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2 AUTHORS:

Shiyu Fu
South China University of Technology
170 PUBLICATIONS **710** CITATIONS

Lucian Amerigo Lucia
North Carolina State University
238 PUBLICATIONS **3,062** CITATIONS

APPLIED CHEMISTRY

Investigation of the Chemical Basis for Inefficient Lignin Removal in Softwood Kraft Pulp during Oxygen Delignification

Shiyu Fu and Lucian A. Lucia*

Center for Advanced Bioproducts and Bioprocesses, Institute of Paper Science and Technology, Georgia Institute of Technology, 500 10th Street NW, Atlanta, Georgia 30318-5794

In this study, an industrial softwood kraft pulp sample was subjected to an oxygen–alkali treatment over three consecutive times as part of a broader research effort to identify methods for selectivity improvements and lignin reactivity inefficiencies. Chemical properties of the pulp were determined that included active functional group analysis of the residual and effluent lignins. Further data for the analysis of the chemical reactions were obtained by collecting and identifying the low molecular weight compounds in the effluent liquors. We determined that the residual lignin cannot be removed beyond 75% of the original levels, although the first oxygen delignification reaction can remove nearly half of the original resident kraft residual lignin. The main factor limiting lignin removal during the oxygen delignification process is the penetration of oxygen and oxygen-active species into the lignin matrix along the microfibrils in the pulp. The matrix structure of carbohydrate and the lignin carbohydrate complex constitute the main barriers against oxidative reactions. We have evidence that the hemicelluloses in the pulp are part of the lignin–carbohydrate complexes, and the robust nature of the native cellulose crystal structure in the pulp fiber is partly responsible for the barrier to lignin removal during oxygen–alkali treatment. In fact, xylan-linked lignin is more resistant to oxidative reactions and tends to remain in the pulp, while galactan-linked lignin tends to dissolve during oxygen delignification. The reduction of reactive groups including hydroxyl and carboxyl groups during oxygen delignification is also responsible for the low level of subsequent delignification. We also support the finding that the *p*-hydroxylphenyl structures and 5,5′-biphenolic units in residual lignin are stable and accumulate during oxygen delignification.

Introduction

Conventional kraft pulping technologies are responsible for removing most of the resident lignin in wood as part of industrial processes to manufacture paper and paperboard products. Topochemical research has demonstrated that the middle lamella lignin dissolves quite easily, leaving native residual lignin in the secondary wall after approximately 50% delignification has been achieved.[1-3] In principle, the removal of this recalcitrant residual lignin in pulp during the ensuing post-delignification stages (bleaching) is an extension of the delignification of the secondary fiber wall.

Because environmental regulatory pressures have come to the fore over the past decade, oxygen delignification has become an increasingly important delignification technology for extending kraft pulping. However, extending oxygen delignification without loss of fiber strength or pulp yield is a crucial topic in this area. For example, a lower lignin level (i.e., lower κ number) following the oxygen delignification stage results in a lower active chemical charge required to bleach the pulp and thereby achieve target brightness. However, one of the major drawbacks of oxygen delignification is its lack of selectivity for delignification beyond 50% in a single stage, beyond which there is excessive cellulose damage manifested as a decrease in the viscosity and a loss of pulp strength.[4]

In a now famous set of recent experiments, Chirat and Lachenal investigated the limits of oxygen delignification using several softwood and hardwood kraft pulps.[5] In all of these experiments, delignification essentially stopped after three successive medium-consistency oxygen stages, which were performed at 100 psi. They found that the limits to oxygen delignification were 75% and 60% for softwood and hardwood kraft brownstock pulps, respectively. It was concluded that the residual lignin was most likely attached to carbohydrates by the notorious lignin–carbohydrate complex (LCC) linkages that are quite robust to oxygen bleaching. Tamminen and Hortling speculated that the difference in delignification was caused by differences in the hemicellulose to lignin bonded structure.[6] Zou demonstrated that pulps with a high xylan content were more difficult to delignify but had improved selectivity when compared to pulps with a low xylan content. Nevertheless, the reactions of oxygen delignification are compromised by diminished accessibility to lignin due to the presence of increased amounts of xylan.[7]

It is widely known that mill oxygen delignification stages can typically remove less than approximately half

* To whom correspondence should be addressed. Tel.: 404 894 9712. Fax: 404 894 4778. E-mail: Lucian.lucia@ipst.edu.

of the lignin from softwood kraft pulps, and if delignification is pushed, unacceptable losses in pulp strength are observed from the depolymerization of cellulose (vide infra). Thus, our study was conducted to determine the limiting factors for lignin removal from pulp during oxygen delignification by subjecting the pulp to oxygen delignification in three stages: fractionating both the residual lignin kept in the pulp and the soluble lignin dissolved in the liquor, analyzing the change of constituents to demonstrate the LCC's effect on restricting delignification and the reactive groups in all lignin fractions, and determining the relative crystallinity of pulp to show that the intrinsic crystal structure is to some extent recalcitrant to cellulose degradation. Finally, we ascertained the level of strength loss in pulp during lignin removal.

