Kraft Green Liquor Pretreatment of Softwood Chips.
Part III: Lignin Chemical Modifications

By Weiping Ban, Jaimal Singh and Lucian A. Lucia

Georgia Institute of Technology, Institute of Paper Science and Technology, Atlanta, GA, USA

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Summary

Quantitative ^{31}P NMR analysis of residual lignin structures isolated from pulps pretreated by green liquor (GL) as a function of various operating parameters are discussed. Uncondensed phenolics and condensed hydroxyl groups decreased as the GL charge increased, but increased with increasing pretreatment temperature. During the cooking of pulps employing variable sulfidities and the addition of anthraquinone (AQ) or polysulfide (PS), various hydroxyl groups exhibited no obvious differences in the case of AQ addition, but dramatic changes were observed at variable sulfidities when the PS was used. The results implied that PS can exert a stronger catalytic effect under a higher sulfidity and result in more cleavage of the lignin macrostructure. The results also demonstrated a correlation between the nature of residual lignin and the efficiency of oxygen delignification based on the finding that the residual lignin in GL modified pulp exhibited a higher reactivity toward oxygen delignification.

Introduction

Softwood kraft pulp lignin contains both condensed and uncondensed guaiacyl moieties. The proportion of both of these lignin structures has been acknowledged to influence the course of delignification during subsequent bleaching operations. Condensed structures present in lignin are known to exhibit increased resistance to elimination in the bleaching operation as compared to uncondensed lignin structures. Some past literature reports have explored and established a correlation between the presence or absence of various lignin hydroxyl groups and the degree of delignification (Hortling *et al.* 1993; Chang *et al.* 1996; Froass *et al.* 1996a, b; Ede *et al.* 1997; George *et al.* 1997).

Extended delignified pulps exhibit higher phenolic hydroxyl group concentrations than conventionally cooked kraft pulps (Chang *et al.* 1996). Analyses of the residual lignins of different kraft pulps revealed that pulps with a lower kappa number contain higher amounts of free phenolic structures (Froass *et al.* 1996a). In fact, the content of phenolic hydroxyl groups in residual lignins correlates well with established data concerning the concentration of phenolic groups and lignin reactions under different bleaching conditions (Hortling *et al.* 1993). Continuous-processed pulps have been more easily delignified in a DE bleaching sequence than batch pulps. However, the higher quantity of phenolic hydroxyl groups in the batch pulps did not result in better bleachability (Van Lierop *et al.* 2000). The residual lignin in the batch pulps also showed more extensive degradation than observed in the continuous-process pulps (George *et al.* 1997).

A novel and powerful way to improve conventional kraft pulping is by means of green liquor (GL) pretreatment. It has been shown to improve delignifying selectivity, save on the consumption of cooking chemicals, and provide better pulp qualities (Andrews and Chang 1985; Klevinska and Treimanis 1997; Chivukula *et al.* 1998). The benefits of GL pretreatment for improvements in bleaching have also been reported (Svedman *et al.* 1997).

The objective of the present investigation is to provide an in-depth analysis of the nature of residual lignin in pulps as modified by GL impregnation under variable parameters and how the changes in lignin structure relate to pulp performance during oxygen delignification. The correlation among pulp pretreatment, specific residual lignin structures, and the performance of oxygen delignification was explored and provided several important findings.

Materials and Methods

Wood chips

US southern pine wood chips from industrial supporting members of the Institute of Paper Science and Technology (IPST) were obtained. The size of chips used for the experiments was $2–3 \times 20 \times 25–30$ mm. The dry content of all the wood chips was determined to be 45.25 % and all bark and knots were removed for any pulping work.

Green liquor

The green liquor (GL) used in all of the experiments was provided by industrial sponsors of IPST. It consisted of 19.18 g/l NaOH, 31.70 g/l Na_2S and 107.89 g/l Na_2CO_3 (all concentra-

Table 1. Pulping and oxygen delignification data

GL charge on wood (l/kg)	0.5	1	1.5	2	1
Pretreatment temperature °C	20	20	20	20	135
Cook A.A. %	15	15	15	15	15
Sulfidity %	30	30	30	30	30
Cooking time (min)	150	180	180	150	150
Brown stock kappa number	54.6	38.32	38.2	57.1	56.3
Kappa number after oxygen delignification	21.88	16.47	18.26	15.75	20.29
Reduction in kappa number	32.72	21.85	19.93	41.35	36

