalytic reactions. Besides being environmentally more benign, the catalytic oxidation of organic compounds with oxidants, such as dioxygen and hydrogen peroxide, is less economically waste-ful than traditional methods and is now an important reaction in both research laboratories and industry [Cozzi 2004; Manickam, Kulandaivelu 2012; Sandaroos et al. 2012].
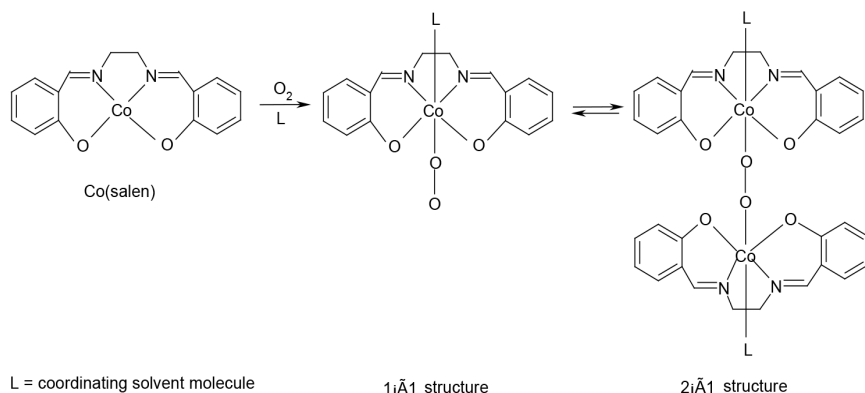

Fig. 1. Two possible structures for the O_2 adduct of Co(salen)
Rys. 1. Dwie możliwe struktury adduktu Co(salen) z O_2

Salen-catalysed oxidations of organic compounds have been widely studied. These complexes can catalyze the oxidation of substrates that serve as models for lignin phenolic subunits. In the studies of Meguro et al. [1984a; 1984b; 1989], Co(salen) was the most active Co-complex in the oxidation of the phenolic lignin model compound guaiacol. In the O_2-oxidation of veratryl alcohol in an alkaline solution, Kervinen et al. [2003] compared several cobalt catalysts, namely Co(salen), Co(α-CH₃salen), Co(4-OHsalen), Co(sulfosalen), Co(acacen) and Co(*N*-Me-salpr). The unsubstituted Co(salen) was the most active and the oxida-tion was selective at the benzylic position as veratryl aldehyde was the sole product. Reactivity increased linearly with increased O_2 pressure. In one study [Sippola 2006], the decomposition of Co(sulfosalen) catalyst was higher in the absence of oxygen. In particular it was demonstrated that they were able to oxidize high

yields of lignin model compounds. Arylglycerol-β-aryl ethers, phenylcoumarans and apocynol showed very high conversion values within 30 min [Haikarainen 2005; Rajagopalan et al. 2008; Badamali et al. 2011]. A series of biomimetic oxidations of lignin and a lignin model compound using Co(salen) were successfully studied in our laboratory [Zhou et al. 2011; Zhang, Zhou 2012; Zhou, Liu 2012]. From this and related studies, it was found that salen-type complexes of cobalt had an ability to selectively catalyse oxidation reactions in all experiments and a high catalytic activity was reached with the complex. Co(salen)-catalysed oxidations appeared to allow the creation of high-value products to extend the role of lignin for future biomass and biofuel applications [Crestini et al. 2010; Aresta et al. 2012].

On the basis of these studies, in this paper a synthetic lignin polymer was chosen as the model substrate for further studies on the reactions of lignin and the effect of O$_2$ (O$_2$ effect) because synthetic lignin polymer is more able to resemble natural lignins in their structures, even though it does not have a γ-hydroxymethyl group. Model polymer studies in lignin are important as they can clarify the mechanism occurring during catalytic reaction [Kishimoto et al. 2005; Katahira et al. 2006; Megiatto et al. 2009].

Materials and methods

Reagents

Co(salen), and 4-hydroxy-3-methoxy-acetophenone, 4-hydroxy-3,5-dimethoxy-aceto phenone were obtained from Sigma-Aldrich. 1,4-dioxane, diethyl ether, bromine, K$_2$CO$_3$, DMF, NaBH$_4$, DMSO, NaOH, H$_2$O$_2$, pyridine, O$_2$, CH$_2$Cl$_2$, HCl, and Na$_2$SO$_4$ were purchased from Sinopharm Chemical Reagent Co. Shanghai, China. The chemicals were used as received, without further purification.