Experimental Section

Pulp and Oxygen Delignification. An industrial softwood kraft pulp was received and kept in a cold room (3 °C). The pulp was subjected to oxygen−alkali delignification in a Parr reactor with 4840 temperature control in three separate stages according to the following protocol: the oxygen delignification in each stage took place with 2.5% sodium hydroxide on a pulp oven-dried (odw) basis, 1.5% magnesium sulfate (odw), and 0.5% phenol (odw) with a consistency of 12%. Runs were done in two phases: the first phase was under an oxygen pressure of 135 psi at 193 °F for 30 min, while the other phase was at 80 psi, 210 °F, and 60 min.

Residual Lignin Preparations. After the industrial kraft pulp underwent oxygen delignification, the residual lignins in pulps were extracted and the effluent lignins were precipitated. Extraction of the residual lignin was done according to the following protocol: 30 g of pulp was treated with 2000 mL of 0.1 mol·L^{-1} HCl in dioxane aqueous solutions in a 5000-mL three-neck flask and refluxed for 120 min under an argon atmosphere; then the extracted solution was passed through Celite that removed the dioxane according to the method described by Chakar and Ragauskas,[8] and the effluent lignin in the solution after oxygen−alkali delignification was precipitated by adjusting the pH to 2.3, washing with 0.002 mol·L^{-1} HCl three times, and freeze-drying for the final structural analysis according to Figure 1.

X-ray Diffraction Chromatography and Crystallinity of the Pulp. Pulp was dried under vacuum and determined by X-ray diffraction according to Ahtee et al.'s method.[9]

Determination of the Carbohydrate Contents. Pulp or lignin samples were treated with 72% H_2SO_4 at 20 °C for 60 min and then diluted to a 3% H_2SO_4 solution. The solutions were hydrolyzed at 120 °C for 60 min, converting them to monomeric carbohydrates. The content of the carbohydrates was determined by HPAEC-PAD using a Dionex HPLC system equipped with a GP40 gradient pump, an ED40 electrochemical detector, and an AS40 autosampler. The separation was carried out on a Dionex's anion-exchange separator column, CarboPac PAI, preceded by a CarboPac PAI guard column. The postcolumn eluent, 0.5 mol·L^{-1} NaOH, was delivered using the Dionex PC 10 pneumatic controller to give a total flow of 1.5 mL·min^{-1} through the detector.[10]

Quantitative ^{31}P NMR Analyses for Hydroxyl Groups. ^{31}P NMR spectra were acquired on lignin samples that were derivatized with 2-chloro-4,4,5,5,5-
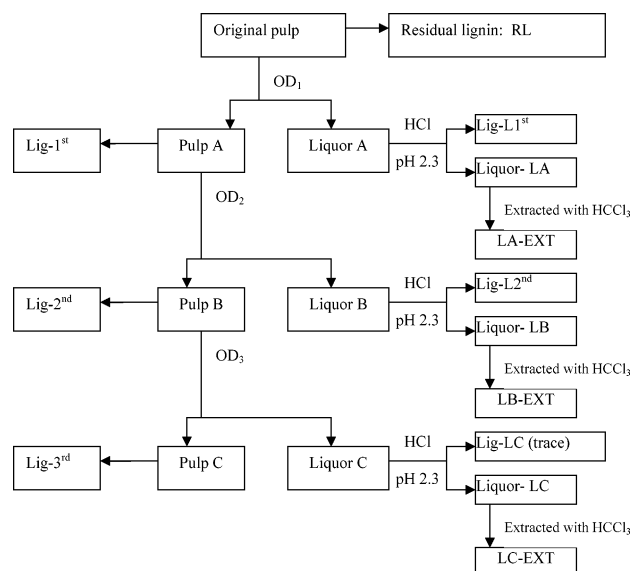

Figure 1. Sketch of the three-stage oxygen delignification and lignin preparation protocol that was used. OD: oxygen delignification.

tetramethyl[1.3.2]dioxaphospholane.[11] 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 was 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 of the chemical shifts were calibrated to the product of the phosphitylating agent with water that gives a sharp ^{31}P signal at 132.2 ppm. Integration regions used to analyze the spectra were obtained from the literature and are listed in Table 5.

Gas Chromatography/Mass Spectrometry (GC/MS) Analysis. The low molecular weight degraded lignin compounds were extracted with chloroform from the filtrate of oxygen-delignified pulp after the pH was adjusted to 2.5. The silylated lignin degradation products were separated and analyzed with a HP 5890 series II GC coupled with a HP 5971A mass-selective detector. The GC was equipped with a DB-5 column with the dimensions of 60 m × 025 mm × 0.25 µL. The initial temperature was set at 100 °C for 10 min, and the oven temperature was increased to a ratio of 20 °C/min until a 280 °C maximum temperature was achieved. The final time at maximum temperature was 10 min. The solvent delay was set to 8 min.

