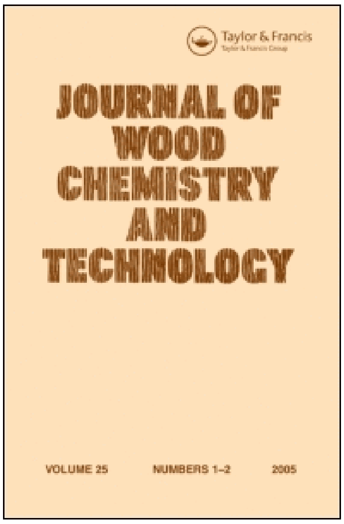

Journal of Wood Chemistry and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597282

Investigation of the Chemistry of Oxygen Delignification of Low Kappa Softwood Kraft Pulp using an Organic/Inorganic Chemical Selectivity System

Shiyu Fu[a]; Jai M. Singh[a]; Shuangfei Wang[a]; Lucian A. Lucia[a]
[a] The Institute of Paper Science and Technology Center Georgia Institute of Technology, Atlanta, Georgia, USA

To cite this Article Fu, Shiyu , Singh, Jai M. , Wang, Shuangfei and Lucia, Lucian A.(2005) 'Investigation of the Chemistry of Oxygen Delignification of Low Kappa Softwood Kraft Pulp using an Organic/Inorganic Chemical Selectivity System', Journal of Wood Chemistry and Technology, 25: 3, 95 — 108

To link to this Article: DOI: 10.1080/02773810500191526

URL: http://dx.doi.org/10.1080/02773810500191526

Journal of Wood Chemistry and Technology, 25: 95–108, 2005

ISSN 0277-3813 print/1532-2319 online
DOI: 10.1080/02773810500191526

Investigation of the Chemistry of Oxygen Delignification of Low Kappa Softwood Kraft Pulp using an Organic/Inorganic Chemical Selectivity System

Shiyu Fu, Jai M. Singh, Shuangfei Wang, and Lucian A. Lucia
Georgia Institute of Technology, The Institute of Paper Science and
Technology Center, Atlanta, Georgia, USA

Abstract: Oxygen delignification (OD) of low kappa softwood kraft pulp was examined in two steps without inter-stage washing as part of an overall program to evaluate the efficiency of a selectivity enhancement system consisting of phenol and magnesium sulfate. Black liquor carryover in the reaction system did not substantially affect delignification and the selectivity of these OD reactions. The residual lignins from both the original pulp and oxygen-delignified pulp with and without the phenol/$MgSO_4$ selectivity enhancement system were prepared and characterized using NMR spectroscopy. The effluent lignins after oxygen delignification were also prepared and characterized. The lignin characterizations provided the basis for the rationalization of the selectivity observed. A significant finding of this study was that the phenol/$MgSO_4$ system in the oxygen delignification reaction appeared to hinder phenolic guaiacyl unit condensation. It also appeared to enrich the levels of *p*-hydroxyphenyls in the residual lignin.

Keywords: Oxygen delignification, selectivity enhancement, NMR spectroscopy, GC-MS spectroscopy

The authors gratefully acknowledge the United States Department of Energy for financial support (Contract DE-FC07-02ID14261) as well as the supporting companies of the Institute of Paper Science and Technology at the Georgia Institute of Technology.

Address correspondence to Lucian A. Lucia, North Carolina State University, College of Natural Resources, Forest Biomaterials Laboratory, Campus Box 8005, 3108 Biltmore Hall, Raleigh, NC 27695-8005, USA. E-mail: lucian.lucia@ncsu.edu

INTRODUCTION

Public and societal pressures on the pulp and paper industry to regulate their effluents are a result of EPA environmental regulations that require the implementation of improved bleaching process to partially or totally eliminate the use of chlorine or its derivatives. Oxygen delignification has become an important industrial process to offload bleaching demands and increase the selectivity of delignification. After the first oxygen-alkali bleaching installation made by SAPPI in South Africa,[1] many pulp mills in Europe and a large number of mills in North American have successfully installed oxygen delignification systems.

