NMR studies, Part 5: Nature of residual lignin in kraft pulps

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ABSTRACT

Recent advances in kraft pulping have extended the degree of practical delignification while improving selectivity. Despite these improvements, little is known about the nature of the residual lignin in low-kappa-number kraft pulps. This paper examines the structure of residual lignin for seven conventional kraft pulps (kappa no. 33–13) and six Lo-Solids® kraft pulps (kappa no. 29–11). The residual lignin in each pulp was isolated and characterized by proton nuclear magnetic resonance (^{1}H NMR). The results of these analyses demonstrate that the overall structure of residual lignin is influenced by both the extent of delignification and the nature of the pulping process.

Application:

These results provide a theoretical basis for further improvements in kraft pulping technology.

ENVIRONMENTAL AND MARKET pressures have sparked a decade of progress in pulping technology. One important innovation was the evolution of modified kraft processes that reduce pulp lignin content prior to bleaching. The continuing evolution of extended kraft delignification is a useful development because it facilitates environmentally compatible bleaching practices, reduces operating costs, and may assist in the development of low-effluent pulp production.

The fundamental principles involved in extending kraft delignification while retaining pulp strength properties were established in the late 1970s and early 1980s *(1–3)*. These principles include leveling out the alkali concentration, maintaining a high sulfidity (particularly at the beginning of the cook), reducing the dissolved lignin concentration, and cooking at lower temperatures. Recently, further improvements have been made in continuous modified kraft cooking technology to enhance delignification while improving pulp strength and uniformity *(4, 5)*. Despite these significant advances in pulping technology, very little is known about how changes in the kraft pulping process can influence the structure of residual lignin. To address this issue, several researchers have begun to characterize the nature of residual lignin in kraft pulps *(6–12)*. As a preliminary study in this field, we have previously reported that the functional groups of lignin can be influenced by the extent of delignification and the type of pulping process employed *(13)*. In this paper, we examine the fundamental changes in lignin structure that occur when loblolly pine is cooked under simulated conventional and Lo-Solids® kraft pulping conditions. (The Lo-Solids process is a modified continuous kraft pulping process that minimizes dissolved wood solids during bulk and final delignification.)

EXPERIMENTAL PROCEDURES

Kraft pulping

A single mature loblolly pine tree grown in the southeastern United States was employed for all pulping results reported in this study. The tree was debarked, chipped, and carefully screened (average chip thickness, 2–8 mm). The kraft pulping experiments were performed at Ahlstrom Machinery in Glens Falls, NY. Established procedures *(4, 5)* were used to simulate conventional kraft (CK) and Lo-Solids (LS) kraft pulping processes. Pulp properties and process conditions are summarized in **Table I**.

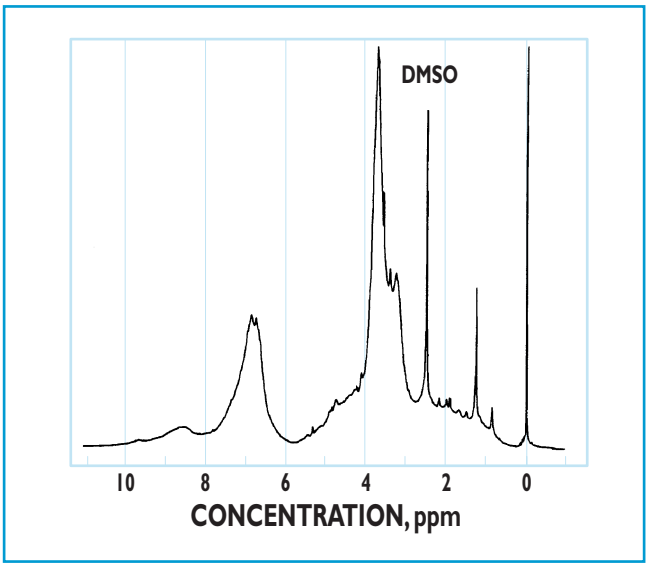
Residual lignin isolation and characterization

Residual lignin was isolated from the various pulps by employing an aqueous acidic dioxane solution following procedures described in the literature *(9)*. This procedure afforded, on average, 55% yield of residual lignin. Lignin samples were then analyzed by quantitative ^{1}H NMR (proton nuclear magnetic resonance) following the procedure described by Lundquist *(14)*. Lignin samples were dissolved in anhydrous DMSO-D_6 (dimethyl sulfoxide). Pentafluorobenzaldehyde (or sodium-3-trimethylsilyl propionate-2,2,3,3-D_4) was added as an internal standard, and all NMR analyses were accomplished using a Bruker 400-MHZ DMX spectrometer employing a $\pi/2$ pulse, 25-s delay, 12,000-Hz sweep width, and 240 transients.