κ **Number and Viscosity Determination.** The κ number and viscosity of the pulp were determined according to T236 cm-85 and T230 om-94.

Results and Discussion

Lignin Removal and Viscosity Loss during Oxygen Delignification. In general, most of the lignin in softwood is removed after the kraft pulping process, with about 3% residual lignin remaining in the fiber of the pulp; more precisely, it remains within the secondary layer (S_2) of the cell wall because the middle lamella lignin was dissolved after the bulk phase of cooking. Nevertheless, chlorine and most of its derivatives can practically remove most of the residual lignin without incurring much damage to the cellulose. However, a more environmentally appealing oxidant such as oxygen can remove lignin to no more than 50% in a single stage

Table 1. κ Number and Viscosity of the Original Pulp after Being Subjected to Three Consecutive Oxygen Delignification Stages

pulp	κ number	viscosity (mPa·s)	degree of κ number decrease (%)	degree of viscosity decrease (%)	selectivity[a]
original pulp	20.4	27.6			
stage 1	11.2	21.9	45	20.8	2.2
stage 2	7.1	19.4	36	11.4	3.2
stage 3	5.7	18.2	20	5.9	3.4

[a] Selectivity: ratio of change in the κ number decrease to change in the viscosity decrease. 2.5% sodium hydroxide on pulp oven-dried weight (odw) basis, 1.5% magnesium sulfate (odw), and phenol 0.5% (odw) at a consistency of 12%. Runs were done in two phases: the first phase is under an oxygen pressure of 135 psi at 193 °F for 30 min, while the other phase is at 80 psi, 210 °F, and 60 min.

and about 75% in a multistage sequence before incurring significant cellulose damage. There have been a number of research efforts focused on this 50% threshold as previously indicated. Chirat and Lachenal[5] proposed that the linkage between residual lignin and carbohydrate is highly resistant toward oxygen delignification. In the present research effort, we therefore examined the latter issue by subjecting softwood kraft pulp to three consecutive oxygen delignification runs. The lignin removal (κ number drop) and viscosity loss are shown in Table 1. In the first stage, about 45% lignin can be removed after oxygen–alkali treatment, but in the second and third stages, it became much more difficult to remove the remaining lignin. Interestingly, it was found that the degree of viscosity decrease was much less in the second and third stages than that in the first stage and the selectivity of delignification increases from the first stage to the third stage. It is obvious that the cellulose damage becomes less pronounced in the second or third stage of oxygen delignification. During the second and third stages, the viscosity loss was less as compared to the result with only magnesium sulfate[12a] owing to the use of the magnesium sulfate and phenol mixture as a synergistic protector system in the present experiment as described in past reports.[12b,c] Part of the rationale for this reduced damage of the fiber or cellulose is the decrease in the concentration of transient metals such as Mn^{2+} from 16 to 9 ppm (determined by the inductively coupled plasma method) in the pulp after the first-stage oxygen–alkali treatment because these metals exacerbate the generation of indiscriminate radicals that harm cellulose. Yet, the composition and structural characteristics of the resident lignin likely influence the delignification response of the pulp.

Composition of the Residual Lignin. Residual lignins extracted from softwood kraft pulp and oxygen-delignified pulps typically contain carbohydrates. For oxygen-delignified pulps, the amount of carbohydrate accounts for about 10% in lignin preparations but only 1% in the original brown stock pulp (see Table 2). Furthermore, the Klason lignin in lignin preparations is very different between brown stock residual lignin and oxygen-delignified residual lignins. In the original residual lignin, there is 99% Klason lignin and only 0.1% acid-soluble lignin; however, the Klason lignin decreased and acid-soluble lignin greatly increased with the oxygen delignification process, concurrent with the lignin depletion in the pulp. It is clear that the majority of residual lignin is on the surface of the fibers for the original brown stock pulp and contained a small content of carbohydrate, similar to the alkali lignin that underwent chemical changes during pulping. There is 0.95% lignin in the brown stock pulp that cannot be extracted by acidolysis in dioxane/water (9:1, v/v). After the first-stage oxygen delignification, the nonextracted residual lignin was 0.46%, which was maintained at about 0.15–0.17% and virtually did not change during the second and third oxygen delignification stages. We conjecture that this residual lignin either is linked to a carbohydrate in a chemical bond or is strongly encrusted by carbohydrates. During oxygen–alkali treatment, the active oxygen species can cleave the bonds between lignin substructures or the glycosidic linkages in cellulose and hemicellulose, which can lead to lignin removal and viscosity loss.