GL charge on wood (l/kg)	1	1	1	1	2
Pretreatment temperature °C	135	135	135	135	135
	AQ	AQ	PS		
Additive %	0.1	0.1	1.2	PS 1.2	None
Cook A.A. %	15	15	15	15	15
Sulfidity %	15	30	15	30	30
Cooking time (min)	180	180	180	180	150
Brown stock kappa number	38.3	31.7	31.3	42.7	56.6
Kappa number after oxygen delignification	14.95	15.99	14.86	21.35	16.69
Reduction in kappa	23.35	15.7	16.44	21.36	39.91

tions are expressed as Na_2O), which were analyzed by standard TAPPI test methods (TM 624cm-85).

Pretreatment and pulping

Pretreatment and cooking were carried out by using a multi-unit stainless steel bomb digestive system designed in the pulping and bleaching labs of IPST. Eight different samples could be treated simultaneously. Pretreatment and cooking procedures were controlled by the computer programmed oil bath; temperature ramps were on the order of 1.2 °C/min and each bomb could accommodate a volume of 500 ml and approximately 50 ml headspace was allowed after 50 g of oven dried (o.d.) wood chips was placed in each bomb. Pretreatment conditions consisted of the following: the ratio of pretreatment liquor to wood chips was 4:1, GL charge on wood chips varied from 0.5–2.0 l/kg, GL concentration varied from 12.5–100 %, pretreatment temperature were 20 °C and 135 °C, and impregnating time 60 min and 120 min.

When the pretreatment run was finished, the pretreatment liquor was drained. A new cooking liquor of a particular alkali charge and sulfidity was added to the digester to continue the post cooking process. A charge of 15 % active alkali and 1.5 h hold time under temperature 170 °C was used for all pulping samples, and the variable sulfidity was 15 % and 30 %.

Oxygen delignification

The oxygen delignification experiments were carried out using an autoclave; 10 g o.d. pulp was dispersed and loaded in the autoclave. The pulp concentration = 10 %, temperature = 100 °C, hold time = 60 min, oxygen pressure = 0.6 MPa, the charge of NaOH = 5 % (on pulp o.d.), and $MgSO_4$ charge = 0.5 % (on pulp o.d.). The data of pulping and oxygen delignification are summarized in Table 1.

Lignin isolation and ^{31}P NMR spectroscopy

Lignin samples were isolated from the pulps according to a method previously described (Gellerstedt and Lindfors 1991; Gellerstedt *et al.* 1994). The pulp samples were extracted by acetone refluxing for 24 h in a Soxhlet extractor, washed with deionized water and air dried. The residual lignin was isolated by refluxing with an acidic dioxane solution (0.1M HCl in a 9:1 dioxane:water solution) for 2 h, after which the mixture was

filtered and the filtrate was neutralized to pH 6.0 with a saturated sodium bicarbonate solution. The dioxane was removed under reduced pressure. Lignin was precipitated by adding 1.0M HCl solution at pH 2.0. The acidic mixture was transferred to centrifuge bottles and frozen to allow for lignin coalescence. Then the samples were thawed, centrifuged and decanted. After this washing procedure, all of the lignin samples was freeze dried. The yield of residual lignin was 60 % – 70 % based on the kappa numbers of the pulps before and after acidic hydrolysis.

The samples were derivatized with 2-chloro-4,4,5,5-tetraethyl-1,3,2 dioxaphospholane and analyzed by ^{31}P NMR following the procedure described in previous reports (Argyropoulos 1994; Granata and Argyropoulos 1995). NMR spectral acquisition and analyses were controlled by a Bruker XWinNMR 2.1 software running on a SGI (Silicon Graphics Indigo) server under the Irix 7.0 operating system.

Results and Discussion

Structural characteristics as a function of pretreatment conditions

It is well known that the uncondensed structures in lignin that contain free phenolic hydroxyl groups exhibit higher reactivity toward oxygen delignification (Ljunggren 1986; Ljunggren *et al.* 1991; Johansson and Ljunggren 1994). Conversely, aromatic condensation reactions decrease the reactivity of residual lignin during oxygen delignification in which condensed lignin structures, such as diphenylmethane and biphenyls, were found to display resistance to oxygen delignification (Lai *et al.* 1994; Argyropoulos and Liu 2000). Based on several research efforts, it has been discovered that the condensation profile of residual lignin is a critical factor for influencing the course of oxygen delignification.