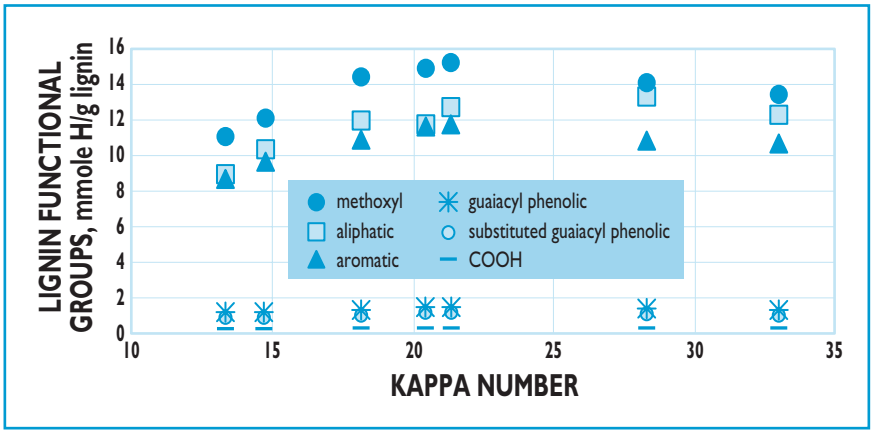
The lignin extraction procedure with acidic dioxane has been used by several researchers to isolate lignin from pulp. Although these isolation conditions can modify the structure of native lignin *(15)*, several studies have shown that the lignin isolated from a kraft pulp using an acidic dioxane solution is representative of the lignin in the pulp *(13, 16)*.

Pulp	Kappa no.	Vis-cosity, mPa	Max. temp., °C	*H*-factor	EA consumed, % NaOH (on wood)
CONVENTIONAL KRAFT PULPS					
CK33	33.0	32.6	168	1201	14.8
CK28	28.3	24.8	170	1213	14.0
CK21	21.3	22.6	170	1999	15.4
CK20	20.4	22.4	170	2311	14.9
CK18	18.1	18.5	171	2987	15.3
CK15	14.7	13.3	171	3496	16.7
CK13	13.3	13.1	171	3499	16.4
LO-SOLIDS KRAFT PULPS					
LS29	29.3	43.4	160	2003	14.1
LS26	26.1	36.1	163	2442	15.2
LS19	19.1	25.5	166	3362	15.0
LS16	16.0	19.2	170	4489	16.6
LS11	11.0	12.1	170	4474	17.8

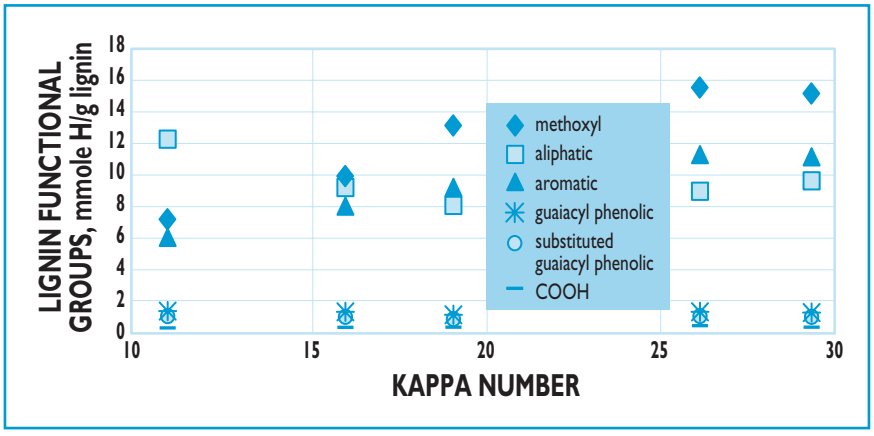
I. Pulping conditions and pulp properties for the conventional and LS kraft pulps



1. Quantitative ^{1}H-NMR spectrum of lignin samples



2. Content of different structural moieties in lignin samples isolated from CK pulps as determined by ^{1}H NMR



3. Content of different structural moieties in lignin samples isolated from LS pulps as determined by ^{1}H NMR

RESULTS AND DISCUSSION

To minimize experimental variation from different wood sources, a single wood sample was used for all of the studies described in this paper. To fully explore the dependency of lignin structure on the type of kraft pulping process, we elected to prepare a series of CK and LS kraft pulps covering the kappa number range of 33.0–11.0. Table I provides a brief description of the physical properties of these kraft pulps.