It is well known that oxygen delignification of kraft pulp can remove up to 50% of the residual lignin in the original pulp, which allows for a lower chemical consumption in subsequent bleaching stages.[2] Ideally, further lowering pulp lignin content entering the bleach plant will not only reduce chemical consumption, but lower effluent production. However, it is well known that beyond the 50% level of lignin removal in chemical pulp, severe cellulose damage takes place during oxygen delignification that results in deterioration of pulp viscosity and physical strength.[3]

The success of the first oxygen bleaching installation was only possible by using magnesium oxide as a viscosity protector. It is well known that radicals are present in oxygen delignification and are formed quickly following ionization of the phenolic hydroxyl groups. In general, under strongly alkaline conditions, the phenoxy anions are converted to phenoxy radicals by electrophilic oxygen attack, the oxygen being converted to the superoxide anion radicals or hydroperoxy radicals. The reaction of lignin with these latter oxidants results in lignin fragmentation through side chain elimination, ring opening, and demethoxylation.[4] However, the presence of transition metals can catalyze the production of highly active hydroxyl radicals, which can cause cellulose deterioration. The addition of magnesium oxide and like compounds has been believed to eliminate the catalytic effect of metal ions. In actuality, many chemical additives have been used as cellulose protectors in oxygen delignification processes including sodium silicate,[5] magnesium salts,[6] borax,[7] and polyhydric alcohols.[8] A magnesium sulfate and phenol protector system was used for the oxygen delignification experiments in the present study as a result of significant effort expended over the last few years in this lab.[9–11]

We obtained a softwood kraft pulp with a kappa number of 20. Oxygen delignification of this low kappa softwood kraft pulp was performed in two steps without washing between the two steps (see Experimental for more detail). In order to reduce the load on chemical bleaching, the kappa number of kraft pulp should be decreased as much as possible without the concomitant loss of selectivity. Because oxygen can also react with cellulose and damage the strength of the pulp, the selectivity of the lignin reactions with oxygen has become a key research issue during the last several decades. The purpose of this research was to study the chemical changes within the residual lignin structure brought about by oxygen delignification in low kappa softwood kraft pulps using the present selectivity enhancement system.

EXPERIMENTAL

Oxygen Delignification

The softwood kraft pulp used in this study was obtained from industrial sources immediately after the brown stock washers. Oxygen delignification was done in PARR pressure reactors under the conditions shown in Table 1. Kappa number and viscosity measurements were performed according to TAPPI test methods.

The oxygen delignifications were run in two phases, with the first phase having the experimental parameters listed in what follows. All chemicals (with or without 60% solids black liquor) were added to deionized water that was heated to 89°C to which was added sufficient pulp to achieve a solids content of 12%. Thermal equilibration to the set temperature was rapid (within 10 min) and the reaction was allowed to continue for 30 min. At that point, the pressure of the reaction was reduced and the temperature increased over a short ramp time (10 min) to 99°C at which time it was also allowed to react for 60 min.

Table 1. Conditions used in the oxygen delignification experiments

1st Phase[a]	$MgSO_4$	0.5%
	Phenol	0.5%
	NaOH	2.5%
	Black liquor	60% solids: added at this point if added
	Consistency of pulp	12%
	Oxygen pressure	135 psi
	Temperature	193°F (89°C)
	Reaction time	30 min.
2nd Phase	No washing and no additional chemical	
	Oxygen pressure	80 psi
	Temperature	210°F (99°C)
	Reaction time	60 min.

[a] Control conditions: No $MgSO_4$ or phenol was added into the reaction system during the 1st phase.

Lignin Extraction and Collection

The residual lignin in pulp was extracted with 0.1 mol. L^{-1} HCl in aqueous dioxane according to the method described by Chakar and Ragauskas.[12] We were able to obtain average yields of 45–55% of the available residual lignin which is an accepted typical range for this chemical procedure.[12] We obtained not only the residual lignins from this study, but the effluent lignins and have assigned the following special nomenclature.

RL: Residual lignin from original pulp

RL-O: Residual lignin from pulp after oxygen delignification (OD) ($MgSO_4$ 0.5% and Phenol 0.5%)

SL-O: Soluble lignin from OD effluent ($MgSO_4$ 0.5% and Phenol 0.5%)

Con-RLO: Residual lignin from pulp after OD without selectivity enhancement

Con-SLO: Soluble lignin from OD effluent without selectivity enhancement

Elemental Analyses

Elemental analyses of the lignin samples was conducted at Atlanta Microanalytical Laboratories Inc. (Atlanta, GA, USA).