The relative abundances of specific hydroxyl groups are shown in Figure 1. As the GL charge is increased, the concentration of the phenolic hydroxyl groups decreases until 1.5 l/kg GL concentration in a manner con-
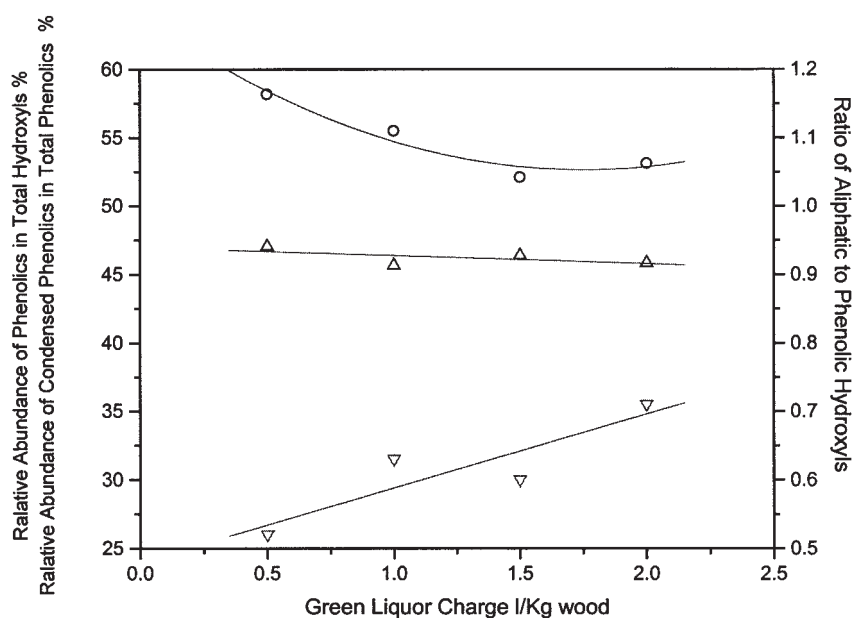
Fig. 1. Changes in the concentrations of specific hydroxyl groups as a function of GL charge (○ = phenolics/total hydroxyls; △ = condensed/total phenolics; ▽ = aliphatics/phenolics).

Table 2. ^{31}P NMR integration results of functional group concentration as a function of variable GL concentrations and pretreatment temperatures

Pretreatment Temp. °C	20	20	135	135
GL Concentration %	50	100	50	100
Total Phenolic OH %	55.49	53.12	56.67	55.44
Condensed Phenolic OH %	25.33	24.34	26.43	25.58
Uncond. Phen/Conden. Phen OH	1.19	1.18	1.14	1.17
p-hydroxyphenyl OH %	3.23	3.23	3.44	3.43
Carboxylic OH	9.43	9.4	8.22	8.8
Aliphatic OH	35.08	37.48	35.11	35.76
Guaiacyl Phenolic OH	26.92	25.54	26.8	26.43

sistent to what was observed for the total hydroxyl group concentration. However, and more importantly, the concentration of condensed structures linearly decreased as the GL charge increased. This result indicates that green liquor pretreatment of wood chips before the kraft cook can effectively reduce or eliminate lignin condensation structures, which implies that the bleachability of kraft pulps may potentially be significantly improved. Although the concentration of phenolic hydroxyl groups was diminished by GL pretreatments, increasing GL charge increased the concentration of aliphatic hydroxyl groups. The ratio of the concentration of aliphatic to phenolic hydroxyl groups was observed to linearly increase as a function of increasing GL charge. This result suggests that increased side chain cleavage in lignin macromolecules occurs as well as phenolic hydroxyl group consumption during GL-modified pulping.

