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Mechanism of Co-salen Biomimetic Catalysis Bleaching of Bamboo Pulp

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1. Introduction

Biomimetics have enzymatically and chemically the catalytic performance and the advantage to reduce pollution (Xie, 1999), and thus have been introduced into the pulping and bleaching field (Huynh, 1986; Cui & Dolphin, 1994). Co-salen can be easily synthesized with high yield. It was shown, in our studies, that Co-salen biomimetic pretreatment improved the bleachability of pulp with a small loss of carbohydrate, increased the brightness of 5.3 % ISO compared to the control when bamboo kraft pulp was bleached with total chlorine free (TCF) sequence. In this work, structural changes in residual lignin isolated and their effects on the bleached pulp were elucidated to provide fundamental basis for the biomimetic catalytic bleaching.

2. Important

Besides being environmentally more benign, catalytic oxidation of organic compounds based on the use of terminal oxidants such as molecular oxygen and hydrogen peroxide is less wasteful from the economical points of view, and is now an important reaction in both research laboratories and industry. Metal salen compounds have been investigated as catalysts in several different reactions, for example epoxidation, epoxide ring opening, carbonyl addition, cycloaddition and oxidation of sulphides to sulphoxides. Earlier work on the Co-salen catalyzed oxidation of phenols with oxygen has been extended to include substrates that serve as models for lignin subunits to provide fundamental basis for the improvement in pulp bleaching industry.

Our laboratory has been investigating the process parameters of Co-salen catalyzed bleaching of bamboo pulp. The mechanism for the oxidation of residual lignin of pulp using Co-salen as catalyst is largely unstudied. In the present study, we studied the structural changes in residual lignin isolated of bamboo pulp across the Co-salen catalytic treatment in the presence of molecular oxygen and hydrogen peroxide using pyridine as axial ligand with GPC, FTIR, ^{1}H-NMR, ^{31}P-NMR and element analysis. It was found that the methoxyl group, phenolic hydroxyl group, aliphatic hydroxyl group, guaiacyl and syringyl were reduced; the content of carbonyl group increased; the aromatic ring was opened, the linkages of β-O-4, β-1, β-5 and β-β were cleaved; the molecular weight of residual lignin decreased. The chromophore of the bleached pulp with Co-salen biomimetic pretreatment was reduced and its crystallinity increased. The experimental formulas(C_9) of the residual lignin of the oxygen delignified bamboo pulp before and after biomimetic treatment were also obtained.

3. Experimental

3.1 Material

Co-salen was synthesized following the procedure of published literature (Liu et al., 1991; Liu et al., 2002).

Oxygen delignified kraft pulp of bamboo (OKP) used was prepared in our laboratory with the property as follows: kappa number 9.1, viscosity 1043 ml/g, brightness 39.5 % ISO.

3.2 Experimental methods

3.2.1 Co-salen treatment of OKP

The treatment was carried out in a 1 L stainless steel tank. Reaction tank was tempered at 90 °C for 5 h by contant-temperature water bath. Oxygen flow was directed into the tank at the pressure of 0.2 MPa. The charge of chemicals (o.d.p.), 0.03% Co-salen, 1:1 pyridine/Co-salen (molar ratio), 3% NaOH, 1.5% H_2O_2, was used at 5 %pulp consistency.

3.2.2 Bleaching of OKP with TCF sequence

OKP was bleached with the sequence of Co-salen pretreatment (Co), alkali extraction with addition of H_2O_2 (Ep), peracetic acid (Pa) and hydrogen peroxide (P) bleaching. Control trial was also performed instead of any chemicals with distilled water at pretreatment stage.

3.2.3 Isolation of residual lignin in pulp, oxygen delignified and Co-salen pretreated pulp

The pulps acetone-preextracted were extracted with 0.1 M HCl in dioxane/water (82 : 18) under nitrogen positive pressure and subsequently worked up according to established procedures (Shi & He, 2003).

3.2.4 Acetylation of lignin samples

Lignin samples were acetylated with pyridine-acetic anhydride solution (1 : 2, v : v) for ^{1}H-NMR analysis.

