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DISSOLVING LIGNIN COMPONENTS IN SPENT LIQUOR OF SIMPLE INORGANIC COMPLEX BLEACHING EUCALYPTUS PULP

*Promising results from the catalytic bleaching (Cat-bleaching) of oxygen-delignified hardwood kraft pulp (*Eucalyptus urophylla* × *Eucalyptus grandis*) with simple inorganic complexes prompted interest in discovering the soluble lignin components. The dissolved substances can be harmful to the environment and some dissolved substances may also have toxic effects on the environment. For these reasons, study of the the composition and structure of dissolved lignin components are of great importance. This investigation is part of a project on Cat-bleaching to obtain more information regarding the lignin components of bleaching effluents. The Cat-treatments of the pulp were performed at bench scale using simple inorganic complexes composed of $(\text{NH}_4)_2\text{S}_2\text{O}_8$ plus $\text{Cu}(\text{CH}_3\text{COO})_2$ (Cu) or $\text{Co}(\text{CH}_3\text{COO})_2$ (Co). The spent liquors obtained after Cat-bleaching were extracted using chloroform, in portions, and the compounds of interest from both the chloroform extracts were isolated using gravity column chromatography with the aid of the UV technique. The samples were analyzed by spectrometric (FT-IR, HSQC 2D-NMR, GC-MS) methods. The dissolved components extracted from the spent liquors from the Cat-bleaching were confirmed to be structurally similar to lignin. The major constituents extracted by organic solvents were identified as phenols, benzaldehydes, phenylethanones, benzoic acid and benzoic acid ethyl ester, which indicated extensive oxidation reactions on the pulp lignin including $\text{C}_\alpha\text{-C}_\beta$ and alkyl-aryl cleavage in the lignin upon catalytical attack. The 2-methoxy phenol predominated, and its proportion was higher from the Cu-bleaching. But the carbonyl compounds (benzaldehyde + phenylethanone) released from the pulp after Co-bleaching had a higher ratio than those after Cu-bleaching. Identification of these carbonyl compounds from among the dissolved compounds contributed to the relation between lignin oxidation and lignin removal.*

Keywords: simple inorganic complex bleaching, eucalyptus pulp, dissolved lignin component, bleaching effluents, spectrometry

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Introduction

In recent years, a trend in pulping and bleaching has been moving towards total chlorine free [TCF] bleaching; this has been prompted by both technological and environmental incentives. New bleaching technologies have been developed to replace environmentally detrimental chlorine-based bleaching technologies. The use of different chemical agents and enzymes as alternative delignification agents has been examined and, in some cases, implemented [Karim 2011; Hart, Rudie 2012].