Synthesis of lignin model polymer

Referring to the methods of Kishimoto et al. (2005), the lignin model polymer composed of only the β-O-4 structure was prepared using simple aromatic compounds as starting materials (fig. 2). The commercially available 4-hydroxy-3-methoxy-acetophenone, 4-hydroxy-3, 5-dimethoxyacetophenone was dissolved in anhydrous 1,4-dioxane-diethyl ether (3:4, v/v), adding bromine to the mixture, then kept at 0ºC for 1 hour to prepare the bromide. Adding K$_2$CO$_3$ as the catalyst, the bromide was dissolved in anhydrous DMF, stirred under nitrogen at 50ºC for 3 hours, and polymerized to obtain the given polymer. The given polymer was reduced with NaBH$_4$ in DMSO to obtain the G- and S-type lignin model polymers composed of the β-O-4 structure. The molecular weight (Mw) was determined by gel permeation chromatography (GPC). The Mw of the guaiacyl type polymer (G-type polymer) was 5753, where the value for the syringyl type (S-type poly-

mer) was 7501. The Mw of the polymers was comparable to that of technical lignin. The chemical structure of the lignin model polymers was characterized by FTIR and ^{13}C-NMR.
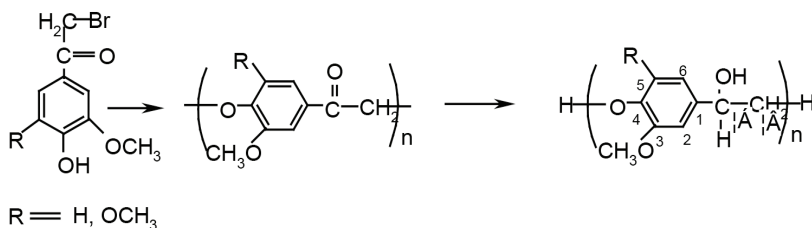

Fig. 2. Synthesis of S- and G-type lignin model polymers
Rys. 2. Synteza modelowych polimerów ligniny typu S- i G-
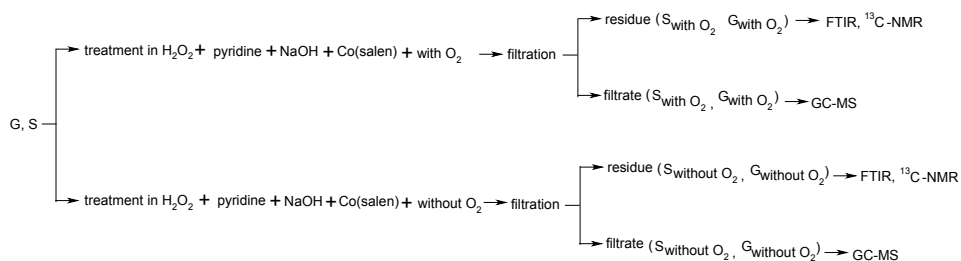
Catalytic experiments

Fig. 3. Programmable route of experiment
Rys. 3. Programowalna ścieżka doświadczenia

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 O_2 was evaluated in the oxidation of the S- and G-type lignin model polymers in the presence/absence of O_2, the standard procedure was to dissolve the lignin model polymers (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). Following this, the Co(salen) (4.0 mL, 0.5 g·L^{-1}) was added, the reaction flask was evacuated and the ambient oxygen pressure ($\geq$99.5%) was bubbled constantly through the solution at a rate (2.5 cm^3/min) low enough to avoid evaporation of the solvent. The mixture was then stirred at 90ºC for 1 hour. The reaction was stopped by cooling the solution to the ambient temperature, after which the reaction mixture was filtered using a fritted glass filter. The final residue ($S_{with\ O2}$, $G_{with\ O2}$) was collected for FTIR and ^{13}C-NMR analysis. The pH of the filtrate was adjusted to 12 with 2M NaOH and the soluble organic products were extracted with methylene dichloride. The organic phase was separated. The residual filtrate was adjusted to pH 2 with 2M HCl and the soluble organic products were

similarly extracted. The two organic phases were merged and dried with sodium sulphate, filtered and finally concentrated to 1mL for reaction product analysis with GC-MS (S$_{with\ O2}$, G$_{with\ O2}$) (fig. 3).

