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Structural change of lignin in catalytic oxidation by Co(salen)

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In order to improve the catalytic performance, Co(salen) catalysis was performed on Indulin lignin. The structural changes of the lignin during the biomimetic treatment were characterized by ^{13}C-NMR, HSQC and ^{31}P-NMR spectroscopy. As a result of the biomimetic treatment, a decrease of β-O-4, β-β and β-5 linkage was observed, especially a cleavage of β-O-4 linkage. The fact that the condensed substructures were significantly decomposed explained the lignin degradation in-deep. In addition to these changes, the proposed route was applied to the lignin oxidation by Co(salen) catalysis based on the subtraction of phenolic hydrogen atoms.

Keywords: Biomimetic catalysis; Indulin lignin; Co(salen); HSQC; ^{13}C and ^{31}P-NMR spectroscopy

INTRODUCTION

Lignin contains a variety of different C-C and C-O linkages, which is related to the physicochemical and degradable properties of lignin. In addition, many chemical reactions such as alkylation, oxidation or reduction and condensation occur in lignin conversion *via* carbonyl, aliphatic hydroxyl and other active functional groups [1]. Moreover, the C-C and C-O linkages are refractory to the degradation of lignin [2], and the S/G ratio in the lignin structure is characteristically an important factor affecting the degradability of lignin [3, 4]. In summary, the reactivity is related to its lignin structure.

In recent years, scientists have made great efforts in catalytic oxidation of lignin, for example, biomimetic catalysts were used to oxidize lignin. M(salen) complex is a biomimetic catalyst, which has both enzymatic and chemical catalytic activity. Some studies have demonstrated the potential of M(salen) as a catalyst in lignin oxidation [5-7]. The activity was affected by the oxygen species in the catalytic system of M(salen). Compared with the binuclear peroxo-complex, the mononuclear superoxo-complex showed a strong catalytic activity in capturing phenolic hydrogen atoms from the substrates [8, 9]. Carmen *et al.* [10] found that the phenoxy cobalt radicals correlated with the formation of the oxidation products and the conversion rates of the substrates.

The reaction properties of lignin have yet to be further explored due to the complex mechanism involved. In addition, biomimetic catalysis has not been practically utilized in lignin conversion because the mechanism is still not clear. Therefore, it is necessary to find out the reaction mechanism of the biomimetic oxidation of lignin. In this paper, Co(salen) was applied to catalyze the oxidation of lignin. The structure of lignin was analyzed by ^{13}C-NMR, 2D HSQC NMR and ^{31}P-NMR. This may be a useful study for providing a mechanistic insight into the application of a biomimetic catalyst in lignin transformation.

Materials and methods

Indulin lignin: Indulin lignin was purchased from Sigma-Aldrich. It was an alkaline lignin derived from pine.

Catalytic oxidation of lignin by Co(salen): The treatment was carried out at 90 °C in a 1 L pressure reactor for 3 h. Typical processing conditions were as follows: 1g of Indulin lignin, 0.1 % dosage of Co(salen) (based on lignin), 1:1 molar ratio of pyridine to Co(salen), 0.5 MPa oxygen pressure,

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100 ml deionized water. After filtration, the residue was dissolved in tetrahydrofuran and filtered. The filtrate was evaporated in vacuum to obtain the residual lignin.

NMR analysis: The NMR analyses of the lignin samples were performed using DMSO-d6 as a solvent on the Bruker DRX500 MHz spectrometer. The frequency of 101.39 MHz was used for the quantitative ^{13}C-NMR with an inverse-gated decoupling sequence, 90° pulse angle. ^{31}P-NMR spectra were obtained after derivatization of the lignin with 2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane (TMDP) using cyclohexanol as internal standard. 2D HSQC NMR spectra were recorded using a standard Bruker pulse sequence with a 90° pulse, 0.12 s acquisition time, 1.3 s pulse delay, and a $^{1}J_{C\text{-}H}$ of 143 Hz. The quantitative analysis of the lignin functional groups by ^{13}C- and ^{31}P-NMR had a standard deviation of ~3.0 % and ~1.2 %, respectively.