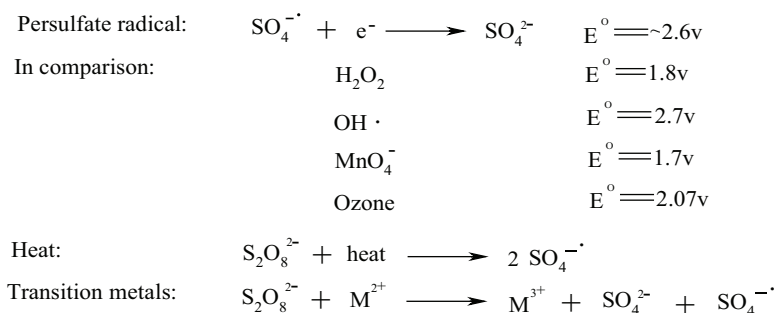


Fig. 1. Persulfate decomposition

Persulfate (also known as peroxydisulfate) is one of the strongest oxidizing agents, and its oxidation of aromatic compounds is believed to be due to its major decomposition product $\text{SO}_4^{\cdot-}$. Persulfate anions $[\text{S}_2\text{O}_8^{2-}]$ can be thermally or chemically activated by transition metal ions to produce sulfate free radicals $[\text{SO}_4^{\cdot-}]$ which are very powerful oxidants (fig. 1). High aqueous solubility, high stability in the subsurface, the relatively low cost and benign end products makes persulfate oxidation a promising choice among oxidation processes [Johnson et al. 2008; Yang et al. 2008]. As simple inorganic complexes, persulfate plus Cu[II], Co[II], Ag[I], Fe[II] and Mn[II] have been successfully reported in the oxidative degradation of phenols and lignin model compounds providing an environmentally benign technology for pulp bleaching. They also have the advantages of chemical and biological agents. Simple inorganic complexes can resemble ligninases in the oxidative degradation of dihydroanisoin, veratrylglycerol- β -guaiacyl ether and veratryl alcohol. The reaction pathways in both chemical and enzymatical systems are similar [Crawford et al. 1981; Huynh 1986; Criquet et al. 2010; Olmez-Hanci, Arslan-Alaton 2013]. Zhao and Ouyang [2012] investigated the effect of ammonium persulfate on the structures and properties of modified lignin. Compared to hydrogen peroxide, ammonium persulfate exhibited a relatively strong oxidation of lignin. A low dosage of oxidant resulted in an increase in the content of active phenolic hydroxyl and carboxyl groups, and β -O-4 and C-C linkages were cleaved in the lignin molecule.

The Cat-bleaching of oxygen-delignified hardwood kraft pulp [*E. urophylla* × *E. grandis*] with simple inorganic complexes $[(\text{NH}_4)_2\text{S}_2\text{O}_8$ plus $\text{Cu}[\text{CH}_3\text{COO}]_2$, $\text{Co}[\text{CH}_3\text{COO}]_2$] was studied. Lignin detection for bleaching effluents has generally been performed with a UV detector at a wavelength of 280 nm, but, thus far, no reports have appeared dealing with the composition and structure of the lignin components of these bleaching liquors. This study reports on the isolation and detailed characterization of lignin components dissolved in the Cat-bleaching of oxygen-delignified eucalyptus kraft pulp. Comparisons were made of the lignin components extracted from the Cu- and Co-bleached spent liquor of the pulp. The dissolved substances can be harmful to the environment and some dissolved substances may also have toxic effects on the environment because they can penetrate through the membranes of living organisms [Tarkpea et al. 1999; Sponza 2003; Pessala et al. 2010; Suess 2010]. For these reasons, the study of the composition and structure of dissolved lignin components are of great importance. The results may provide a basis for the development of modifications to the industrial process which would reduce environmental pollution.

Materials and methods

Materials

The raw material for pulping and bleaching was hybrid eucalyptus chips (*E. urophylla* × *E. grandis*), supplied by Yunjing Forestry Development Co. Ltd of Yunnan.

All the chemicals were purchased commercially (Sinopharm Chemical Reagent Co. Ltd.) and used without further purification, unless otherwise noted. Deionised water was used in the all experiments.

Pulping and bleaching

The chips were kraft pulped (K) in a laboratory digester (HK ZZ01, Dongguan Hengke Automation Equipment Co., Ltd.). The K-pulp was oxygen delignified (O) at 10% consistency. The O-pulp was freeze-dried and extracted in a Soxhlet apparatus with acetone-water (9:1, v/v) for 24 h to remove all lipophilic materials [Puro 2011]. The extractive-free O-pulp was catalytically bleached in a neutral solution at 5% consistency in a laboratory for the preparation of laboratory spent liquors. The liquors from each bleaching were collected in plastic bottles for further processing. In order to obtain a representative sample of spent liquor, five separate bleachings were performed and the five spent liquors were combined into one. In order to extract the lignin present in the liquor, the pH of the liquor was adjusted to 2 with 0.1 M HCl which was slowly added under vigorous stirring.

The characteristics and parameters obtained during pulping and bleaching are given in table 1.