FTIR

The FTIR spectra of the lignin model polymers (S, G) and residual lignin model polymers (S$_{with\ O2}$, G$_{with\ O2}$) obtained from the 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}.

C-13 NMR spectrometry

All ^{13}C-NMR spectra were recorded under quantitative 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, was 10 seconds.

The samples were dissolved in d$_6$-DMSO and the spectra were recorded on Bruker DRX 500 apparatus at 318 K with TMS as the internal reference (δ 0.00) 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 usec, pl 1 = 1.00 db), 222 ppm sweep width, and a 10-second pulse delay. The total acquisition time for recording each spectrum was typically quite long, ranging from 24 to 36 hours. During the processing, a line broadening of 10.0 Hz was used to obtain acceptable line widths.

GC-MS

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

Results and discussion

Two types of lignin model polymers were synthesised: a G-type with one elec-tron-donating CH_3O-group and S-type with two electron-donating CH_3O-groups. The reactions and reaction conditions of biological systems were mimicked by carrying out the oxidation experiments in aqueous solutions. The capability of the Co(salen) complex was tested in the catalytic oxidations of the lignin model polymers, G- and S-type lignin model polymers. In addition, a study was made of the O_2 effect of the catalyst at the rate of the oxidation of the lignin model polymers. Polymeric β-O-4 lignin model compounds G- and S-type were the first model compounds to be tested. The oxidation of lignin model polymers lead to the formation of degradation products by the superoxocobalt complex initially formed [Nishinaga, Tomita 1980; Lyons, Stack 2013]. The species formed under these conditions have been spectrally observed in the lignin oxidations [Zhang, Zhou 2012]. The oxidation products consisted of mixtures of benzaldehyde, phe-nol, and quinone compounds (fig. 6: 7.2 min, 13.9 min, 21.50 min; fig. 7: I, II, III). The main oxidation products were benzaldehydes with good selectivities. Iden-tification was based on the NMR and mass spectra, as well as comparison with authentic samples [Schmidt 2010]. Compounds were formed by a rapid oxidation of α-C alcohol of the polymers. Some minor structural components (compounds II and III) in the oxidation mixtures were formed by other oxidative cleavage, but the amount was usually very low [Zhou et al. 2011].

The results obtained in the oxidations of the lignin model polymers with the use of the Co(salen) complex as a catalyst depended on the oxidant O_2 and the structure of the polymer, such as the CH_3O-group. The different results obtained in the reactions were compared in the spectra from fig. 4 to fig. 6. The effect of O_2 was tested by conducting the oxidations in the presence/absence of O_2. According to the results, the catalytic oxidations with the Co(salen) catalyst benefitted from the addition of O_2; adding O_2 to the reaction mixture in most cases markedly increased the reaction rate. This was because, by adding O_2, more of the superoxo complex was formed to more easily oxidise the lignin model polymers. In addition, the de-gree of degradation in the experiments varied with the CH_3O-group of lignin model polymers in the Co(salen)-catalysed oxidations. The G-lignin model polymer gave products with a high degree of degradation, whereas this was low with the S-lignin model polymer, suggesting that the CH_3O-group of the polymer has a significant effect on the oxidations. This is probably because the polymer was more stable towards destruction when the second electron-donating CH_3O-group was intro-duced into the ring [Lebo Jr. et al. 2001]. Kervinen et al. [2003] investigated oxi-dations of 3,4-dimethoxybenzyl alcohol to 3,4-dimethoxybenzaldehyde in aqueous alkaline media using Co(salen) and its derivatives as catalysts, and dioxygen as the terminal oxidant, when the catalyst substrate ratio dropped to 1:5950, a TON (turnover number) as huge as 330 was obtained at ambient dioxygen pressure, the