The data in Table I clearly demonstrate that the LS process can produce lower-lignin pulps while retaining higher viscosity. Our interest in the CK and LS pulps was twofold. First, we wanted to find out if pulps with different lignin contents would have different lignin structures. Second, we were interested in establishing whether differences in pulping technology—such as the differences between conventional and LS pulping methods—would also impact lignin structure. To examine these issues, the residual lignin from kraft pulps CK33–CK13 and LS29–LS11 was isolated and characterized by NMR. Following literature methods, residual lignin was extracted from each of these pulps by employing an acidic dioxane solution. After purification,

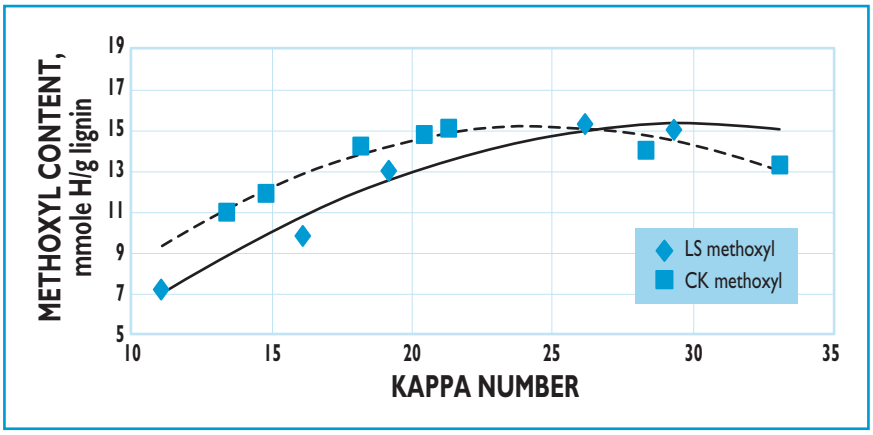
typical yields were in the range of 45–65%. The lignin isolated from the kraft pulps was then characterized by employing the quantitative ^{1}H NMR methods developed by Lundquist *(14)*. **Figure 1** provides a representative spectrum of a lignin sample analyzed by ^{1}H NMR.

The analysis of lignin structure by NMR is well described in the literature. NMR analysis provides a facile means for characterizing a variety of functional groups of lignin, including acid groups and methoxy, phenoxy, and aliphatic units. The results of these analyses for the 13 pulps studied in this paper are summarized in **Figs. 2 and 3** for CK and LS pulps, respectively. **Figures 4–7** provide direct comparisons of methoxyl, guaiacyl phenolic, substituted guaiacyl phenolic, and aromatic units, respectively, for CK and LS pulps.

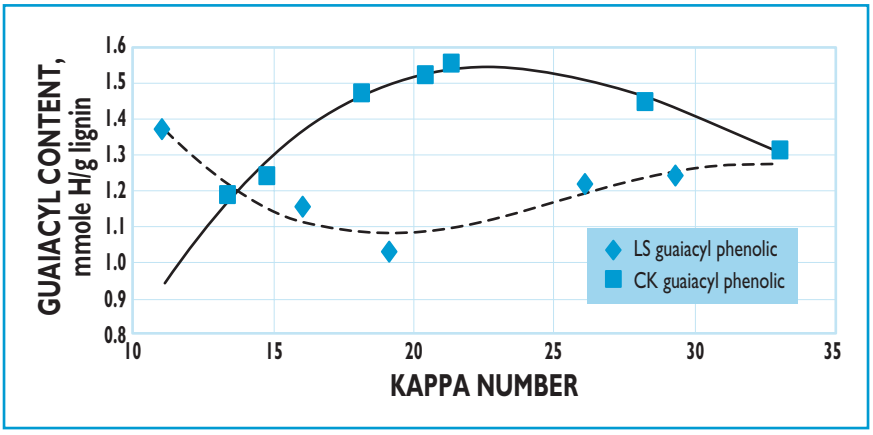
Figures 2 and 3 show the content of methoxy and aromatic hydrogens in residual lignin isolated from the conventional (CK) and modified (LS) pulps, respectively. This analysis indicates that the methoxy content of residual lignin decreases as the extent of delignification increases. Furthermore, the aromatic proton content of residual lignin samples is also decreasing, suggesting that the lignin remaining in the pulp is more condensed as delignification proceeds.

For the CK pulps, the aliphatic and guaiacyl units also decrease as delignification proceeds. In contrast, for the LS pulps, the aliphatic and guaiacyl units appear to be at a minimum value for the kappa no. 19 pulp. The lignin acid groups for both the CK and LS pulps remain approximately constant.