Table 1. Characteristics and parameters of pulp obtained during pulping and bleaching

Pulp	Kappa number TAPPI T236	Viscosity [ml g ⁻¹] TAPPI T230	Brightness [%ISO] TAPPI T452	Yield [%]	Process
K	17.6	1127	35.2	52.2	Kraft pulping. Active alkali charge 17% [on o.d. wood], sulfidity 28%, liquor ratio 1:4, maximum temperature 165°C, 120 min to 165°C, 165°C for 90 min
O	11.3	967	45.3	50.1	Oxygen delignification. O ₂ pressure 0.6MPa, NaOH charge 2.5% [on o.d.p], MgSO ₄ charge 0.5% [on o.d.p], 100°C for 60 min
Cu	10.9	826	48.2	48.6	Cu-bleaching. Cu[CH ₃ COO] ₂ charge 0.01% [on o.d.p], 2:1 M/M portion of [NH ₄] ₂ S ₂ O ₈ / Cu[CH ₃ COO] ₂ , 70°C for 120 min
Co	10.5	779	49.0	47.8	Co-bleaching. Co[CH ₃ COO] ₂ charge 0.01% [on o.d.p], 2:1 M/M portion of [NH ₄] ₂ S ₂ O ₈ / Co[CH ₃ COO] ₂ , 70°C for 120 min

Yield: calculated on the basis of dried raw material

Extraction of the Cat-bleaching liquor

A 4L sample of the Cat-bleaching liquor was filtered using a glass fiber filter [GF 50] to remove micro-fines, and extracted using approximately 12L of chloroform in portions. The organic phase was dried over anhydrous Na₂SO₄ and evaporated on a rotary evaporator at 30°C.

General chromatography

All the compounds from both the chloroform extracts were extracted successively with dichloromethane, hexane, ethyl acetate and methanol using gravity column chromatography packed with silica gel. The compounds of interest were isolated with the aid of the UV technique.

HSQC 2D-NMR

All HSQC 2D-NMR spectra were recorded at room temperature on a 400 MHz Varian UNITY-INOVA spectrophotometer using standard Bruker pulse sequences. The solvents used were deuterated acetone(CH₃COCH₃-d₆). The chemical shift values were all recorded in ppm relative to TMS (tetramethylsilane).

The central solvent peak (δ_{H} 2.04 ppm, δ_{C} 29.83 ppm) was used as the internal reference. The assignment of the observed correlations was based on lignin model compound data [Ralph et al. 2006; Ralph, Landucci 2010].

FT-IR

FT-IR spectra of samples on KBr pellets were recorded using a Nicolet Impact 400D Fourier-Transform Infrared (FT-IR) spectrometer. All the data were acquired using the OMNIC software.

GC-MS

The separation and identification of the lignin components 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 \times 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 and using He as the carrier gas ($\sim 1.0\text{ mL min}^{-1}$). The GC oven was programmed from 80°C (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, 70eV). Compound identification was performed using GC retention times, model compounds and the Mainlib database.

Results and discussion

After pulping, about 10% of the lignin is left in the pulp [Sixta 2006]. Due to the selectivity of simple inorganic complexes which mimic the reaction pathways for the ligninases, most oxidation products formed during Cat-bleaching can, therefore, be expected to be related to the residual lignin. With the progression of Cat-bleaching, lignin dissolution may occur as a result of lignin fragments involving aryl cation radical intermediates (fig. 2) [Kersten et al. 1985; Huynh 1986; Wong 2009].