RESULTS AND DISCUSSION

Quantitative ^{13}C-NMR analysis

The structure of the lignin samples was elucidated by ^{13}C-NMR before and after treatment with Co(salen). The quantitative determination was performed for different lignin moieties using the integral region of δ 162.3-102.7 ppm as a reference of six aromatic carbons [11].

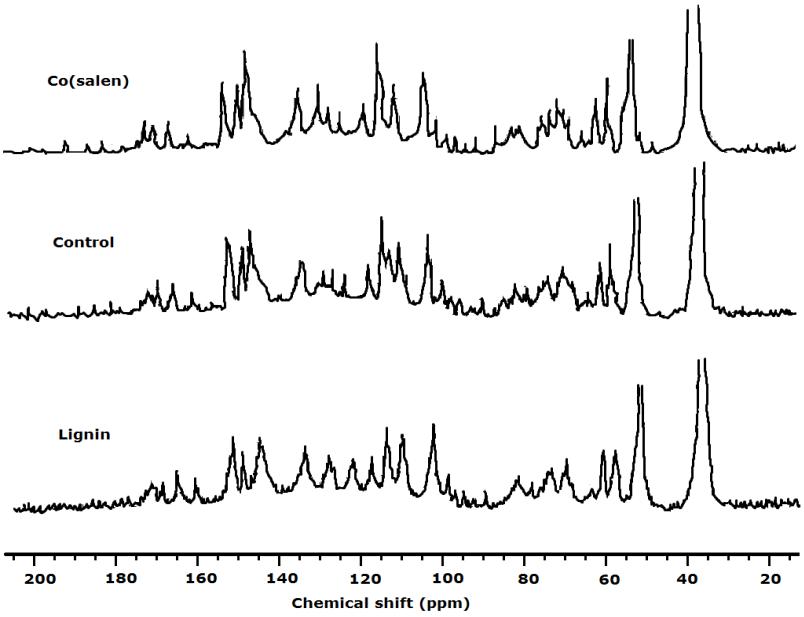

Figure 1. Quantitative ^{13}C-NMR spectra of the lignin samples.

Table 1. Content of functional groups by ^{13}C-NMR analysis.

Chemical shift (ppm)	Assignment	Amount (Ar)		
		Lignin	Control	Co(salen)
182.7-180.6	C=O in spirodienone structure	0.03	0.05	0.08
173.2-168.1	C=O in phenyl-COOR	0.24	0.28	0.35
167.7-165.8	C=O in conjugated phenyl-COOR	0.12	0.17	0.23
162.3-157.6	C_4 in p-hydroxyphenyl structure	0.02	0.04	0.07
155.2-141.7	C_3/C_4 in guaiacyl structure, C_3/C_5 in syringyl structure	1.57	1.72	2.13
140.4-122.8	C_1 in guaiacyl, syringyl, and p-hydroxyphenyl structure C_4 in syringyl structure, C_2/C_6 in p-hydroxyphenyl structure	2.26	2.05	1.68
122.6-118.3	C_6 in guaiacyl structure	0.38	0.47	0.71
116.5-112.6	C_5 in guaiacyl structure, C_3/C_5 in p-hydroxyphenyl structure	0.92	0.76	0.42
112.6-110.3	C_2 in guaiacyl structure	0.35	0.48	0.73
108.5-102.7	C_2/C_6 in syringyl structure	0.83	0.74	0.54
90.4-77.8	C_β in β-O-4, C_α in β-5 and β-β	0.81	0.62	0.33
65.2-61.7	C_γ in β-5 and β-O-4 with C_α=O in guaiacyl and syringyl structure	0.42	0.31	0.16
61.3-56.6	C_γ in β-O-4 structure without C_α=O	0.46	0.32	0.17
58.4-56.9	methoxyl group	0.84	0.64	0.37
52.7-51.3	C_β in β-β and C_β in β-5 structure	0.17	0.12	0.06