Quantitative ^{31}P-NMR Analyses for Hydroxyl Groups

^{31}P-NMR spectra were acquired on lignin samples that were derivatized with 2-cloro-4,4,5,5,5-tetramethyl-1.3.2-dioxaphopholane.[13] Each ^{31}P-NMR acquisition was performed with a 25 s delay between 90° pulses. The inverse gated decoupling pulse sequence was used to obtain quantitative spectra. A minimum of 200 transients were acquired for each sample. The acquisitions were performed at room temperature, using a 61.9 ppm sweep width and a 4 Hz line broadening. All the chemical shifts were calibrated to the product of the phosphilylating agent with water that gives a sharp ^{31}P signal at 132.2 ppm. Integration regions used to analyze the spectra have been previously published.[13]

Quantitative ^{13}C-NMR Analyses

The ^{13}C-NMR samples were prepared by adding 100 mg of dry lignin to 0.5 mL of DMSO-d^6 in a 4 mL vial. The solution was transferred to a 5 mm NMR tube using a pipette. The quantitative ^{13}C- NMR experiment was performed using a 90° pulse with an inverse gated decoupling pulse

Table 2. Elemental and methoxyl analyses of lignin samples

Lignin sample	C %	H %	N %	O %	OCH_3 mol/benzene
RL	62.55	5.52	0.09	31.84	0.75
RL-O	61.66	5.35	0.11	32.89	0.62
SL-O	56.39	4.82	0.17	38.58	0.60
Con-RL-O	61.87	5.11	0.20	32.83	0.82
Con-SL-O	56.67	4.70	0.20	38.43	0.76

RL: Residual lignin from original pulp.
RL-O: Residual lignin from pulp after OD ($MgSO_4$ 0.5% and phenol 0.5%).
SL-O: Soluble lignin from OD effluent ($MgSO_4$ 0.5% and phenol 0.5%).
Con-RLO: Residual lignin from pulp after OD without selectivity enhancement.
Con-SLO: Soluble lignin from OD effluent without selectivity enhancement.
All methoxyl data obtained from ^{13}C NMR.

sequence, which is needed to remove the nuclear Overhauser effect. All integration for the carbon signals was based on normalization of the integration value for the benzene protons (107.5–163 ppm).

RESULTS AND DISCUSSION

Lignin and Carbohydrate Changes during Oxygen Delignification

In the present two-phase oxygen delignification set of experiments, more than 50% of the residual lignin in the well-washed pulp was removed with approximately less than 25% viscosity loss. In these experiments, the final kappa number was 20.20 for the washed pulp, but 24.85 for the unwashed pulp which corresponds to a 6.5% kraft black liquor carryover level (on a pulp mass basis). Yet, there was not much difference in the kappa number decrease and viscosity loss even at 11% black liquor carryover (60% solids) on dried pulp weight as shown in Table 3.

The selectivity enhancements with magnesium sulfate or phenol individually were not as effective as demonstrated with the combination.[9,10] Therefore, we do not show that data for the purposes of focusing on the two-member selectivity system. In general, the selectivity of the present system is not compromised under these conditions. The residual lignin in these pulps can be characterized as belonging to four different types of fractions: wash loss lignin, easily leachable, slowly leachable, and stagnant fractions.[14]

The wash loss lignin and easily leachable fractions are very fast reacting components. The added black liquor in our experiments possesses the character of those two fractions, whose artificially added levels caused a drop in total delignification by up to 1.5 units because of its reactivity with the oxygen and caustic. The removal of the stagnant fraction of residual

Table 3. Kappa numbers and viscosities of the pulp after oxygen delignification

Sample	Additional black liquor, %	Kappa number	Viscosity, mPas
Original pulp	—	20.20	27.64
Pulp after oxygen delignification[a]	0	9.89	20.92
	0.2	10.68	21.43
	0.5	10.34	20.71
	0.9	10.58	20.74
	1.8	11.01	20.72
	2.2	10.82	21.86
	4.5	11.22	19.29
	6.7	11.26	20.25
	11.2	11.50	19.41

[a] Oxygen delignification conditions: 0.5% $MgSO_4$, 0.5% phenol, and 2.5% NaOH.

lignin in pulp, however, is crucial for oxygen delignification. The distribution of this residual lignin in the pulp fiber does indeed affect oxygen delignification. Li[15] described the distribution of lignin between the surface and bulk of fiber and demonstrated that the deposition of dissolved lignin from pulping liquors on fibers was the primary cause of lignin enrichment on fiber surfaces. For high kappa number pulps, the surface lignin accounts for approximately 50% or more of the total residual lignin. Because the concentration of lignin in high kappa pulps on the fiber surface is large, oxygen delignification may be enhanced to a degree. However, for low kappa number pulps such as evident in these runs, the concentration of lignin on the fiber surfaces drops precipitously. Because the reactivity differences between surface lignin and bulk lignin in fibers are generally minor, the chemical features of residual lignin in pulp are therefore the most important factor for lignin removal during oxygen delignification and constituted a major focus of this study.