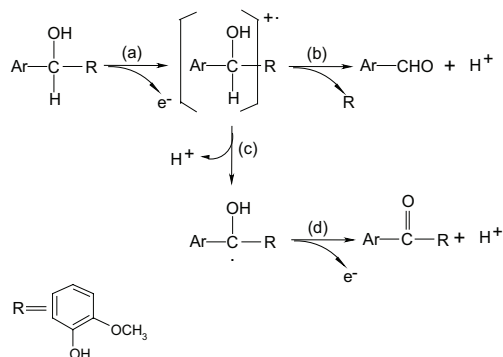


Fig. 2. Formation of phenol, aldehyde, and ketone from residual lignin

2D-NMR results

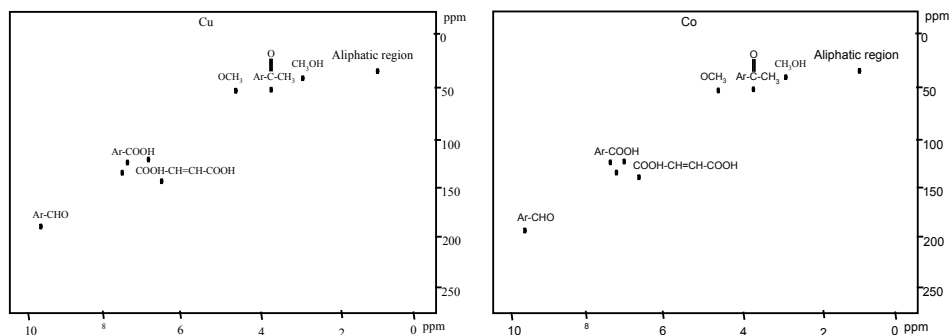


Fig. 3. HSQC 2D-NMR of solvent extracts from Cat-bleaching liquors

2D-NMR is a powerful tool for lignin structural characterization [Kim et al. 2008; Rencoret et al. 2009; Wen et al. 2013]. The HSQC 2D-NMR spectra (fig. 3) showed that both extracts contained lignin-like aromatic C–H correlations (aromatic region C/H, 100–130/6–8.5 ppm), methoxyl correlations typical for aromatic ring methoxyl shifts (OCH_3 , 56–57/3.7–4.2 ppm), benzaldehyde (Ar-CHO , 191–193/9.8–10.2 ppm) and benzoic acid (Ar-COOH , 129.23–133.68/7.49–8.03 ppm) groups. Aromatic moieties appeared more abundant than aliphatic moieties in both the extracts (aliphatic region C/H, 10–40/0–3 ppm).

An important correlation found in the spectra of the extracts at C/H 49.8/3.30 ppm was consistent with the methyl groups of methanol (CH_3OH). Methanol identified in the extracts indicated the occurrence of demethoxylation reactions. Consistent with this result was lignin demethoxylation during Cat-bleaching based on the results of a methoxyl analysis of the residual lignin isolated from O- (19.27%), Cu- (11.81%), and Co- (11.31%) pulp. In addition, the correlations observed at 52.84/3.83 ppm may be indicative of Ar-CO-CH_3 structures. The occurrence of maleic acid (COOH-CH=CH-COOH) at 132.59/6.37 ppm in both the Cu- and Co-extracts would offer evidence that Cat-bleaching involved ring opening.

FT-IR results

FT-IR is a useful technique for analyzing chemical and structural changes that occur in wood components due to different treatments [Colom, Carrillo 2005; Popescu et al. 2007]. The FT-IR spectra of the Cu-, Co-extracts showed the same basic structure as all pulp lignins isolated from kraft pulp, oxygen delignified pulp using a two-step mild enzymatic/acidolysis isolation procedure [Lachenal et al. 1995] (fig. 4): strong broad OH stretching ($3300\text{--}4000\text{ cm}^{-1}$), C–H stretching in methyl and methylene groups ($2800\text{--}3000\text{ cm}^{-1}$), and a strong broad superposition with sharp and discrete absorptions in the region from $1000\text{ to }1750\text{ cm}^{-1}$ [Owen, Thomas 1989; Faix 1991; Pandey 1999; Rana et al. 2010]. Comparing the spectra

of the extract and the pulp lignin revealed that the absorptions situated at 1510 and 1600 cm^{-1} (aromatic skeletal vibrations) were caused by the lignin, and the absorption located at 1730 cm^{-1} indicated the C=O stretch in non-conjugated ketones, carbonyls and in ester groups. The appearance of the band near 2935, 2830, 1460, 1425 cm^{-1} was strongly associated with the aromatic OCH_3 stretching mode. On the other hand, it is seen from fig. 4 that a band of phenolic groups existed at 1260–1234 cm^{-1} .