Besides GL concentration, pretreatment temperature also plays an important role in inducing changes in the structure of lignin (Table 2). It clearly demonstrates that residual lignin is enriched in more phenolic hydroxyl groups pretreated by green liquor at a high temperature (135 °C) than at a low temperature (20 °C). This result indicates that more lignin β-O-4 ether bond cleavage reactions occur under the higher temperature. In the case of GL concentration of 50% or 100%, the concentration of condensed lignin structures at the higher pretreatment temperature is slightly higher than at the lower temperature. At the 50% GL concentration, the ratio of uncondensed structures to condensed structures decreased as the pretreatment temperature increased agreeing with what has been observed for the decrease in both phenolics and increase in condensed structures. From Table 2, similar changes are also seen in the concentration of the *p*-hydroxyphenyl group, a group whose origins and importance have been discussed previously for limiting the degree of oxygen

delignification (Akim *et al.* 2001). An increase in the pretreatment temperature resulted in increased *p*-hydroxyphenyl group formation in residual lignin, regardless of the GL concentration used in pretreatment; however, at same pretreatment temperature, an increase in the GL concentration appeared to have little impact on increasing the concentration of *p*-hydroxyphenyl structures.

Our previous work, in which the chemical absorption during GL pretreatment was investigated, indicated that various chemicals such as sodium hydroxide, sulfide, and sodium carbonate displayed different absorption characteristics (Ban *et al.* 2003). As the GL charge increased, alkali was absorbed more rapidly into wood chips than sulfide, which indicated that the ratio of sulfide ions to hydroxide ions absorbed decreased under higher GL charge levels. Since sulfide ions contribute to limiting lignin condensation reactions in the early part of the cooking stage, it is reasonable to confirm that the chemical absorption and the relevant optimal GL pretreatment condition are critical factors for improving delignification, specifically in the control of the lignin condensation reaction profile.

Lignin hydroxyl group changes as a function of sulfidity, PS, and AQ

To investigate the impact of variable sulfidity and additives on changes in residual lignin structure, wood chips were pretreated by using a 50 % concentration of GL at 135 °C for 1 h, followed by kraft cooking. Lignin NMR functional group integration results are shown in Table 3. When the sulfidity was increased from 15 % to 30 %, various hydroxyl groups in lignin increased in both the case of anthraquinone and polysulfide treatments. This indicated that there is a critical concentration of sulfide necessary to degrade the lignin macrostructure. The most remarkable data are observed when applying polysulfide additive cooking. When the sulfidity was increased from 15 % to 30 %, the total hydroxyl group content increased dramatically, but the same phenomenon was not exhibited in the anthraquinone case. This observation proved that a different effective mechanism was in operation between AQ and PS, in which polysulfide exhibited a strong catalytic effect on the cleavage of lignin macromolecules. Nonetheless, sufficient sulfidity is an important basic criterion to ensure polysulfide-catalyzed lignin degradation.

As the sulfidity increases from 15 % to 30 % with either AQ or PS addition, only slight changes in the concentration of hydroxyl groups for the AQ-treated pulp could be observed, but for the PS additive pulp, sulfidity seemed to play a more significant role in the nature of residual lignin. Not surprisingly, as the sulfidity increased, the concentration of the phenolic hydroxyls increased, whereas that of the aliphatic hydroxyls decreased. The data supported an enhanced cleavage by PS of the lignin β-ether bond at higher sulfidity. The data further indicate that increasing sulfidity results in a reduction of the ratio of aliphatic to phenolic hydroxyl group for PS pulp, but little change for AQ pulp. The increase in cooking sulfidity showed a different impact on ratio of uncondensed to condensed hydroxyl groups for the AQ and PS pulps. The higher sulfidity exhibited a positive impact on AQ additive pretreatment pulping to reduce condensed lignin structure. For the PS case, the ratio of uncondensed to condensed hydroxyl groups slightly decreased with increasing sulfidity, a result that requires further investigation.

Lignocellulosics contain a distinct amount of the *p*-hydroxyphenyl structure, whose content varies in each particular substrate. Softwood lignin usually contains fewer *p*-hydroxyphenyl groups than hardwood. *p*-Hydroxyphenyl structures also derive from the cleavage of methoxyl groups in guaiacyl units during cooking process. The impact of *p*-hydroxyphenyl structure on oxygen delignification is still not clearly understood. Argyropoulos *et al.* (2000) and Akim (2001) concluded that the *p*-hydroxyphenyl structure has a higher stability under oxygen delignification by analogy to their model compounds experiments. Table 3 demonstrates that the *p*-hydroxyphenyl group in the residual lignin increased significantly as the sulfidity increased from 15 % to 30 % in PS-modified pulp as compared to the AQ-treated pulps. The implications of this result for oxygen delignification are not clear based on the following data.