With regard to the carbohydrate component of the pulp, there was almost no change in the pulp saccharides as shown in Table 4 (all fall within a 5% experimental error of the experimental protocol), yet, the crystallinity of cellulose (the crystallinity or crystallinity index) increased after oxygen delignification. The crystallinity of cellulose is one of the factors that affect the fiber degradation because crystalline cellulose is more difficult to degrade than amorphous cellulose. The increase in crystallinity of the pulp is most likely caused by reducing the levels of amorphous cellulose[16,17] and/or removing lignin or lignin carbohydrate complexes during the oxygen delignification process, a phenomenon that we also observed during the control oxygen delignification runs. It did not appear that the additive system improved the crystallinity of the pulp to any great extent.

Table 4. Carbohydrate components of the pulp before and after oxygen delignification

Sample ID	CrI %	Ara %	Gal %	Glu %	Xyl %	Man %	Total[b] %
Original pulp	82.2	0.5	0.3	76.6	6.6	4.8	88.8
Oxygen delignification pulp[a]	87.3	0.5	0.3	76.4	6.4	5.9	89.5

CrI: Crystallinity index is equal to (1-1/PVR), in which PVR (peak to valley ratio in the x-ray spectrum, the valley is that between peak 101 and peak 002) = I_{002}/I_v. (18).

Ara = arabinose, Gal = galactose, Glu = glucose, Xyl = xylose, Man = mannose

[a] Conditions: 0.5% $MgSO_4$, 0.5% phenol, and 2.5% NaOH without black liquor.

[b] The content of carbohydrates is based on the total weight of pulp.

CrI for control oxygen run was 87.1.

The Influence of Phenol/$MgSO_4$ on Oxygen Delignification

The easily leachable fractions in pulp, such as the residual black liquor, can be oxidized and degraded during oxygen delignification, which accounts for the kappa number increase shown in Table 3. The residual lignin, however, is a stagnant lignin, which can be attacked during oxygen delignification and the subsequent bleaching process, albeit more slowly than the easily leachable fractions. It is desirable to remove as much as possible of the stagnant residual lignin through oxygen delignification without incurring significant damage to the carbohydrates. Enhanced selectivity may be obtained by a protector system. We have determined from past work[9,10] that the phenol/$MgSO_4$ mixture improves selectivity and demonstrates approximately 46% improvements in the current work as shown in Table 5.

It is demonstrated in Table 5 that both magnesium ion and phenol can preserve pulp viscosity during oxygen delignification, although in different

Table 5. The chemical properties of a representative pulp after oxygen delignification as a function of inclusion of additives

	Kappa number	Viscosity, mPa.s	Selectivity
Original brownstock	20.38	30.77	—
NO additives	8.03	14.44	0.756
Phenol, 0.5%	8.68	15.30	0.756
$MgSO_4$, 0.5%	9.14	19.12	0.965
$MgSO_4$, 0.5%, phenol, 0.5%	9.28	20.70	1.102

The error for the viscosity has a precision of within 0.15 mPa.s (three duplicates/run), whereas the kappa measurement has a precision of within 0.05 kappa units (three duplicates/run).

chemical ways.[11] The addition of 0.5% phenol improved pulp viscosity by <1 mPa over that without additives, but the selectivity of delignification, which is defined as the ratio of decrease of kappa number to decrease of viscosity, remained unchanged. The addition of 0.5% magnesium ion improved pulp viscosity by 4.7 mPas and selectivity by 28%. However, the addition of 0.5% phenol and 0.5% magnesium sulfate improved viscosity by 6.3 mPas and selectivity by 46%, which are statistically significant values within the scope of this work that has been supported by our past work.[9–11] This indicates that phenol and magnesium ions work in tandem during oxygen delignification for selectivity improvements. The action of phenol during oxygen delignification may be due to its free radical scavenging potential under alkaline conditions,[19] whereas the action of magnesium may be to entrap transition metals (such as Mn), which can catalyze the production of hydroxyl radicals through a Fenton-type mechanism.