mechanism involved the initial formation of a superoxo complex, which performed a two-electron oxidation of the substrate [Kervinen et al. 2003; Kervinen et al. 2005]. Sippola [2006] found that the best conversion of the substrate to the corresponding aldehyde was 15.1% at atmospheric pressure of dioxygen in the oxidation of 3,4-dimethoxybenzyl alcohol using Co(sulfosalen) as the catalyst. Das and Punniyamurthy [2003], Velusamy and Punniyamurthy [2003] used cobalt and copper complexes of tetrahydrosalen ligand to oxidize benzylic alcohols with H_2O_2, as dioxygen was found to be an ineffective oxidant with these tetrahydrosalen catalysts.
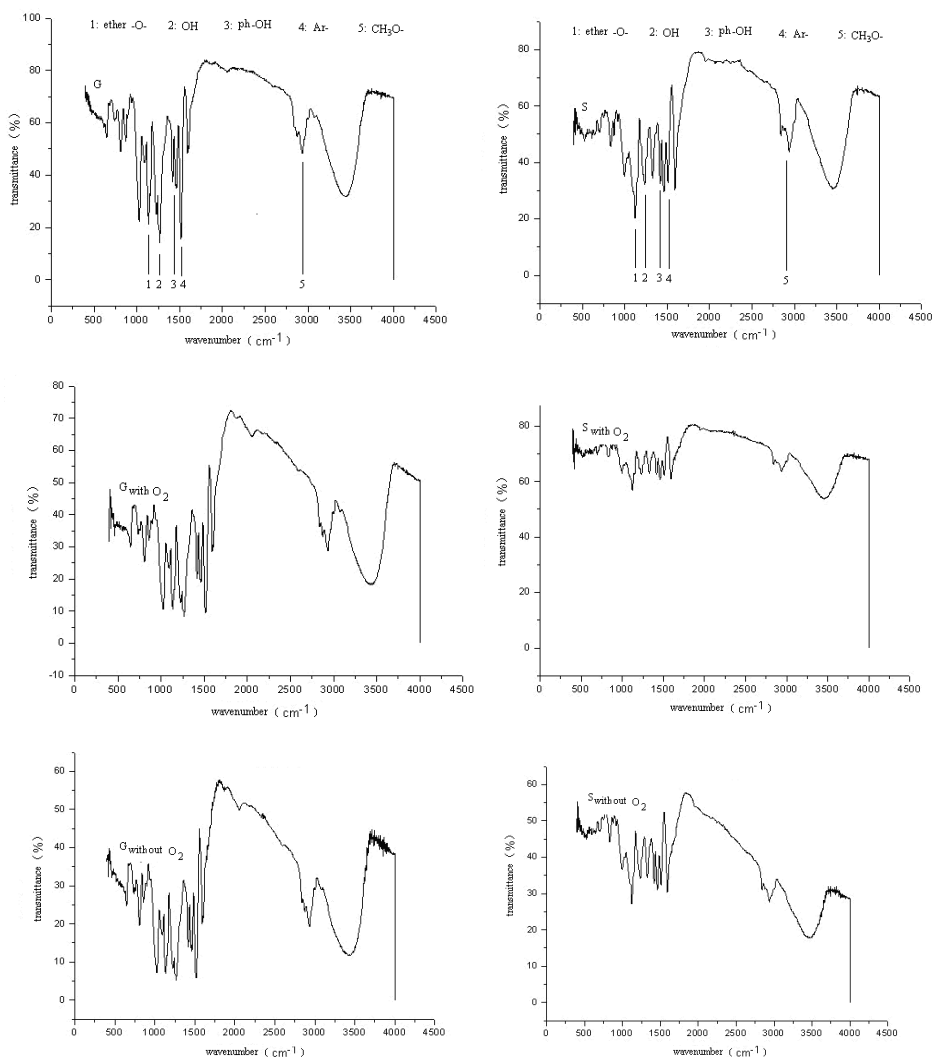

Fig. 4. FTIR spectra of lignin model polymers
Rys. 4. Widma FTIR modelowych polimerów ligniny