Besides lignin removal, the lignin substructure cleavage also accounts for the increase of acidic-soluble lignin in lignin preparations after oxygen delignification. From the knowledge of the recalcitrant residual lignin, we can deduce that there is sufficient lignin in pulp (~0.15%) that is difficult to remove by oxygen delignification. Part of the κ number measured is from a contribution of hexenuronic acids in the kraft pulp because hexenuronic acid cannot be removed during oxygen delignification.[13a,b] Nevertheless, the lignin in the pulp after three stages of alkaline oxygen delignification demonstrated its stability and recalcitrant nature, likely in a matrix surrounded by polysaccharides that is inaccessible. During the second and third stages of oxygen delignification, although the viscosity loss decreased with delignification, the relative selectivity increased, which can be explained by the robust nature of the native crystalline cellulose remaining.

Crystallinity of Pulps and Carbohydrate Components in Pulps and Lignins. The crystallinity of cellulose is the main reason that accounts for its robust nature and lack of hydrolysis by either chemical or microbial attack.[14] During oxygen delignification, although active oxygen species can cleave the glycosidic linkage in the cellulose chain, the crystalline structure of cellulose is recalcitrant to cleavage. The relative degrees of crystallinity measured by X-ray diffraction

Table 2. Residual Lignin Extracted from the Pulp after Oxygen Delignification

	total lignin in the pulp calculated from the κ number (%)[a]	extracted with dioxane and HCl in 9:1 (%)	yield of extracted lignin to the total lignin in the pulp (%)	Klason lignin in the lignin sample (%)[b]	acid-soluble lignin in the lignin sample (%)[c]	sugar in the lignin sample[d]	nonextracted residual lignin in the pulp (%)[e]
original pulp	2.65	1.7	64	~99	0.1	0.9	0.95
stage 1	1.45	1.1	76	83.5	6.1	10.4	0.46
stage 2	0.93	0.84	90	73.0	17.2	9.8	0.17
stage 3	0.74	0.65	88	54.9	35.6	9.5	0.15

[a] Total lignin content = 0.13% κ number value. [b] Klason lignin was determined according to Tappi method T222 os-74. [c] Acid-soluble lignin in the lignin sample = 100% − Klason lignin (%) − sugar (%). [d] Data are from the determination of sugar by HPAEC. [e] Nonextracted residual lignin in pulp = total lignin content − lignin extracted with HCl–dioxane.

Table 3. Crystallinity and Carbohydrate Content of Pulps

sample	crystallinity (%)[b]	monosaccharide composition in the pulps (%)[a]				
		arabinose	galactose	glucose	xylose	mannose
cotton	93.6					
original pulp	82.2	0.5	0.3	76.6	6.6	4.8
stage 1	87.3	0.5	0.3	76.4	6.4	5.9
stage 2	88.4	0.5	0.3	79.4	6.8	5.3
stage 3	88.3	0.5	0.2	80.3	6.6	5.2

[a] The value was measured by HPAEC in duplicate with 2−5% error. [b] Measured by X-ray diffraction.

for softwood kraft pulps and cotton are shown in Table 3. The first oxygen delignification treatment causes the pulp crystallinity to increase by about 5%, but the subsequent two stages of oxygen−alkali treatment do not improve the crystallinity of the pulp.

The initial increase can be explained using a fringed micelle model proposed by De Souza, which describes the removal of easily accessible amorphous polysaccharides that promote the increase of the crystalline/amorphous ratio of the fiber.[15] The components on the surface of the fiber including residual lignin and hemicellulose are first removed during the first-stage oxygen delignification. With an increase in the crystallinity of the fiber, oxygen and its derivatives have much more difficulty penetrating into the fiber, an explanation which partly explains the difficulty of lignin removal during subsequent oxygen delignification stages.

The monosaccharide composition of polysaccharides in the pulps was determined by HPAEC (in Table 3). The results showed that there are not too many differences in the hemicellulose contents of arabinose, galactose, xylose, and mannose, but glucose appears to increase slightly in the pulp after the second and third oxygen delignification stages. In the wood, the hemicelluloses are substances deposited along the microfibrils and the middle lamella, yet because parts of the hemicellulose are removed and degrade during kraft pulping, any residual hemicellulose almost exclusively resides within the secondary wall. Oxygen delignification treatment does not remove this hemicellulose selectively, but it uniformly accesses the surface of the fiber, and the relative amount of these carbohydrate components therefore remain virtually the same, despite the number of stages.

Components of Carbohydrates in Lignin Samples. Lignin samples were extracted from the pulps to provide a representative residual lignin fraction, and the lignin from the effluents was precipitated to give effluent lignin. The amount of effluent lignin (Lig-L) becomes quite low because of the reduced amount of resident lignin available. The effluent lignin Lig-L3rd was very low (trace) and is not sufficient for compositional analysis (see Figure 1), especially after the third oxygen delignification stage. Components of carbohydrates in lignin samples determined by HPAEC are shown in Table 4. The lignin from the original pulp (brown stock pulp) contains lower levels of carbohydrate for this sample because it mainly comes from the surface of the fiber. After the first oxygen−alkali treatment, the remaining lignin in the pulp is contained within the matrix along the microfibrils.