Chemical Characteristics of Lignin

The residual lignin in pulp was separated into two fractions after oxygen delignification: one fraction was stagnant (residual), whereas the other fraction was the effluent lignin in the alkaline liquor. The elemental and methoxyl group content of these lignin fractions are shown in Table 2. It was found that the elemental components were not very different from either the original pulp residual lignin or oxygen delignified pulp residual lignin; the only significant difference is that the oxygen content in the effluent lignin was higher than both other lignins due to the extensive oxidation of lignin by oxygen, a finding that has already been documented.[20] During the oxygen delignification process, part of the total methoxyl groups were depleted from lignin, that is the methoxyl group content in RL-O was less than that in RL. The methoxyl group content in dissolved lignin SL-O was even less than that in RL-O. Thus, the oxygen delignification system with the additives removes more methoxyl groups than without the additives. This suggests that demethoxylation reactions are enhanced with the additive system. This may be indicative of the functioning mechanism of the additive system.

There is not much difference in the elemental data for the residual lignin between RL-O and Con-RLO after oxygen delignification, as well as for the effluent lignin between SL-O and Con-SLO, but the elemental concentration in the residual lignin RL of the original pulp is different for the lignin after oxygen delignification. The relative oxygen content increased, whereas the content of carbon and hydrogen decreased after OD.

Hydroxyl groups, especially the phenolic hydroxyl groups in lignin, are important as active points for oxidation during oxygen delignification.[21] The hydroxyl group contents in various lignins were determined using ^{31}P-NMR spectroscopy, as shown in Figure 1 and in Table 6. The aliphatic hydroxyl groups in the ^{31}P-NMR spectra are not accounted by the hydroxyl

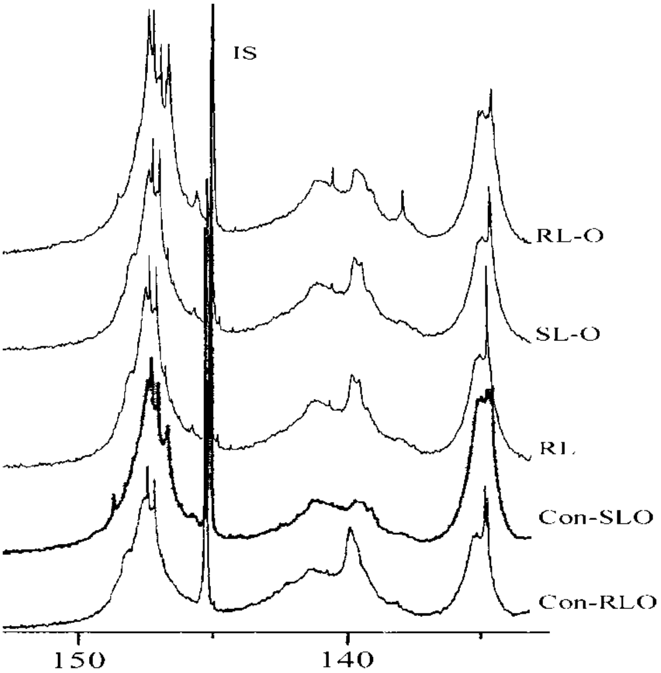

Figure 1. ^{31}P-NMR spectra of residual lignin in pulp and dissolved lignin.

Table 6. Comparison of hydroxyl group content in different lignins

Functional group	Shift (ppm)	RL mmol/g lignin	RL-O mmol/g lignin	SL-O mmol/g lignin	Con-RLO mmol/g lignin	Con-SLO mmol/g lignin
Aliphatic OH	149.0–145.6	1.391	1.516	1.980	1.71	2.02
Condensed phenolic OH	144.4–140.4	0.895	0.814	0.938	1.07	0.84
Guaiacyl phenolic OH	140.4–138.6	0.858	0.616	0.646	0.83	0.55
p-hydroxyl phenolic OH	138.6–137.0	0.080	0.153	0.134	0.10	0.085
Carboxyl OH	136.0–133.8	0.342	0.842	0.956	0.90	1.35

group in side chain of lignin due to the contamination of carbohydrates; those residual carbohydrates are possibly from the sugar moiety of a lignin-carbohydrate complex,[22] which will be evaluated in a subsequent publication.