3.3 Analytical methods

3.3.1 Molecular weight of lignin samples

Molecular weight of lignin samples were determined with Waters 515 Gel Permeation Chromatography (GPC).

3.3.2 Elemental analysis

Analysis of C, H, N in lignin samples was performed on Vario EL Organic Elemental Analyser. Content of O was as calculated from that of C, H, N.

3.3.3 FTIR analysis

Bruker Tensor 27 FT-IR Spectroscopy was used at 400-4000 cm^{-1}.

3.3.4 NMR analysis

The analytical techniques of ^{1}H-NMR and ^{31}P-NMR are employed for the determination of residual lignin structural features on Bruker DRX 500 NMR Spectroscopy.

3.4 Methoxyl content of lignin samples

Vieböck method was used for the determination of methoxyl content of lignin samples (Shi & He, 2003).

3.5 C_9 experimental formula of lignin samples

C_9 experimental formula of lignin samples was obtained based on the elemental and methoxyl analysis according to the formula $C_xH_yO_z(OCH_3)_n$ provided by Vazquez et al (Vazquez et al., 1997).

4. Results and discussion

4.1 Elemental and methoxyl analysis of isolated residual lignins before and after Co-salen biomimetic treatment

The data are listed in Table 1 on elemental composition, methoxyl content and experimental formula of residual lignins isolated from pulps obtained during Co-salen biomimetic treatment. Content in methoxyl was reduced possibly due to the cleavage of methyl aryl ether. Molecular weight of structural uint (C_9) was also increased due to the increase in oxygen element content which resulted from the catalytic oxidation of aryl ring and side chain by Co-salen.

Samples	C/%	H/%	O/%	N/%	OCH_3/%	Experimental formulas (C_9)	Unit molecular weight
Untreated	59.03	6.455	33.74	0.780	17.67	$C_9H_{9.82}O_{3.18}(OCH_3)_{1.18}$	205.3
Treated	55.84	6.423	37.34	0.396	12.85	$C_9H_{11.00}O_{4.08}(OCH_3)_{0.88}$	211.5

Table 1. Results of elemental and methoxyl analysis of isolated residual lignins before and after Co-salen biomimetic treatment

4.2 Molecular weight analysis of isolated residual lignins before and after Co-salen biomimetic treatment

Molecular weight (Mn, Mw) and polydispersity of residual lignin was all decreased across the oxidation degradation in Co-salen biomimetic treatment according to the data obtained by GPC (Table 2).

Samples	RT/min	Mn	Mw	Polydispersity
Untreated	7.2	4813	5418	1.12
Treated	7.2	4759	5199	1.09

Table 2. Molecular weight of isolated residual lignins before and after Co-salen biomimetic treatment

4.3 FTIR analysis of isolated residual lignins before and after Co-salen biomimetic treatment

AS seen in Table 3, the band of ~ 3430 cm^{-1} was assigned to hydroxyl, it was reduced according to the relative intensity, which was just because of the oxidation reaction in which obvious increase in carbonyl (1640 cm^{-1}) was observed. This increase can enhance the

No.	Assignment (Jiang, 2009)	Wavenumber / cm^{-1}		Rel. intensity	
		Untreated	Treated	Untreated	Treated
1	OH stretching vibration	3425	3432	0.555	0.485
2	CH asymmetrical stretching vibration in CH_3, CH_2, CH	2924	2923	0.198	0.191
3	CH symmetrical stretching vibration in CH_3, CH_2, CH	2853	2852	0.016	0.036
4	C=O stretching vibration in β-C=O, COOH, ester	1721	1720	0.086	0.072
5	C=O stretching vibration in α-C=O, conjugated C=O	1640	1630	0.030	0.210
6	Benzene skeleton vibration	1600	1603	0.240	0.015
7	Benzene skeleton vibration	1509	1508	0.092	0.060
8	CH deformation vibration in CH_3, CH_2	1462	1462	0.140	0.101
9	Benzene skeleton vibration	1422	1422	0.047	0.033
10	CH deformation vibration in benzene ring	1380	1381	0.012	0.018
11	C-O stretching vibration in syringyl ring	1326	1327	0.030	0.016
12	C-O stretching vibration in guaiacyl ring	1267	1266	0.013	0.010
13	C-O stretching vibration in syringyl ring	1216	1217	0.056	0.038
14	C-H stretching vibration in syringyl ring	1121	1125	0.015	0.018
15	C-O bending vibration in secondary alcohol, ether	1085	1084	0.018	0.364
16	C-O bending vibration in primary alcohol, ether	1051	1052	0.529	0.027
17	C-H bending vibration in benzene ring	898	899	0.023	0.006