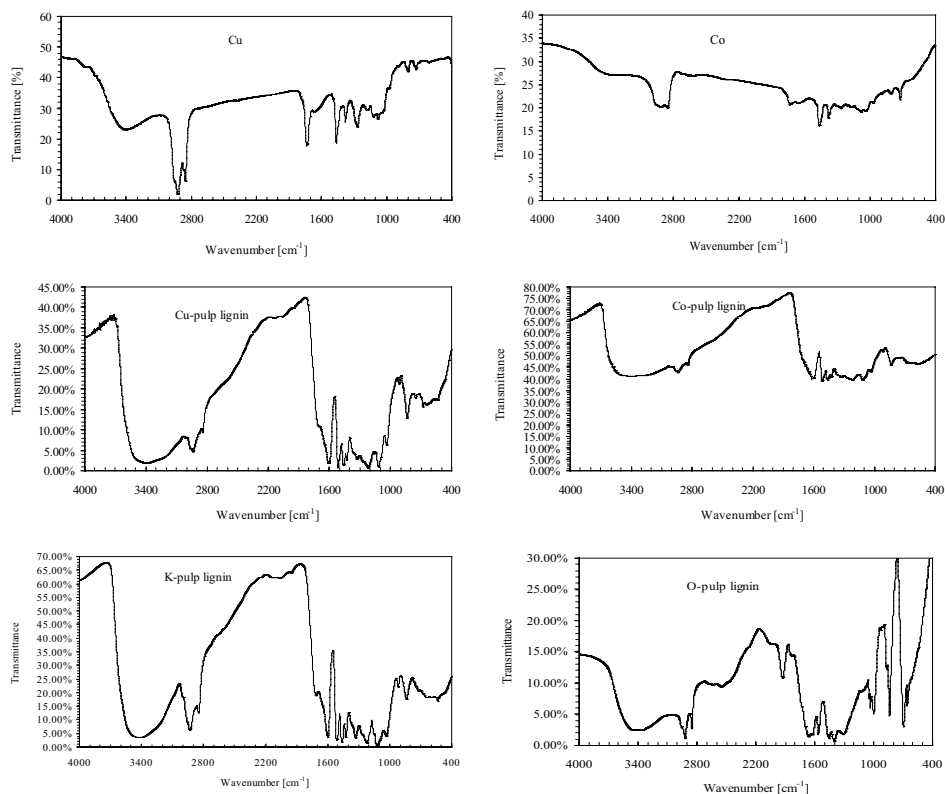


Fig. 4. FT-IR of solvent extracts from Cat-bleaching liquors

The FT-IR spectra contained signals characteristic of lignin and provided evidence of lignin structure in the extracts from the Cat-bleaching liquors. The differences were found in the region 1600–1750 cm^{-1} , particularly in the absorption bands of carbonyl groups. The band related to C=O stretch in non-conjugated ketones, carbonyls and in ester groups at 1730 cm^{-1} was much broader and abundant for the dissolved lignin components versus the pulp lignins. Interestingly, on the other hand, a more or less pronounced band assigned to carbonyl stretch, particularly assigned to conjugated p-substituted aryl ketones around 1660 cm^{-1} existed in the spectra of both the Cu- and Co-extracts, but not in the spectra of all the pulp

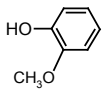
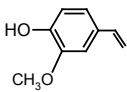
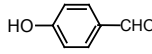
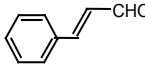
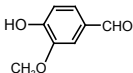
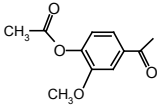
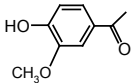
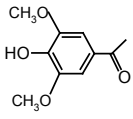
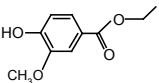
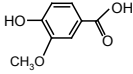
lignins. This is probably explained by the fact that the lignin enriched in carbonyl groups was easily degraded and dissolved from the pulp during bleaching due to the oxidation of the lignin at in? the carbonyl group [Fengel, Wegener 1989; Silverstein et al. 1991], which is known to be one of the main mechanisms in simple inorganic complex oxidation [Huynh 1986].