The phenolic hydroxyl group derives from both the condensed guaiacyl structures and the uncondensed guaiacyl structures. Interestingly, unlike typical research findings, the former group decreased after selectivity enhancement-supported oxygen delignification for the residual lignin in pulp, and increased for the dissolved lignin (SL-O).[23] It is possible that the lignin degraded and leached from the pulp fiber and underwent condensation in the alkaline solution. However, OD without the selectivity enhancement was as reported in the literature: the condensed guaiacyl hydroxyl increased for the residual lignin in pulp, and decreased for the effluent lignin, which indicates that more condensed guaiacyl units were formed and retained in the residual lignin of pulp as opposed to what was found in the selectivity system. Not surprisingly, the level of uncondensed guaiacyl phenolic groups was lower for both residual lignin and dissolved lignin with and without the selectivity enhancement after oxygen delignification than for the residual lignin in the original pulp.

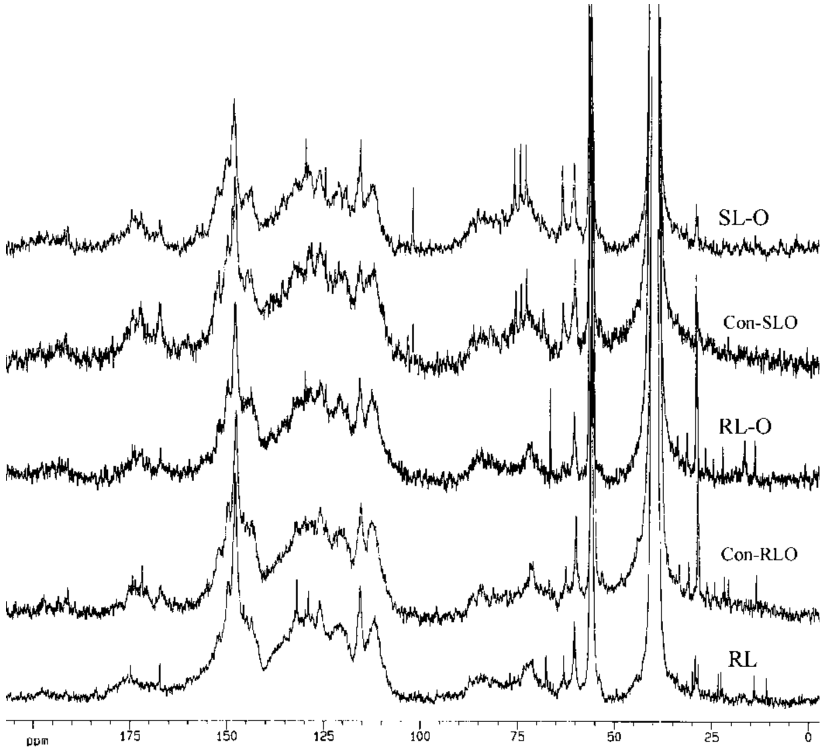

Figure 2. ^{13}C-NMR spectra of residual lignin in pulp and dissolved lignin.

Table 7. ^{13}C-NMR analyses of lignin from softwood kraft pulps

Shift region (ppm)	Structure	Carbons corresponding to each benzene				
		RL	RL-O	SL-O	Contr.-RL	Contr.-SL
199.9–188.4	C═O	0.10	0.20	0.20	0.20	0.20
180.4–170.6	Unconjugated COOH	0.29	0.28	0.44	0.41	0.57
170.6–165	Conjugated COOH	0.11	0.13	0.18	0.16	0.23
163–140	G, C_3/C_4	2.31	1.85	1.98	1.99	1.9
140–127	G, C_1	1.49	1.88	1.59	1.54	1.64
127–124.5	G, C_5-C (condensed)	0.53	0.67	0.57	0.60	0.62
124.5–117	G, C_6-H	0.67	0.63	0.74	0.74	0.76
117–114	G, C_5-H (uncondensed)	0.38	0.39	0.39	0.41	0.37
114–107.5	G, C_2-H	0.60	0.58	0.70	0.72	0.71
107.5–101	C_1 in Xylan	—	—	*0.09*	—	*0.09*
90–78.5	C_β in β-O-4,	0.34	0.31	0.35	0.38	0.45
76–67.7	C_α in β-O-4,	0.36	0.27	*0.58/0.31*[a]	0.56	0.71/0.50[a]
67.7–64.5	Dioxane	0.08	0.06	—	—	—
64.5–62	C_γ in β-O-4 with α-C═O	0.08	0.05	*0.09/0*[b]	0.16	0.16/0.07[b]
62–58.2	C_γ in β-O-4,	0.19	0.11	0.17	0.27	0.26
58.2–54.1	OCH_3	0.75	0.62	*0.60*	0.82	0.76
54.1–52.5	$C\beta$ in $\beta - \beta$ and in β-5	0.04	0.04	0.04	0.12	0.11
29.6–27.5	CH_2 in diaryl methane	0.08	0.15	0.07	0.22	0.13
24.2–20.8	Aliphatic chain	0.03	0.08	—	—	—
	$H\text{-}C_{5\ \text{uncond.}}/C_{5\ \text{cond.}}$	0.72	0.62	0.68	0.68	0.60