The spectra are presented in Figure 1, and the data are summarized in Table 1 [12, 13]. It is observed that the biomimetic treatment resulted inconsiderable changes in recovered lignin structure. The peak at δ 160 ppm confirmed the presence of p-hydroxy phenyl (H) units. The units of guaiacyl (G) and syringyl (S) in the lignin were evidenced by the chemical shifts between *δ* 125.6-110.3 and *δ* 108.5-102.7 ppm, respectively. Rencoret *et al.* [14] have reported that wood lignins are mainly composed of syringyl and guaiacyl units. The S/G ratio was found to decrease from 0.76 to 0.46 after the treatment with Co(salen). It was noticed that after the treatment the content of β-β and β-5 linkages decreased according to the amount per C_6 by the integration of C_β at *δ* 51.3-52.7 ppm. The β-O-4 linkages in lignin without C_α=O were quantified based on the C_γ at *δ* 56.6-61.3 ppm. There was about 34 % decrease after the biomimetic treatment compared to the control.

HSQC NMR analysis

HSQC NMR was applied to analyze the lignin structure before and after the biomimetic treatment by Co(salen). The results are shown in Table 2 [15, 16]. In HSQC NMR analysis, the spectrum is usually divided into high-field (0-50 ppm/0-3 ppm), aliphatic (50-100 ppm/3-6 ppm) and aromatic region (100-150 ppm/6-9 ppm). On the whole, the strength of the peaks decreased after the lignin was treated with Co(salen), which was the result of lignin degradation, as shown in Table 2. After the lignin was catalytically treated with Co(salen), the peak intensity of the guaiacyl, syringyl and p-hydroxyphenyl structures in the HSQC spectra decreased, indicating the degradation of these structural units in the biomimetic oxidation of lignin. Moreover, HSQC also confirmed the results obtained by ^{13}C-NMR analysis, in which the linkages of β-O-4, β-β, β-5 and methoxyl group were cleaved. The decrease in the content of methoxyl groups may be due to the degradation of syringyl structure and the demethylation of methoxyl groups. In addition, the α-5 structure in lignin (39.6-39.5 ppm/2.26-2.85 ppm) was found to decompose by the biomimetic oxidation. The functional groups at the side chains were oxidized according to the peak intensity, such as -CH_3 in aliphatic structure (13.6-19.2 ppm/0.76 ppm-0.84 ppm), -CH═CH- in guaiacyl structure (127.4 ppm/7.33 ppm), resulting in an increase in carbonyl content in the lignin (24.3-24.6 ppm/1.23-1.62 ppm, 37.3 ppm/1.98 ppm, 38.5 ppm/2.04 ppm, 73.5 ppm/3.26, 119.7 ppm/7.38 ppm).

Table 2. Analysis of functional groups by HSQC.

Chemical shift (ppm)		Functional group	Signal		
			Lignin	Control	Co(salen)
13.6-19.2	0.76~0.84	-CH_3 in aliphatic structure	s	w	vw
24.3-24.6	1.23-1.62	-CO-CH_3	vw	w	s
37.3	1.98	-CH_2-CH_2-COOH	vw	w	s
38.5	2.04	-CO-CH_2-CH_3, -CO-CH_2-COOH	vw	w	s
39.6-39.5	2.26-2.85	C_α-H in α-5 structure	s	w	vw
55.7	3.16	C_γ-H in β-β structure	s	w	vw
73.5	3.26	Ph-OCH_2-COOH	vw	w	s
59.6-61.3	3.35-3.57	C_γ-H in β-O-4 structure	s	w	vw
55.4	3.73	-OCH_3	s	w	vw
92.4-93.2	3.94-4.35	C_β-H in β-O-4 structure	s	w	vw
101.8	4.25	C_1-H in carbohydrate structure	s	w	vw
93.2-93.4	4.42-4.46	C_β-H in β-β structure	s	w	vw
71.6	4.65	C_α-H in threo β-O-4 structure	s	w	vw
71.6	4.88	C_α-H in erythro β-O-4 structure	s	w	vw
92.6	5.06	C_β-H in β-5 structure	s	w	vw
114.6-115.3	6.43-6.52	C_2-H in quinoid structure	vw	w	s
104.3	6.76	$C_{2/6}$-H in syringyl structure	s	w	vw
128.3	6.84	C-H in coniferol structure	s	w	vw
7.7	6.94	C_2-H in guaiacyl structure	s	w	vw
118.5-119.4	6.74~6.85	C_6-H in guaiacyl structure	s	w	vw
119.7	7.38	C_6-H in guaiacyl structure containing C=O	vw	w	s
114.5-115.6	6.89~7.14	C_5-H in guaiacyl structure	s	w	vw
142.7	7.44	C_6-H in quinoid structure	vw	w	s
128.3	7.05	$C_{2/6}$-H in p-hydroxyl phenyl structure	s	w	vw
127.4	7.33	-CH═CH- in guaiacyl structure	s	w	vw