For the above oxidations of phenolic lignin model polymers, a reaction mechanism is postulated (fig. 8) [Becker 1980]. First, the catalytically active species removes a hydride ion from the benzylic position. The resulting cation loses a proton, and after tautomerization the oxidised product is obtained. Since the main observed products were aldehydes, the reaction appears to be a two-electron oxidation.
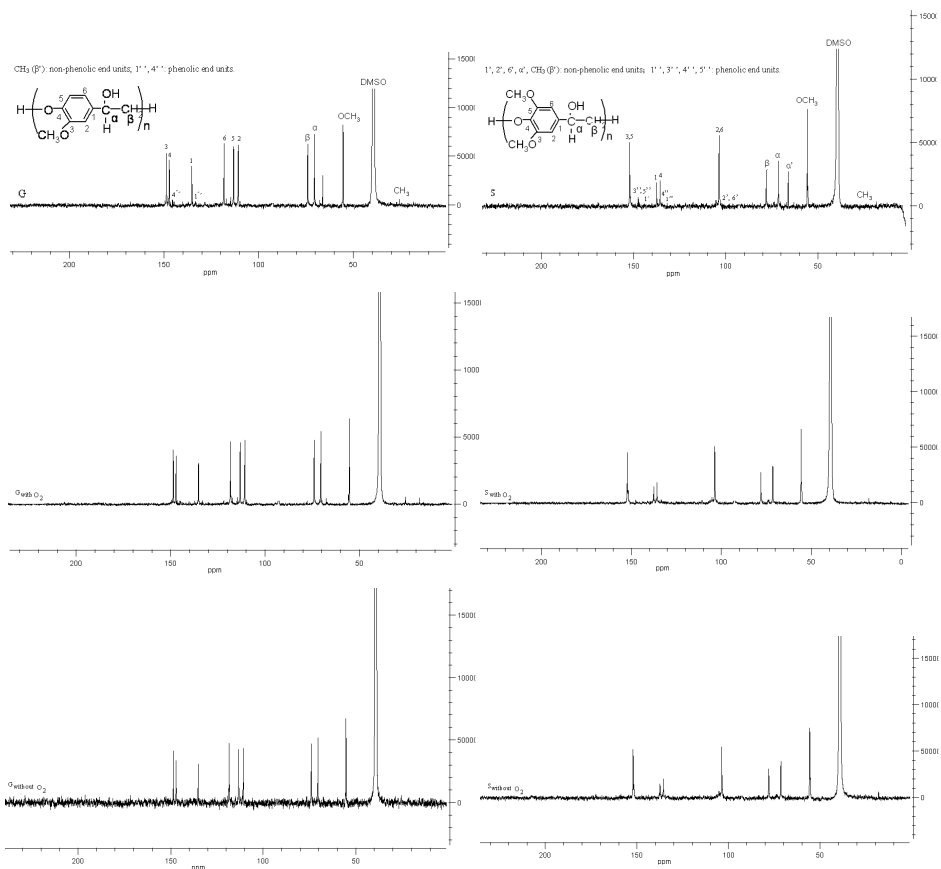

Fig. 5. C-13 NMR spectra of lignin model polymers
Rys. 5. Widma C-13 NMR modelowych polimerów ligniny