GC-MS results

In addition to FT-IR and HSQC 2D-NMR characterizations, even if they are useful in elucidating changes in functional groups, GC-MS analysis was also performed on the product mixture extracted from the Cat-liquors. The GC-MS method has proven useful for a comparison of lignin products of different origin [Louchouart et al. 2010; Chan et al. 2013; Lee et al. 2013]. The compounds identified in the extracts from both the Cu- and Co-liquors resulting from the bleaching of the pulp are shown in table 2, in descending order of proportion detected. The composition was in agreement with the results reported for polyoxometalate (POM) liquors from kraft pulp bleaching [Bujanovic et al. 2007] and in disagreement with those for thermomechanical pulping (TMP) effluent [Andersson et al. 2008]. Details of the composition of the extracts obtained by HSQC 2D-NMR and FT-IR spectroscopy were mainly confirmed by the results of the GC-MS analysis. It verified the similarity in chemical structure of the lignin components extracted from both the Cu- and Co-liquors. By normalization of the peaks in the chromatograms, differences were observed in the proportion of lignin components.

2-methoxyphenol predominated in both the Cu- and Co-extracts from the spent bleaching liquors. After Cu-bleaching, the proportion of 2-methoxyphenol in the extract from the liquor was higher (63.3%). The proportion of 2-methoxyphenol in the extract from the Co-bleaching liquor was, on the contrary, lower (33.8%). 2-methoxy-4-vinylphenol was also found in the spent liquors. This compound constituted about 2.7% of the total components in the Cu-extract, and 5.4% in the Co- extract from spent bleaching liquor. All these phenol compounds can be attributed to the cleavage of α - and β -ether linkages [Wu, Heitz 1995; Bujanovic et al. 2011]. In fact, the same trend was observed by H-1 NMR spectroscopy in this study of pulp lignin behaviour during the Cat-bleaching of eucalyptus pulp. The phenolic-OH content of the reacted lignin [Cu-lignin, 1.79%; Co-lignin, 1.99%] was lower than that of O-lignin [4.25%].

Table 2 The identity and proportion of compounds identified in both Cu- and Co-pent bleaching liquors, as determined by GC-MS

Compound	Molecular formula	Structure	Proportion [%]	
			Cu	Co
2-Methoxyphenol	C ₇ H ₈ O ₂		63.3	33.8
2-Methoxy-4-vinylphenol	C ₉ H ₁₀ O ₂		2.7	5.4
∑Phenols	–	–	66.0	39.2
4-Hydroxybenzaldehyde	C ₇ H ₆ O ₂		11.0	19.3
[E]-Cinnamaldehyde	C ₉ H ₈ O		7.3	7.9
4-Hydroxy-3-methoxybenzaldehyde [Vanillin]	C ₈ H ₈ O ₃		1.6	3.7
∑Benzaldehydes	–	–	19.9	30.9
4-Acetoxy-3-methoxyphenylethanone	C ₁₁ H ₁₂ O ₄		4.0	8.1
4-Hydroxy-3-methoxyphenylethanone	C ₉ H ₁₀ O ₃		1.9	4.1
4-Hydroxy-3,5-dimethoxyphenylethanone	C ₁₀ H ₁₂ O ₄		1.7	3.7
∑Phenylethanones	–	–	7.6	15.9
4-Hydroxy-3-methoxybenzoic acid ethyl ester	C ₁₀ H ₁₂ O ₄		3.4	7.4
4-Hydroxy-3-methoxybenzoic acid	C ₈ H ₈ O ₄		3.1	6.4
∑Benzoic acids	–	–	6.5	13.8