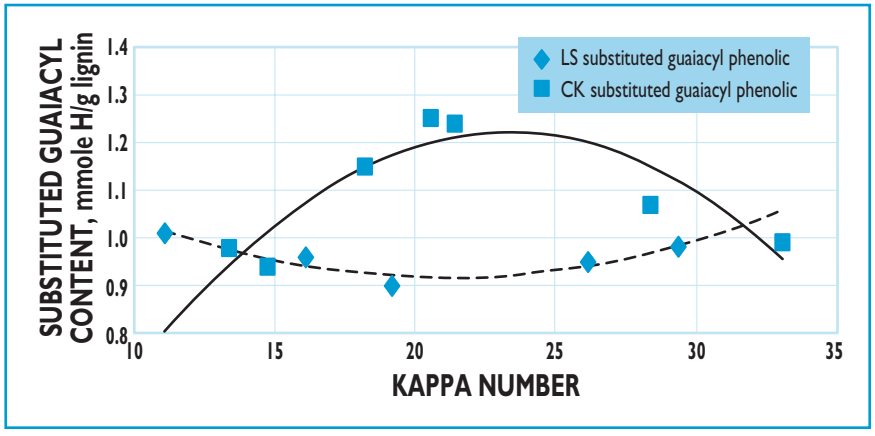
A comparison of the structural groups of residual lignins from the LS and CK kraft pulps provides additional information on the nature of kraft pulping and the influence that process modifications can have on the final product.



4. Changes in methoxyl content of residual lignin samples isolated from LS and CK pulps as determined by ^{1}H NMR

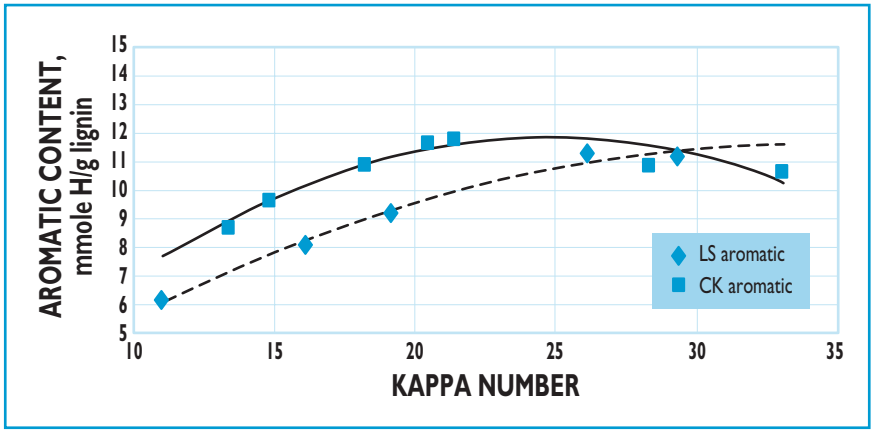


5. Changes in guaiacyl content of residual lignin samples isolated from LS and CK pulps as determined by ^{1}H NMR



6. Changes in substituted guaiacyl content of residual lignin samples isolated from LS and CK pulps as determined by ^{1}H NMR

As shown in Fig. 4, the content of methoxy groups was found to be lower in the modified kraft than in the conventional kraft pulps. The guaiacyl and 5-substituted guaiacyl units of the conventional and modified kraft pulps exhibited a more complex pattern, as seen in Figs. 5



7. Changes in aromatic proton content of residual lignin samples isolated from LS and CK pulps as determined by ^1H NMR

and 6, respectively. At high kappa numbers (ca. kappa no. 30), both the conventional and modified kraft pulps have comparable levels of phenoxy groups. As delignification is extended, the LS pulps exhibit a decrease in free phenols, whereas the conventional pulps show an increase. Finally, at low kappa numbers (<15), the LS pulps appear to have higher contents of free phenols. We have previously noted *(13)* a comparable pattern of residual lignin when comparing a conventional kraft pulp with an EMCC (extended modified continuous cooking) pulp. These differences in lignin structure were attributed to differing amounts of β-O-aryl ethers present in the pulp as delignification proceeds, the result of differences in the two pulping methods.

Figure 7 shows that there is a decrease in the aromatic proton character in residual lignin as delignification proceeds from kappa no. ≈30 to kappa no. 11. Furthermore, as previously noted, the LS pulps appear to have lower amounts of aromatic protons than the conventional pulps, suggesting that they are further substituted. These results again mirror our previous results with EMCC pulps *(13)*.

CONCLUSIONS

This paper provides further evidence that the nature of the residual lignin in kraft pulps is influenced by the extent of delignification. Furthermore, we have noted that kraft pulping process parameters also influence the nature of residual lignin.

The results presented here were all obtained using a single wood source, thus eliminating variations in lignin structure arising from the use of commercial samples. Our results continue to suggest that the kraft pulping process has a tremendous influence on the nature of residual lignin. With further study, we hope to gain a deeper understanding of the relationship between pulping parameters and the nature of the residual lignin. With greater knowledge, we anticipate the possibility of designing kraft pulp processes to optimize subsequent bleaching operations while reducing their environmental impact. **TJ**

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