s, strong; w, weak; vw, very weak.

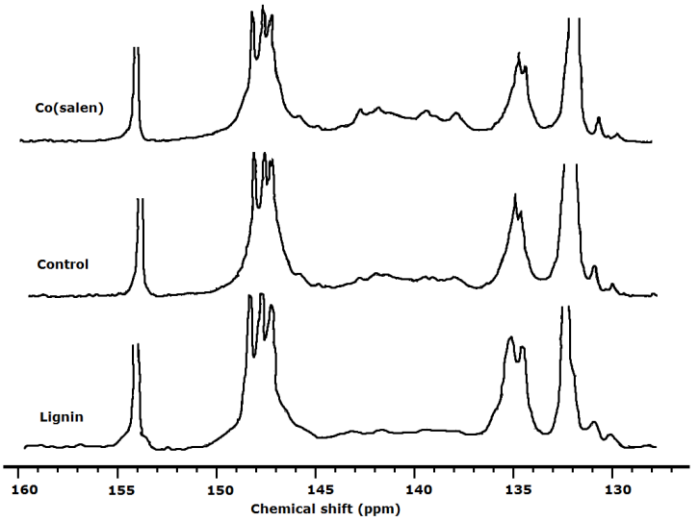

Figure 2. Quantitative ^{31}P-NMR spectra of the lignin samples.

Table 3. Content of functional groups by ^{31}P-NMR analysis.

Chemical shift (ppm)	Functional group	Content (mmol/g)		
		Lignin	Control	Co(salen) catalysis
154.3-153.6	Internal standard	-	-	-
149.5-145.4	Aliphatic hydroxyl groups	1.57	1.23	1.06
144.2-140.4	Condensed phenolic hydroxyl groups	0.62	0.36	0.17
143.3-142.2	Phenolic hydroxyl groups in syringyl structure	0.25	0.38	0.52
140.4-138.7	Phenolic hydroxyl groups in guaiacyl structure	0.16	0.29	0.36
138.6-137.3	p-Phenolic hydroxyl groups	0.13	0.25	0.42
136.2-133.4	Hydroxyl groups in carboxyl groups	0.14	0.48	0.73