Table 3. [31] PNMR integration results of functional group concentration as a function of sulfidity and additives

Sulfidity %	15	30	15	30
Additives %	AQ 0.1	AQ 0.1	PS 1.2	PS 1.2
Aliphatic OH %	33.6	32.31	33.56	28.38
Condensed Phenolic OH %	24.28	24.31	24.06	29.13
Total Phenolic OH %	52.98	54.31	52.23	59.96
p-Hydroxyphenyl OH %	4.42	4.7	4.38	4.65
Aliphatic OH/Phenolic OH	0.63	0.59	0.64	0.47
Uncond. Phen./Conden. Phen. OH	1.18	1.23	1.17	1.06
Guaiacyl Phenolic OH	24.28	25.3	23.79	26.18
Carboxyl OH	13.43	13.37	14.21	11.67
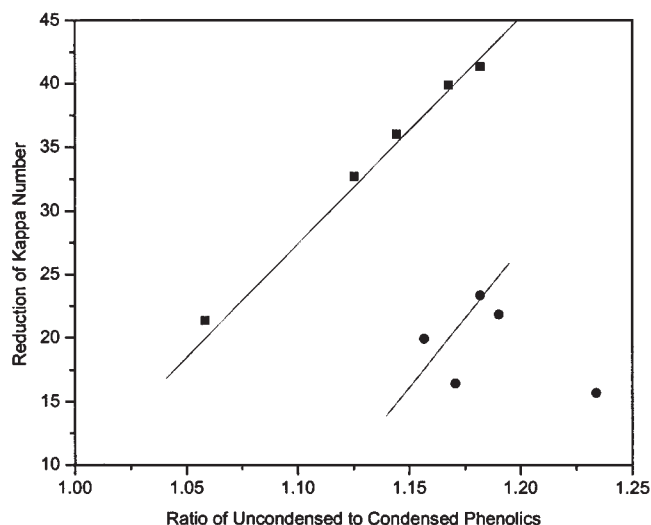
Fig. 2. Reduction of kappa number during oxygen delignification as a function of the ratio of uncondensed to condensed phenolics (■ = high kappa pulp; ● = low kappa pulp).
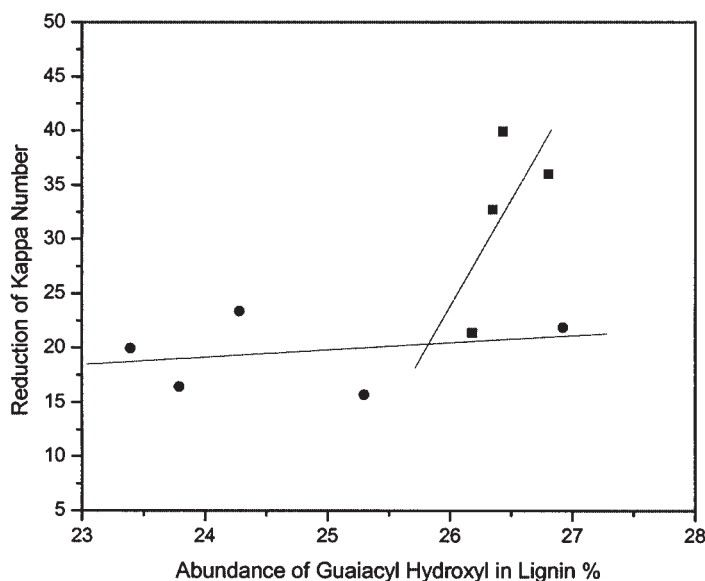
Fig. 3. Kappa number reduction as a function of guaiacyl hydroxyl group concentration (■ = high kappa pulp; ● = low kappa pulp).

Relationship of residual lignin structure to performance during oxygen delignification

For the purposes of comparison of the impact of residual lignin structures in the original pulps on the performance of oxygen delignification, all pulp samples were treated under the same conditions. The changes in pulp kappa number are compared and contrasted to the residual lignin structure from the original pulps to provide insight into the potential extent of oxygen delignification.

In general, the higher the ratio of uncondensed to condensed hydroxyl groups in residual lignin, the greater the potential extent of lignin removal during oxygen deligni-

fication. Figure 2 illustrates that the reduction of pulp kappa number after oxygen treatment increased as the uncondensed to condensed hydroxyl group ratio increased despite the difference in starting pulp kappa number. This result indicated that modifications in the pulping process that tend to reduce the phenomenon of lignin condensation are critical for the improvement of oxygen delignification. Thus, it is reasonable to anticipate that if a pulp was pretreated by GL, it would exhibit enhanced bleachability since pretreatment minimizes the generation of condensed lignin structures.