Table 3. Results of FTIR analysis of isolated residual lignins before and after Co-salen biomimetic treatment

reactivity of residual lignin in pulp. The decrease in relative intensity of 2924, 1462 cm^{-1} indicated that aliphatic side chains were oxidized, in the mean time aryl rings were also seriously degraded as seen the observed significant weakening of signals at 1600, 1509, 1422 cm^{-1}. Syringyl structures (1326, 1216 cm^{-1}) was preferentially degraded, and guaiacyl ones (1267 cm^{-1}) basically did not change in reaction.

4.4 NMR analysis of isolated residual lignins before and after Co-salen biomimetic treatment

4.4.1 ^{1}H-NMR analysis

The results of ^{1}H-NMR analysis on residual lignins isolated from pulps in Co-salen biomimetic treatment were shown in Table 4. It was found that syringyl units were significantly reduced, guaiacyl units changed little, which was in agreement with the results obtained by FTIR, and p-OH benzene ones were increased. Demethylation occured as reaction proceeding leading to the decrese of methoxyl in residual lignin. The decrease in phenolic hydroxyl may be related to the etherification. In accordance with the FTIR analysis the decrease in aliphatic hydroxyl was due to the oxidation, in which H atom of COOH, CHO present in residual lignin was found to be obviously increased based on the ^{1}H-NMR data (Table 4). In addition H atom at 5.7-6.17, 3.03-3.54 ppm was reduced, which indicated that the structures with the linkages of β-O-4, β-1, β-5, β-β were partially cleaved.

No.	δ/ppm	Assignment (Shi & He, 2003)	H/% Untreated	H/% Treated	H/C_9 Untreated	H/C_9 Treated
1	8.01-11.50	H in COOH, CHO	1.01	6.21	0.20	1.23
2	7.50-8.01	H in aromatic nucleus of p-OH benzene	1.64	2.78	0.32	0.55
	6.97-7.50	H in aromatic nucleus of guaiacyl	6.07	5.72	1.19	1.13
	6.17-6.97	H in aromatic nucleus of syringyl	5.06	3.76	0.99	0.74
3	5.70-6.17	H_α in side chain (β-O-4, β-1); H_β (conjugated between α and β)	3.16	2.29	0.62	0.45
4	5.20-5.70	H_α in phenyl coumaran	1.90	2.45	0.37	0.48
5	4.40-5.20	H_α (β-β); H_β (β-O-4); H_γ (cinnamyl alcohol)	4.55	5.88	0.89	1.16
	4.14-4.40	H_γ (β-1, β-5, β-O-4, β-β)	2.91	3.10	0.59	0.60
	3.54-4.14	H in CH_3O	11.25	10.13	2.21	2.00
	3.03-3.54	H_β (β-1, β-5, β-β)	7.96	6.37	1.56	1.26
6	2.20-3.03	Aromatic OH	13.65	13.07	2.68	2.48
7	1.47-2.20	Aliphatic OH	22.00	21.41	4.31	4.23

Table 4. Results of ^{1}H-NMR analysis of isolated residual lignins before and after Co-salen biomimetic treatment

4.4.2 ^{31}P-NMR analysis

No.	δ/ppm	Assignment (Granata & Argyropoulos, 1995)	mmol · g^{-1} Untreated	Treated
1	149.8-145.2	Aliphatic OH	1.12	1.08
2	144.5-143.6	Condensed aromatic OH	0.34	0.23
3	143.6-142.3	Syringyl aromatic OH	0.14	0.08
4	140.1-138.5	Guaiacyl aromatic OH	0.20	0.13
5	138.5-137.0	p-aromatic OH	0.15	0.11
6	136.5~133.6	COOH	0.48	0.51