In general, the residual lignins contain a higher content of glucose, xylan, and mannan, but the effluent lignins contain a higher content of galactan. In all actuality, residual lignins that are in the pulp appear to exist in the LCC form. Thus, from our results in Table

Table 4. Carbohydrate Components in the Lignin Samples

sample	arabinan (%)	galactan (%)	glucose (%)	xylan (%)	mannan (%)	total (%)
RL	0.1	0.1	0.3	0.2	0.2	0.9
Lig-1st	0.9	0.5	3.9	3.5	1.6	10.4
Lig-2nd	0.8	0.4	4.1	3.0	1.5	9.8
Lig-3rd	0.8	0.4	3.6	3.2	1.3	9.5
Lig-L1st	0.3	1.3	1.7	1.3	0.3	4.8
Lig-L2nd	0.4	1.8	1.0	0.8	0.2	4.2

5, the galactan−lignin complex in the pulp is relatively easy to dissolve during oxygen−alkali treatment, but the xylan−lignin complex is more difficult to remove.

Reactive Groups in Residual Lignins. Lignin samples were extracted from the original pulp as well as the various stages of oxygen-delignified pulps using 0.1 N HCl in a mixture of dioxane/water (9:1). The nominal reactive groups, such as the aliphatic hydroxyls, phenolic hydroxyls, and carboxylic hydroxyls, were determined by traditional ^{31}P NMR spectroscopy. These groups are called reactive groups because the delignification reactions initiate from these groups; for instance, the phenolic OH donates an electron to the ground-state oxygen and initializes radical propagation to cause lignin cleavage that is encouraged by the development of carboxyl groups on the lignin. From the results (Table 5), the high content of aliphatic hydroxyl groups is partly attributable to a high content of carbohydrates. The content of either condensed or uncondensed phenolic hydroxyl groups in the lignin resulting from oxygen delignification is less than that from the original pulp, and the decrease in uncondensed phenolic hydroxyl groups is greater. With the concomitant decrease in the level of uncondensed phenolic hydroxyl groups, it becomes more difficult (although not impossible) to delignify in subsequent oxygen stages because the phenolic hydroxyl group is the reactive point for oxidative reactions. This rationale partially accounts for the reduced delignification in the second and third stages. The carboxyl group content in Lig-1st is greater than that in RL, a difference caused by the oxidation of lignin in the first stage, but the carboxyl group contents in Lig-2nd and Lig-3rd are less than that in Lig-1st, which means that the lignin with the carboxyl groups was removed in the second and third stages, and the more stable residual lignin contains less reactive or solubilizing groups.

When the residual lignin is compared with the effluent lignin during oxygen delignification, the effluent lignin contains more phenolic hydroxyl groups and carboxyl groups, but the content of the uncondensed phenolic hydroxyl group was lower than that of the condensed phenolic hydroxyl group. There are two reasons for this difference: one is that the phenolic hydroxyl group took part in a condensation reaction during oxygen delignification under alkali conditions,

Table 5. Quantity of Reactive Groups, Such as Aliphatic Hydroxyls, Phenolic Hydroxyls, and Carboxylic Acid Groups

group		RL (mmol/g)	Lig-1st (mmol/g)	Lig-2nd (mmol/g)	Lig-3rd (mmol/g)	Lig-L1st (mmol/g)	Lig-L2nd (mmol/g)
aliphatic OH	150.0–145.6	1.56	3.52	4.14	3.87	1.87	2.66
condensed phenolic OH	144.7–140.4	1.02	0.77	0.52	0.55	0.91	1.10
guaiacyl phenolic OH	140.4–138.6	0.92	0.55	0.32	0.30	0.57	0.60
p-hydroxylphenolic OH	138.6–137.0		0.09	0.06	0.07	0.13	0.22
carboxyl OH	136.0–133.8	0.43	0.68	0.30	0.32	0.69	1.27

Table 6. Compounds Extracted from Liquors after Oxygen Delignification

compound	relative abundance (%)			retn time (min)	mol. peak mass	peak mass
	38LA-EXT	38LB-EXT	38LC-EXT			
1	3	3	3	8.931	178	178, 179, 135, 105
2	1	6	1	9.416	262	262, 247, 147,
3	3	4	1	10.309	194	194, 179, 151, 135
	9	10	11	11.654		unknown
4	44	46	46	12.146	224	224, 209, 194, 165, 137
5	7	5	8	13.261	238	238, 223, 208, 193, 165, 117
6	7	17	29	13.359	234	234, 219, 175, 145, 89
7	1	<1		14.053	310	310, 295, 253, 192, 147
8	1	<1		14.155	312	312, 297, 223, 209, 165, 149
9	2	1	2	14.543	254	254, 239, 195, 165
10	8	8	5	15.638	312	312, 297, 223, 193
11	1	2		16.663	326	326, 311, 297, 267, 237, 206, 179,
12	3	6		20.922	340	340, 325, 295, 251, 235, 221, 147
13	1	1		23.226	354	354, 339, 265, 235, 147, 117
14	1	2		23.355	340	340, 325, 295, 250, 223, 193

while the other is the ring opening of the phenolic hydroxyls during the process.