As confirmed by HSQC 2D-NMR and FT-IR spectroscopy on the structure of the extracts, benzaldehyde compounds such as 4-hydroxybenzaldehyde, and (E)-cinnamaldehyde, vanillin and phenylethanone compounds as 4-hydroxy-3-methoxyphenylethanone, 4-acetoxy-3-methoxyphenylethanone, and 4-hydroxy-3,5-dimethoxyphenylethanone, resulting from the guaiacyl (G) and syringyl (S) units of lignin respectively [Bose et al. 2009; Tobimatsu et al. 2013] were found. This result was in accordance with the results obtained with POM showing that catalysis included the oxidation of C in the β -O-4 aryl ether structure promoted by catalyst [Evtuguin et al. 2000]. But the carbonyl compounds (benzaldehyde + phenylethanone) released from the pulp after the Co-bleaching had a higher proportion [about 47% of the total components] than those after the Cu-bleaching [about 27% of the total components], because the cobalt acetate was more reactive towards the reaction [Chaplin et al. 1984; Khodakov et al. 2007; Hebrard, Kalck 2009; Zhang et al. 2013]. There is a relation between lignin oxidation and lignin removal [Lachenal et al. 1995; Bujanovic et al. 2005; Hart, Rudie 2012]. As illustrated in table 1, the pulp after the Co-bleaching had a lower kappa number than that after the Cu-bleaching. This confirmed that the rate of carbonyl compound production was in agreement with the efficiency of lignin removal [Pranovich et al. 2005]. In spite of the significance of the Cat-induced lignin depolymerization, part of the oxidized lignin moiety probably became more soluble in the water phase and accumulated in the bleaching liquor. Overall, this probably reflected oxidative changes in the bleached lignin, particularly side-chain cleavage with the formation of C_α-keto compounds by catalysis [Lange et al. 2013; Wang et al. 2013].

C_α carboxylic acids were identified as 4-hydroxy-3-methoxybenzoic acid and its ethyl ester due to the Cat-induced oxidation of side chains in the aromatic moieties [Arpe 2010; Soldán et al. 2013]. They represented a relatively small amount, being about 6% of the total components in the Cu-liquor, and 14% in the Co-liquor (4-hydroxy-3-methoxybenzoic acid:4-hydroxy-3-methoxybenzoic acid ethyl ester, 1:1).

Conclusions

During the Cat-bleaching of eucalyptus pulp with simple inorganic complexes ($[\text{NH}_4]_2\text{S}_2\text{O}_8$ plus $\text{Cu}[\text{CH}_3\text{COO}]_2$, $\text{Co}[\text{CH}_3\text{COO}]_2$), lignin components were released into water. The lignin components dissolved in the Cat-liquors consisted mainly of phenols, benzaldehyde, phenylethanone and small quantities of benzoic acid and benzoic acid ethyl ester, comprising predominantly 2-methoxyphenol, which was proportionally different between the Cu- [63%] and Co- [34%] liquors. The carbonyl compounds (benzaldehyde + phenylethanone) released from the pulp after the Co-bleaching had a higher proportion of the total components (about 47%) than after the Cu-bleaching (about 27%), suggesting that cobalt acetate was more reactive towards oxidation. Identification of these carbonyl

compounds among the dissolved compounds contributed to the relation between lignin oxidation and lignin removal. The rate of carbonyl compound production was in agreement with lignin removal efficiency.

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Acknowledgements

This work was supported by the National Natural Science Foundation of P. R. China (No. 21166011), the Open Research Fund of the State Key Laboratory of Water Resources and Hydropower Engineering Science of Wuhan University (No. 2011B084), and the Open Research Foundation of State Key Laboratory of Urban Water Resource and Environment of Harbin Institute of Technology (No. QA201317).