Table 5. Results of ^{31}P-NMR analysis of isolated residual lignins before and after Co-salen biomimetic treatment

The data obtained by ^{31}P-NMR (Table 5) also showed that aliphatic and phenolic hydroxyls present in residual lignin were reduced, and carboxyls increased after Co-salen biomimetic bleaching of oxygen delignified bamboo pulp, where the change of syringyl-type phenolics was more obvious than other functional groups as listed in Table 5. Especially condensed-type phenolic structures were significantly degraded, which may improved the removal of residual lignin from the pulp.

4.5 FTIR analysis of resultant bleached pulp compared to the control sample

The signals at 1237, 1059, 1032, 987 cm^{-1} in FTIR spectra were assigned to carbonyl group present in cellulose, hemicellulose and lignin. The relative intensity of these signals were weakened compared to the control sample as shown in Table 6, which indicated that Co-salen biomimetic pretreatment may reduced chromophores produced during the bleaching process. In addition the crystallinity of bleached pulp was also increased when oxygen delignified pulp of bamboo was pretreated by Co-salen biomimetic system.

5. Conclusion

During Co-salen biomimetic pretreatment of oxygen delignified bamboo pulp, ary rings were opened, the functional groups of methoxyl, phenolic and aliphatic hydroxyl reduced. Carbonyls were increased due to the oxidation of aliphatic hydroxyls. Structural units of guaiacyl and syringyl-type present in residual lignin were degraded. Structural linkages were cleaved including β-O-4, β-1, β-5 and β-β. Molecular weight of residual lignin was decreased as reaction proceeding, oppositely that of C_9-structural uint was increased due to the increase in oxygen element content according to the C_9-experimental formulas obtained in this study. Besides the structural changes occured in residual lignin mentioned above, Co-salen biomimetic pretreatment may reduce chromophores and increase crystallinity of resultant bleached pulp of bamboo.

No.	Assignment (Stenius & Vuorinen, 1999)	Wavenumber /cm^{-1} Control	Bleached pulp	Rel. intensity Control	Bleached pulp
1	CH asymmetrical stretching vibration in CH_3, CH_2, CH in cellulose	2899	2901	0.141	0.121
2	CH_2 shear vibration in cellulose	1433	1432	0.054	0.055
3	CH bending vibration in cellulose and hemicellulose	1375	1376	0.120	0.116
4	C=O stretching vibration in lignin	1237	1238	0.008	0.001
5	C=O stretching vibration in cellulose and hemicellulose	1059	1059	0.423	0.386
6	C=O stretching vibration in cellulose, hemicellulose and lignin	1032	1032	0.029	0.026
7	C=O stretching vibration in cellulose and hemicellulose	987	988	0.022	0.012
8	C_1 deformation vibration in polysaccharide	896	896	0.060	0.049
9	Crystallinity index (Shi & He, 2003) $O'KI$ = A 1433cm^{-1}/A 896cm^{-1} $N \cdot O'KI$ = A 1375cm^{-1}/A 2899cm^{-1}			 0.783 0.849	 0.903 0.949

Table 6. Results of FTIR analysis of resultant bleached pulp when oxygen delignified bamboo pulp was treated with the sequence CoEpPaP

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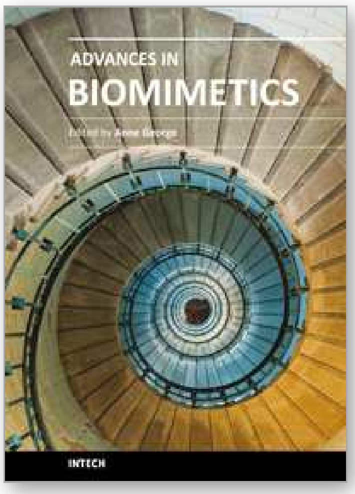

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