G$_{with\ O2}$ S$_{with\ O2}$

G$_{without\ O2}$ S$_{without\ O2}$

G$_{with\ O2}$ S$_{with\ O2}$
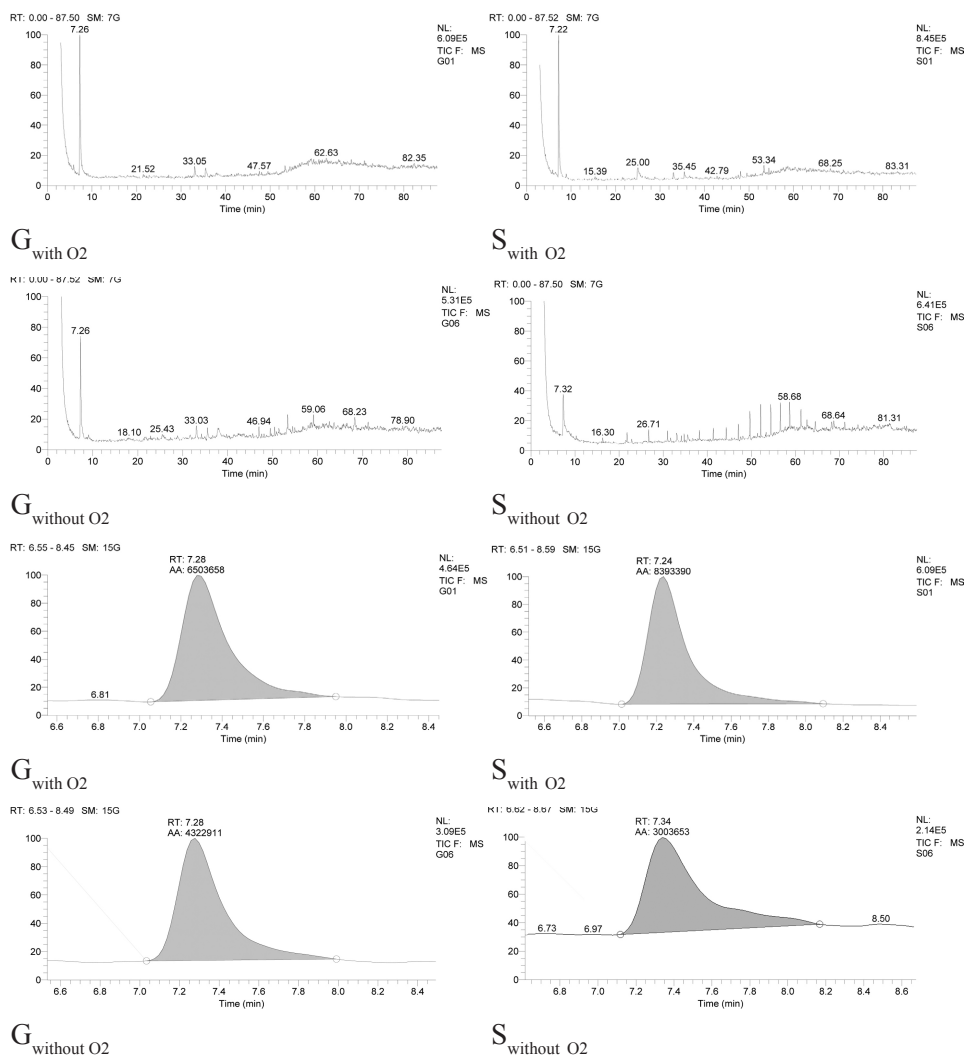
G$_{without\ O2}$ S$_{without\ O2}$

Fig. 6. Total ion chromatograms of S and G samples for GC-MS detection
Rys. 6. Chromatogramy całkowitej zawartości jonów próbek S i G przy zastosowaniu detekcji GC-MS
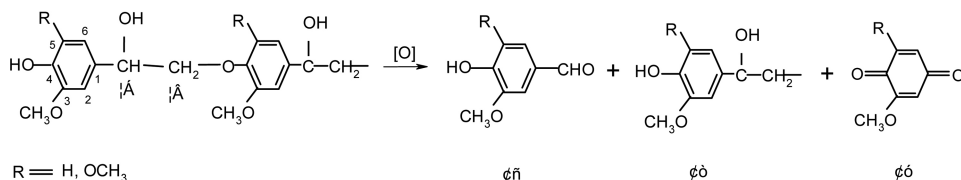

R = H, OCH$_3$

Fig. 7. Formation of products I-III by the oxidative cleavage of lignin model polymers
Rys. 7. Tworzenie się produktów I-III podczas oksydacyjnego rozkładu modelowych polimerów ligniny
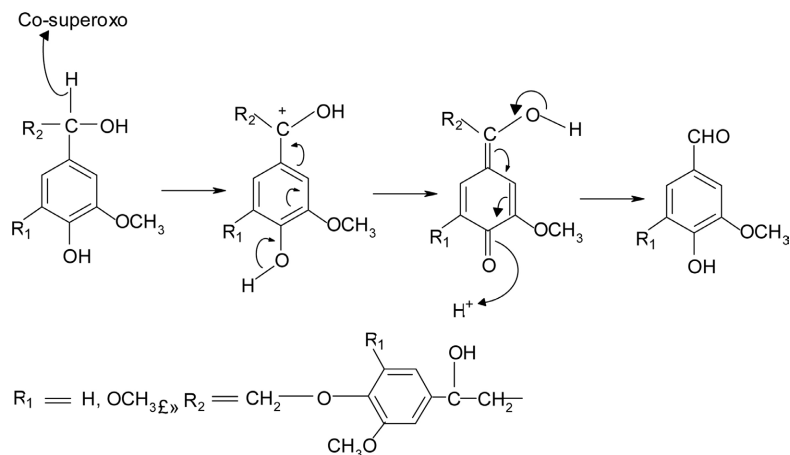
Fig. 8. Postulated mechanism for the oxidation of lignin model polymers
Rys 8. Postulowany mechanizm oksydacji modelowych polimerów ligniny