In the second oxygen delignification process, the effluent lignin contained more phenolic hydroxyl groups and carboxyl groups than that the residual lignin. There are greater levels of hydroxyl groups and carboxyl groups in the effluent lignin of the second oxygen delignification stage than that of the first stage. The lignin underwent oxidative reactions, is cleaved from the pulp, and dissolves in the bulk liquor; therefore, these effluent lignins contained more carboxyl groups and phenolic hydroxyl groups in both the condensed and uncondensed forms than in the residual lignin.

The lignin removal in the pulp during oxygen delignification is relative to both the lignin structure, especially the reactive function groups in the residual lignin, and the location of the lignin in the fiber, i.e., the accessibility of reactive reagent to lignin. The lignin in the original pulp was distributed on the surface of the fiber predominantly, which was easily removed during the first oxygen delignification stage. Meanwhile, some carbohydrates in hemicellulose and amorphous cellulose were degraded, which caused an increase in the crystallinity of cellulose in the pulp. The lignins encrusted between microfibrils or linked with carbohydrates are inaccessible to oxygen reagents and are retained in the pulp even with several oxygen delignification stages. The carboxyl groups in the residual lignin after two stages of oxygen delignification (Lig-2nd and Lig-3rd) are less than that in Lig-1st, which demonstrates that the lignin that remained in the pulp after two or three stages of oxygen delignification was slightly affected by oxygen reagents.

Low Molecular Weight Compounds from Effluent after Oxygen Delignification. The residual lignin in the pulp that had undergone oxygen delignification was divided three fractions; one fraction still remained in the pulp, which was extracted out with an acidolysis method, one fraction was solubilized during oxygen delignification and precipitated by acid, and another fraction was low molecular weight compounds. Although

the features of the first two fractions were discussed in the previous description, the determination of the features of the low molecular weight fraction are helpful in understanding the mechanism of lignin degradation during oxygen delignification.

Extractives from the effluent of various stages of oxygen–alkali treatment were analyzed by GC/MS spectra. The major compounds that were found were vanillin and guaiacyl products, a direct result from the oxidation of guaiacyl units in residual lignin in oxygen delignification. Remarkably, *p*-hydroxyphenyl products and benzyl alcohol were also found. It is a known that softwood lignin contains low levels of *p*-hydroxyphenyl units whose abundance is estimated to range from 5% to 13% of the total lignin moieties. Such moieties may accumulate within the residual lignin during the kraft pulping process and appear to act as blocking or intransient groups toward oxidation. From the first stage to the third stage of oxygen delignification, it was found that the oxalate acid in the extractives increased, more than likely because of oxidation of the carbohydrate. 5-Substituted guaiacyl products in the extractives from the third-stage effluent could not be determined.