[a] The integration of peaks subtracting three peaks of sugar by three repetitions of 0.09 (C_1).

[b] There is no integration for C_γ in β-O-4 with α-C═O after correcting for saccharides.

p-Hydroxyl phenolic hydroxyl groups in the lignin samples were analyzed after oxygen delignification for the pulp with and without the selectivity enhancement. *p*-Hydroxylphenyl structures in lignin are considered inactive units and stagnant to oxygen delignification. Akim et al.[23] proposed that the accumulation of less reactive *p*-hydroxyphenyl structures was one of the factors limiting oxygen delignification of kraft pulp. This finding may be in effect for the system under study because the selectivity enhancement system has enriched levels of the *p*-hydroxyphenyls in the RL and displays higher kappa levels than the control.

The carboxyl groups in residual lignin from OD pulp and effluent lignin were quite different for the OD systems with and without the selectivity enhancement. Without the selectivity enhancement, the residual lignin and the effluent contained more carboxyl groups, which indicated that the lignins were oxidized more efficiently.[24] It is likely that the transition metals in the pulp were not deactivated as well, thus they had the opportunity to catalyze the production of the hydroxyl radical, which can lead to enhanced oxidation of lignin, while simultaneously damaging pulp carbohydrates.

Figure 2 illustrates the spectra of ^{13}C NMR of lignins from the pulp and effluent. The data listed in Table 7 indicates that the content of acidic groups including unconjugated and conjugated COOH increased after oxygen delignification for all lignin samples; RL-O, Con-RLO and SL-O, Con-SLO, and unconjugated and conjugated COOH increased more for Con-RLO and Con-SLO, which is in good agreement with the results obtained by ^{31}P-NMR for the carboxyl hydroxyl groups. The carbonyl group in RL-O, Con-RLO and SL-O, Con-SLO appeared in addition to an increase in the levels of the carboxyl group.

CONCLUSIONS

Changes in the chemical functionality and distribution of the residual lignin were found using the selectivity-enhanced oxygen delignification system. In general, the magnesium ion and phenol in the protector system appear to work in unison for the selectivity enhancement. The lignin was degraded and leached from the pulp fiber under the alkali oxygen system and appeared to undergo condensation in the alkaline solution. The phenol/ $MgSO_4$ system in the oxygen delignification reaction can prevent phenolic guaiacyl unit condensation, which may be beneficial for subsequent bleaching although it appears to enrich the level of *p*-hydroxyphenyl compounds, which may be one reason for the limitation in kappa number reduction. The diaryl structures in residual lignin increased after oxygen delignification despite the presence or absence of the selectivity enhancement system. Finally, we have some very preliminary ^{13}C NMR data that suggests that the residual lignin is bonded to the carbohydrate in pulp, which we will follow up in a subsequent paper.