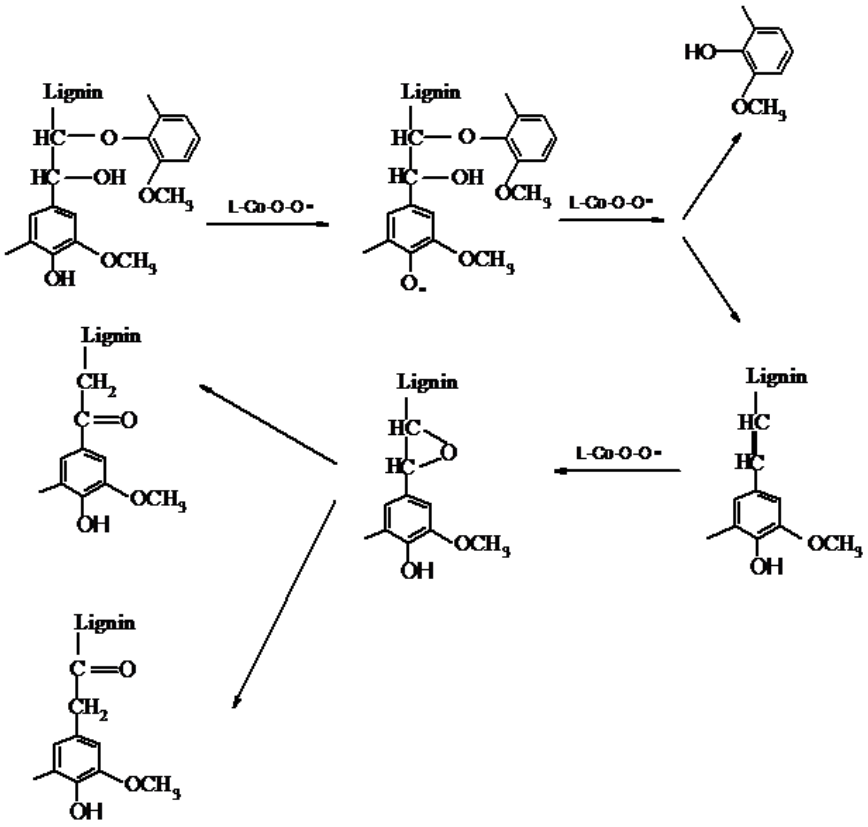

Figure 3. Representative pathways of lignin depolymerization by Co(salen).

Quantitative ^{31}P-NMR analysis

The quantitative ^{31}P-NMR analysis was used to determine the hydroxyl groups in order to elucidate the lignin oxidation. The spectra are presented in Figure 2, and the hydroxyl content is shown in Table 3 [17]. The data clearly illustrated that the most prominent ones in the lignin were aliphatic hydroxyl groups, which was in line with the report by Pu *et al*. [18] that the major hydroxyl groups in the wood lignin were in the aliphatic regions.

After biomimetic treatment, the content of the aliphatic hydroxyl groups decreased from 1.23 mmol/g to 1.06 mmol/g due to the oxidation at the side chains in the lignin, which was confirmed by the increase in the content of the carboxyl groups (136.2-133.4 ppm). The content of the condensed phenolic hydroxyl groups decreased from 0.36 mmol/g to 0.17 mmol/g, indicating that the condensed type substructures in the lignin were obviously degraded. In addition, the data shown in Table 3 suggest that the phenolic hydroxyl content of the syringyl, guaiacyl and p-hydroxyphenyl substructures in the Co(salen)-treated lignin increased when compared with the control. This was due to the cleavage of β-O-4 linkage leading to an increase in phenolic hydroxyl groups. As shown in Figure 1, the superoxocobalt complex initiated the reaction by subtraction of phenolic hydrogen atoms, leading to the cleavage of β-O-4 linkage. Further oxidation at the side-chain gave carbonyl groups [19, 20].

CONCLUSIONS

In accordance with the lignin transformation, in this study the structure of Indulin lignin in the biomimetic treatment with Co(salen) was examined by ^{13}C, ^{31}P-NMR and HSQC. During the biomimetic catalysis, the structural behavior of the lignin significantly changed. It was observed that the cleavage of β-O-4 linkage resulted in an increase in phenolic hydroxyl groups by the treatment. The side chains in the lignin were oxidized. Furthermore, the content of the units wasobserved to decrease in the guaiacyl, syringyl and p-hydroxyphenyl substructure as a result of the biomimetic treatment.

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СТРУКТУРНИ ПРОМЕНИ В ЛИГНИН ПРИ КАТАЛИТИЧНО ОКИСЛЕНИЕ С Co(САЛЕН)

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(Резюме)

За подобряване на ефективността на катализа при окислението на ингулин лигнин е използван Co(сален). Структурните промени на лигнина при биомиметичната обработка са проследени чрез ^{13}C-NMR, HSQC и ^{31}P-NMR спектроскопия. В резултат на биомиметичната обработка е установено скъсяване на връзките β-O-4, β-β и β-5, и по-специално, разцепване на β-O-4 връзката. Фактът, че кондензираните субструктури значително се разлагат, обяснява дълбочинната деградация на лигнина. В допълнение на тези промени, предложеният механизъм е приложен към окислението на лигнин, катализирано с Co(сален) чрез отстраняване на фенолни водородни атоми.