Condensed Units in the Residual Lignin. The typical condensed units in softwood lignin include 5,5′-biphenolic hydroxyls, diphenylmethane (DPM), β-5, and dibenzodioxocin.[16] The now famous octagonal dibenzodioxocin moiety is known to additionally supply 5,5′-phenolic hydroxyls under kraft pulping conditions. The total condensed phenolic hydroxyls in the residual lignin of softwood kraft pulp decreased after oxygen delignification treatment; however, the content of the condensed phenolic hydroxyl group does not change during the second and third oxygen delignification (Table 5). Lai et al. showed that the phenolic lignin DPM dimers and β-5 linkage structures were reactive in mild oxygen–alkali solution and gave monomeric products, e.g., vanilly alcohol and 5-(hydroxymethyl)cresol.[17] Among the low molecular weight compounds extracted from the liquor after oxygen delignification (Figure 3 and Table
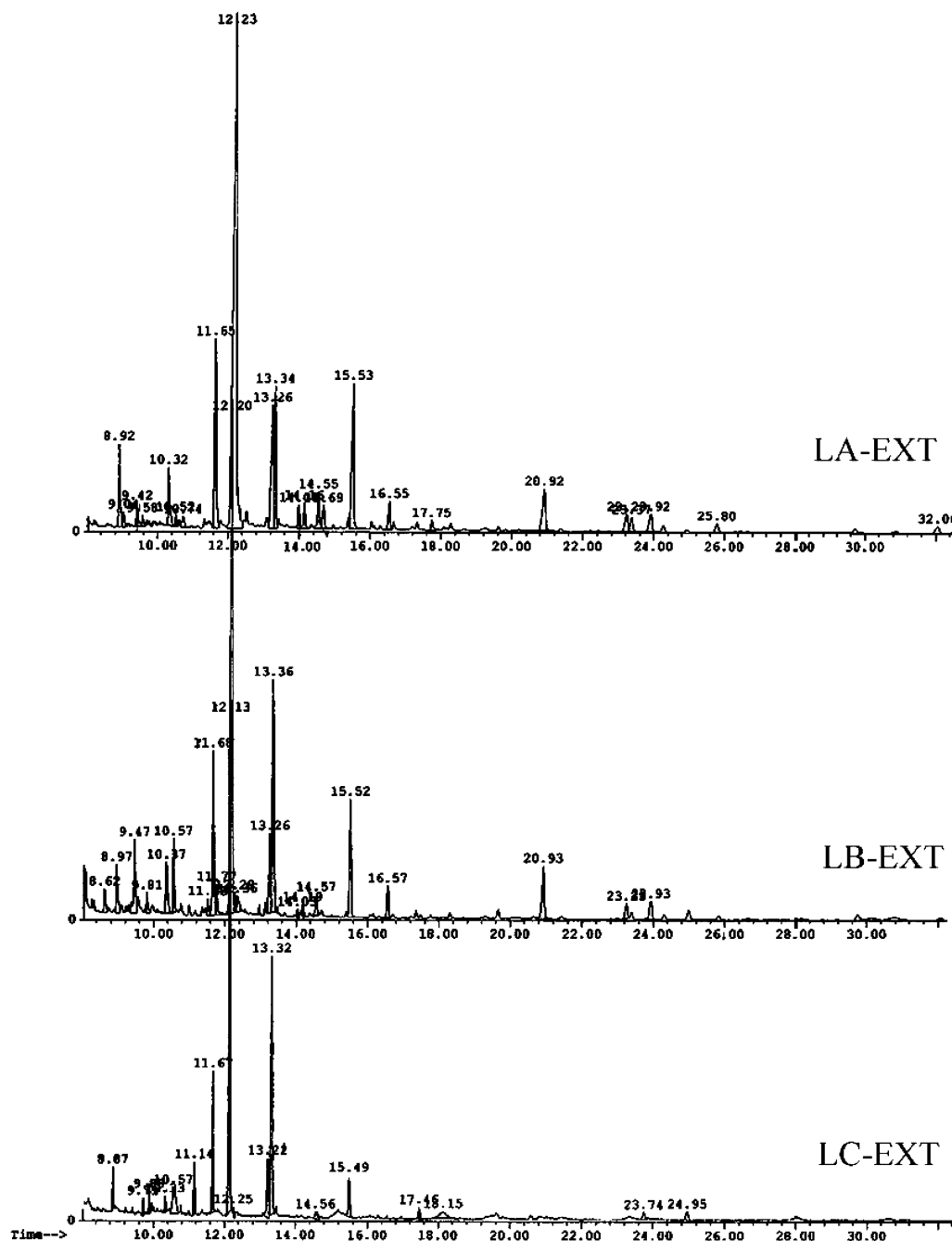
Figure 2. TIC chromatograph of extractives from liquors after oxygen delignification by GC/MS.

6), several 5-carboxyl group compounds, such as compounds 8, 12, and 13, were likely formed from the DPM units or β-5 units in the residual lignin under oxygen–alkali treatment. Argyropoulos demonstrated that 5,5′-biphenolic structures showed the highest oxidative resistance among the condensed structures.[18] Actually, the oxidative resistance of several special lignin structures such as these condensed structures is quite strong. It was found that there is a high content of condensed phenolic hydroxyl groups in the effluent lignin, such as Lig-L1st and Lig-L2nd, which are even higher than that in the original residual lignin (RL). Under oxygen delignification, the DPM and β-5 units are partly oxidized and changed to low molecular weight compounds, and it is therefore reasonable to state that most of condensed structures in the effluent lignin are in 5,5′-biphenolic structures whose increase can be explained in two ways: the accumulation or enrichment of these structures and/or formation during the reaction processes. The first reason is more likely because formation can also cause these structures to increase in the residual lignin in the pulp, which is not the case. The uncondensed structures, DPM and β-5, are subject to oxidation and give monomeric compounds or low molecular weight compounds, and the oxidation-resistant lignin structures accumulate.