Conclusions

A system of Rusing Co(salen) – oxidant for oxidation was investigated. The presented system allowed the oxidation of lignin model polymers, analysing their viability and promoting the production of chemicals. Synthetic lignin-like polymers were synthesized from simple aromatic compounds which offered an additional advantage of enabling the lignin model compounds to resemble natural lignins in their structures. The Co(salen) as the catalyst was capable of catalysing the oxidative degradation of the lignin model polymers. The oxidation of the benzylic positions of both the G- and S-lignin model polymers catalysed by the Co(salen) was studied, and the corresponding aldehydes were identified as the main products with fair yields, especially in the presence of O_2. The effects of O_2 were to make the reaction smooth and increase the catalytic ability of the Co(salen) within the oxidation. There were some influences of the CH_3O-group of the lignin model polymers on the reactions: the presence of the electron-donating CH_3O--group in the lignin model polymers was found to decrease the reaction rate. High yields were obtained with the G-type substrate, whereas low yields were obtained with the S-type substrate. The Co(salen) complexes therefore appear to be promising oxidation catalysts for selective transformations of monomeric, dimeric and polymeric lignin model compounds with H_2O_2 or O_2 as terminal oxidants. To confirm the use of a Co(salen) – oxidant system for lignin transformations, further studies on lignin model compounds followed by lignins are needed.

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KATALIZOWANE Co(salen) UTLENIANIE SYNTETYCZNEGO LIGNINO-PODOBNEGO POLIMERU: EFEKT O_2

Streszczenie

Co(salen) to kompleks koordynacyjny stanowiący pochodną ligandu salenowego (disalicylaloetylenodiaminy) i kobaltu. Jego pochodne znajdują zastosowanie jako katalizatory. Przeprowadzono badania nad biomimetycznym utlenianiem ligniny i modelowych związków lignin z wykorzystaniem kompleksu Co(salen). Stwierdzono, że reakcje utleniania katalizowane kompleksu Co(salen) pozwalają na powstania wartościowych produktów, które umożliwią wykorzystanie ligniny w aspekcie przyszłych zastosowań jako biomasa i biopaliwa.

W pracy zastosowano dwa syntetyczne polimery ligninowe typu S i G, jako modelowe substraty do dalszych badań nad zachowaniem ligniny w reakcjach utleniania katalizowanych kompleksem Co(salen). Jego katalityczną skuteczność i wpływ O_2 analizowano za pomocą spektroskopii FTIR, C-13 NMR i chromatografii GC-MS. Odkryto, że Co(salen) zwiększa stopień utlenienia polimerów typu S i G. Natomiast O_2 wpływa na jego aktywność. Stopień rozkładu omawianych dwóch polimerów zwiększa się wraz z dodaniem O_2. Struktura polimerów wpływa na ich rozkład. W przypadku polimeru z dwiema grupami CH_3O- (typ S) depolimeryzacja zmniejszała się. Niezależnie of typu polimeru (S lub G) w procesie depolimeryzacji tworzyły się znaczne ilości benzaldehydów, jako głównych produktów reakcji, zwłaszcza w obecności O_2.

Kompleksy Co(salen) wydają się być obiecującymi katalizatorami utleniania dla selektywnych transformacji syntetycznych lignino-podobnych polimerów z wykorzystaniem O_2, jako końcowego (ostatecznego) utleniacza. Efekt O_2 zwiększają zdolność katalityczną Co(salen)u w reakcji utleniania.

Słowa kluczowe: Co(salen), katalizator, utlenianie katalityczne, model polimeru ligninowego, efekt O_2, FTIR, C-13 NMR, GC-MS