Uncondensed lignin structures are mainly composed of guaiacyl and *p*-hydroxyphenyl groups. Figure 3 further illustrates the corresponding correlation between the re-
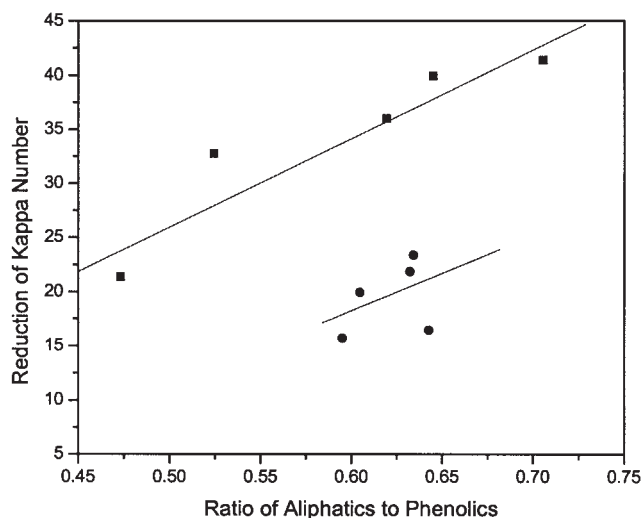
Fig. 4. Kappa number reduction as a function of the ratio of aliphatic hydroxyls to phenolics (● = high kappa pulp; ● = low kappa pulp).

duction of pulp kappa number and the abundance of guaiacyl groups. The enrichment in guaiacyl hydroxyl groups in residual lignin results in an increasing reduction in kappa number for both high and low kappa number pulp samples during oxygen delignification. Surprisingly, no similar trend could be developed between *p*-hydroxyphenyl groups with oxygen delignification. The data implies that the guaiacyl structure in residual lignin has a higher reactivity and is one of the critical factors to increasing pulp delignification in oxygen treatment.

Another particularly important trend associated with the hydroxyl group nature of residual lignin and its effect on oxygen delignification is the relative composition of aliphatic and phenolic hydroxyl groups in the residual lignin. Figure 4 shows that the percent reduction of original pulp kappa number after oxygen treatment increased as the ratio of aliphatic to phenolic hydroxyl group increased. The higher concentration of aliphatic hydroxyl groups indicates that the pulp lignin has undergone more side chain oxidation. Since GL pretreatment can increase the concentration of aliphatic hydroxyl groups (*vide infra*), this would appear to benefit pulp bleachability (Fig. 2).

Conclusion

The residual lignin structure of GL-pretreated pulp is characterized by a reduction in total condensed structures and possesses a greater number of aliphatic hydroxyl groups. The increase in the charge of GL pretreatment liquor contributes to increased uncondensed and aliphatic hydroxyl structure concentrations, whereas a higher pretreatment temperature resulted in a lower concentration of uncondensed lignin structures and a higher concentration of *p*-hydroxyphenyl groups.

A change in the cooking sulfidity from 15% to 30% impacted the nature of residual lignin during PS additive pulping that resulted in an increase in phenolic and *p*-hydroxyphenyl groups. In AQ-treated pulps, slight changes in the lignin structure were observed.

In general, a higher concentration of uncondensed phenolic structures in residual lignin improved oxygen delignification, which resulted in greater kappa number reduction during oxygen treatment. Based on this experimental data, the character and behavior of the uncondensed lignin structure during oxygen delignification can mainly be ascribed to the guaiacyl structure. The aliphatic to phenolic ratio also influences the removal of residual lignin during oxygen delignification, in which a higher ratio results in a higher reduction of kappa number.

Pulping modified by GL pretreatment produces a pulp that is apparently easier to delignify during oxygen delignification. The nature of this residual lignin is characterized by a higher uncondensed to condensed and aliphatic to phenolic hydroxyl group ratio. The results indicate that oxygen delignification of pulp modified by GL pretreatment is significantly improved.

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Weiping Ban
Jaimal Singh
Lucian A. Lucia[1]
Institute of Paper Science and Technology
Georgia Institute of Technology
500 10th St., NW
Atlanta, GA 30318-5794
USA

[1] Corresponding author