p-Hydroxylphenyl Units in the Residual Lignin. From ^{31}P NMR spectra, p-hydroxylphenolic groups appeared at 138.6–137 ppm for phosphilylated lignin with 2-chloro-4,4,5,5,5-tetramethyl[1.3.2]dioxaphospholane. There is no peak at this position in the ^{31}P NMR for the residual lignin from the original pulp, but there are obviously peaks for the lignins after oxygen delignification. The content of p-hydroxylphenolic groups is higher in the effluent lignins, such as Lig-L1st and Lig-L2nd, than that in the residual lignin from pulps.
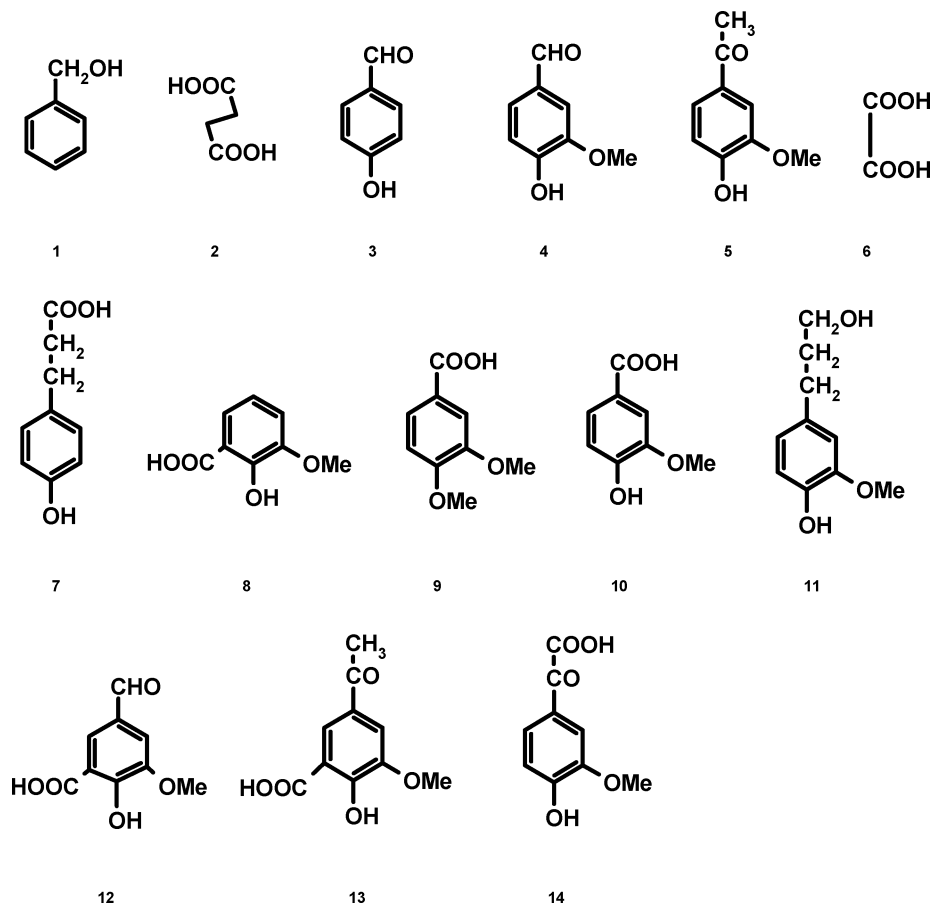
Figure 3. Structure of major compounds extracted from the liquor after oxygen delignification identified by GC/MS.

The higher content of *p*-hydroxylphenolic groups results from their oxidative resistance; in other words, *p*-hydroxylphenolic groups can accumulate during oxygen delignification. Actually, the *p*-hydroxylphenyl unit can also be oxidized during oxygen delignification and gave low molecular weight *p*-hydroxylphenyl products, such as compounds **2** and **7**. However, the reactivity for *p*-hydroxylphenyl and guaiacyl units is different during oxygen delignification; the latter is more reactive under oxygen alkali than the former, which leads to an accumulation of *p*-hydroxylphenyl units in the residual lignin and effluent lignin. In fact, experiments with model compounds demonstrate the higher stability of the *p*-hydroxylphenyl moieties under oxygen delignification.

Conclusions

The industrial kraft pulp was delignified with oxygen alkali in three continual stages, and about 75% residual lignin can be removed, but there are some lignins in the pulp recalcitrant to delignification. During the oxygen delignification process, the penetration of oxygen and oxygen-active species into the lignin matrix along the microfibrils in the pulp is perhaps the main factor limiting lignin removal. The matrix structure of carbohydrate, the robust nature of native cellulose crystal in the pulp fiber, and the LCC constitute the main barriers to oxidative reactions resulting in delignification. Different constituents of hemicelluloses in the pulp are responsible for the barrier of lignin removal during oxygen−alkali treatment. Lignin linked with xylan is more resistant to oxidation and remains in the pulp, but lignin linked with galactan can be dissolved during oxygen delignification. The decrease in reactive groups such as hydroxyl and carboxyl groups during oxygen delignification is responsible for the reduced ability of subsequent delignification reactions. Finally, the *p*-hydroxylphenyl and 5,5′ biphenolic units in the residual lignin are quite stable and tend to accumulate during oxygen delignification.

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