REFERENCES

1. Rowlandson, G. Continuous oxygen bleaching in commercial production. TAPPI J. **1971**, *52*, 962.
2. McDonough, T. Recent advances in bleached chemical pulp manufacturing technology. Part 1: Extended delignification, oxygen delignification, enzyme applications and ECF and TCF bleaching. TAPPI J. **1995**, *78*, 55.
3. Masura, V. Mathematical model for kraft pulping expressed by a logarithmic straight-line equation. TAPPI J. **1993**, *76*, 105.
4. Ljunggrren, S.C.H.; Johansson, E.C. Reaction kinetics of lignin structures during oxygen bleaching. In *Pulp Bleaching-Principles and Practice*; Dence, C.W., Reeves, D.W., Eds.; TAPPI Press: Atlanta, GA, 1996; 218.
5. Hou, J.C.M.; Potlatch, Corp. Oxygen Bleaching of Pulp in the Presence of High Silicate Protector, 1979. Pat no. 1062858, Sept 2, 1979.
6. Smith, L.; Calvert, D.W.; Robert, A. Delignification and Bleaching of Cellulose Pulp. Pat no. 68/3771, June 13, 1968.
7. Bair, C.; Zou, H.; Liukkonen, A. Application of sodium borate in oxygen bleaching, Proceedings of the 1998 Pulping Conference Part 1 (of 3); 1–7.
8. Solinas, M.; Proust, A. Oxygen Bleaching Process for Cellulose Pulps with a Polyhydric Alcohol Cellulose Protector. US. Pat no. 5609723, March 11, 1997.
9. Chen, S.-L.; Lucia, L.A. Fundamental insight into the mechanism of oxygen delignification of kraft pulps: Influence of a novel carbohydrate protective system. Cell. Chem. Technol. **2002**, *36*, 339–351.
10. Chen, S.-L.; Lucia, L.A. Fundamental insight into the mechanism of oxygen delignification of kraft pulps. Part II. Application of surfactants. Cell. Chem. Technol. **2002**, *36*, 495–505.
11. Chen, S.-L.; Lucia, L.A. New method for the evaluation of cellulose degradation. J. Wood Sci. **2003**, *49*, 285–288.
12. Chakar, F.S.; Ragauskas, A.J. The effects of oxidative alkaline extraction stages after laccase $_{\mathrm{HBT}}$ and Laccase $_{\mathrm{NHAA}}$ Treatments: An NMR study of residual lignins. J. Wood Chem. Technol. **2000**, *20*, 169.
13. Granata, A.; Argyropoulos, D.D, 2-Chloro-4, 4, 5, 5, 5-tetramethyl-1.3.2-dioxaphopholane: A reagent for the accurate determination of uncondensed and condensed phenolic moieties in lignin. J. Agric. Food Chem. **1995**, *43*, 1538.
14. Ala-Kaila, K.; Reilama, I. Step-wise delignification response in an industrial two-stage oxygen-alkali delignification process, 2000 International Pulp Bleaching Conference, June 27–30, 2000, World Trade Convention Centre: Halifax, Nova Scotia, Canada, 27.
15. Li, K.; Reeve, D. The origins of kraft pulp fiber surface lignin, 2000, International Pulp Bleaching Conference, June 27–30, 2000 World Trade Convention Centre: Halifax, Nova Scotia, Canada, 197.
16. Dimmel, D.R. Bleaching reactions of amorphous and crystalline cellulose, International Pulp Bleaching Conference, PAPTAC, Montreal, Canada, 1994; 107.
17. De Souza, I.J.; Bouchardm, J.; Methot, M. Changes in cellulose crystallinity during oxygen delignification, 2000, International Pulp Bleaching Conference, June 27–30, 2000, World Trade Convention Centre: Halifax, Nova Scotia, Canada, 41.
18. Ahtee, M.; Paakkari, T.; Puikkonen, K. Crystallinity measurements on thermomechanical pulp by X-ray diffraction. Pap. Ja Puu. **1980**, *4*, 167.
19. McDonough, T.J. Oxygen delignification. In *Pulp Bleaching, Principles and Practice*; Carlton, W.D., Douglas, W.R., Eds.; TAPPI Press, 2000; 215.

20. Lucia, L.A.; Ragauskas, A.J.; Chakar, F.S. Comparative evaluation of oxygen delignification processes for low- and high-lignin-content softwood kraft pulps. Ind. Eng. Chem. Res. **2002**, *41*, 5171.
21. Kadla, J.F.; Chang, H.-M.; Jameel, H. The reactions of lignins with high temperature hydrogen peroxide, Part 2. The oxidation of kraft lignin. Holzfor. **1999**, *53*, 277.
22. Schwager, C.; Faix, O.; Metzger, J. Investigation on lignin-carbohydrates complexes. 1994, Proceedings 3rd European Workshop on Lignocellulosics and Pulp, Sweden; 13.
23. Akim, L.G.; Colodette, J.L.; Argyropoulos, D.S. Factors limiting oxygen delignification of kraft pulp. Can. J. Chem. **2001**, *79*, 201.
24. Fu, S.; Lucia, L.A. Investigation of the chemical basis for inefficient removal of lignin removal in softwood kraft pulp during oxygen delignification. Ind. Eng. Chem. Res. **2003**, *42*, 4269.