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Fundamental Investigations of C1O₂ Delignification

Final Report – 07/10/1996 – 07/09/1999

**T. J. McDonough
A. J. Ragauskas**

May 2001

Work Performed Under Contract No. DE-FC07-96ID13442

**For
U.S. Department of Energy
Assistant Secretary for
Energy Efficiency and Renewable Energy
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**By
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1.1 INTRODUCTION: Over the last decade environmental regulations^{1,2} and renewed consumer activism^{3,4} have substantially impacted many pulp and paper operations. Among the many chemical processes involved in the manufacturing of paper, few processes have drawn as much environmental attention as the bleaching of chemical pulps. Beginning with the detection of polychlorinated dibenzo-p-dioxins and dibenzofurans in kraft bleach plant effluents, the pulp and paper industry has been required to address a series of environmental performance issues.^{5,6} To address these issues the pulp and paper industry has begun to implement a series of process changes including extending the pulping process to yield kraft pulps with low lignin content, improved brownstock washing, use of oxygen delignification technologies, 100% chlorine dioxide substitution, and fortification of extraction stages with oxygen and hydrogen peroxide.^{7,8,9,10} Based upon a variety of performance and environmental considerations, chlorine dioxide remains one of the most attractive bleaching agents for kraft pulp.^{11,12}

Recent research results from the principal investigator's laboratories have shown that although free phenolic structures are important in ClO₂ bleaching chemistry, their content in unbleached kraft pulps cannot simply be related to the observed bleaching response.¹³ Lower kappa number pulps were found to contain a greater content of free phenolic structures, yet bleaching experiments in general show that as the kappa number is decreased there is a slight increase in total available chlorine (TAC) consumption per unit kappa number reduction in the D(EO) sequence. Reactivity studies of ClO₂ with residual lignin suggest that residual lignin in higher kappa number pulp is more reactive towards ClO₂, which is consistent with the observed bleaching response. The goal of the present project was to identify important structural components of kraft pulps that control pulp bleachability and employ this knowledge to develop strategies to improve future bleaching operations.

1.2 PROJECT OBJECTIVES: The overall objective of this project was to develop a fundamental understanding of the mechanisms of chlorine dioxide delignification of low kappa kraft pulps and identify new methods of improving the efficiency and effectiveness of this bleaching agent. The approach adopted was to investigate the fundamental structural components of lignin that contribute to delignification reactions with chlorine dioxide. These results were then used to examine new bleaching technologies that will permit enhanced delignification while simultaneously reducing the generation of chlorinated organic compounds.

1.3 RESEARCH JUSTIFICATION: Efficient delignification during ECF bleaching is believed to be significantly influenced by the reactivity of residual lignin towards chlorine dioxide. The structure of residual lignin is believed to play a key role in this reactivity, particularly the content of free phenolic groups, which have already been shown to have an effect on ClO_2 .

Studies by Froass, et al.¹³ began to examine the fundamental chemical basis for these relationships. In this preliminary investigation, we studied the ClO_2 delignification of five pulps. These were conventional kraft (CK) pulps having unbleached kappa numbers of 28.0 and 18.5 and simulated EMCCTM pulps having kappa numbers of 29.1, 18.5, and 14.5 (see Table 1.1).

Table 1.1. Bleachability parameters for conventional and EMCCTM pulps.

Parameter	Conventional		EMCC TM		
Unbleached Kappa No.	28	18.5	29.1	18.5	14.5
Kappa No. after D ^a	11.0	9.6	11.0	7.5	6.0
TAC/ Kappa	0.30	0.38	0.30	0.31	0.33
Kappa No. after (EO) ^b	3.8	3.8	3.3	3.0	2.3
TAC/ Kappa after (EO)	0.21	0.23	0.21	0.22	0.23
Brightness after (EO)	47.4	49.9	49.8	50.2	53.5

^aD₀ was at 45 °C, 10% consistency, 30 min., kappa factor of 0.187; ^b(EO): 70°C, 10% consistency, 60 min., NaOH charge of 50% of TAC charge, O₂ press. was initially 60 psi and decreased by 12 psi/5 min.

The results of this study indicated that decreasing the unbleached kappa number causes an increase in ClO_2 consumption per unit of kappa number reduction in both the D and D(EO) stages. At a given unbleached kappa no., EMCCTM is more readily delignified in the D(EO) stages than CK, resulting in a lower overall chemical requirement for EMCCTM.

The significance of these results in the present context is that they established the existence of differences in ClO_2 bleachability between pulps, in particular between pulps of similar kappa numbers, and provided an incentive to implement methods for residual lignin structural analysis. These are the same methods that are most appropriate for examining the mechanistic pathways that determine the course of ClO_2 delignification.

Residual lignin was isolated from each of the kraft pulps described in Table 1.1 and analyzed by NMR spectroscopy. ^{13}C NMR analysis indicated that as the kappa number is decreased for both conventional and EMCCTM pulps there is a decrease in etherified linkages in the residual lignin structure, most of which can probably be assigned to aryl ether linkages. The results also show that more substituted aromatic carbons are found in the residual lignins as the kappa number is decreased. This result was substantiated by derivatizing the residual lignin samples isolated from the conventional and EMCCTM kraft pulps with a selective phosphorylation reagent and examining the derivatized material by means of ^{31}P NMR. The ^{31}P -spectra indicated that concentration of condensed phenolic units in the residual lignin increased as kappa number decreased. The ^{31}P NMR data also suggested that the phenolic content of the EMCCTM residual lignins continued to increase with decreasing kappa number while for the CK residual lignins the phenolic content leveled off after kappa number of 18 was reached. At low kappa numbers the EMCCTM residual lignin contains more phenolic structures (both condensed and uncondensed) than the CK residual lignin. Although the increased phenolic content of the former correlates with its easier bleachability, the relationship is not a simple one, since the lower kappa number pulps, which were more difficult to bleach, had a higher content of phenolic structures. Structural analysis revealed that the higher kappa number pulps had a higher content of aryl ether linkages and a lower content of condensed lignin structures. This suggests that such a lignin may be more reactive towards ClO_2 . In summary, work prior to this project indicated that the reactivity of ClO_2 towards conventional and EMCCTM kraft pulps may be related to residual lignin structure. A goal of the current project was to examine this relationship on a broader set of pulps and to determine if these relationships are global to SW and HW kraft pulps.

1.4 SUMMARY OF PREVIOUS WORK: In summary, the bleachability of conventional and EMCC[®] kraft pulps in a D(EO) sequence was related to the residual lignin structure and its reactivity towards ClO_2 . During the delignification stages (D and D(EO)) the ClO_2 consumption per unit kappa number reduction increased slightly as the kappa numbers of both the CK and EMCC[®] pulps decreased. This result suggests that the higher kappa number pulps contain residual lignin that is more reactive towards the ClO_2 . Analysis of the residual lignin structure suggested that the content of free phenolic structures could not be simply related to this result, since the lower kappa number pulps had a higher content of phenolic structures. The structural analysis revealed that the higher kappa number pulps had a higher content of aryl ether linkages and a lower content of condensed lignin structures, possibly including condensed nonphenolic structures. The higher content of aryl ether linkages and lower amounts of condensed structure suggests that such a lignin may be more reactive towards ClO_2 . Experiments in which the isolated residual lignins were reacted with ClO_2 showed that the higher kappa number residual lignins, in spite of their lower phenolic content, had a larger increase in carboxylic acid formation, suggesting a more reactive lignin. The bleachability experiments also showed that EMCC[®] pulps were more readily delignified in the D(EO) stages than the CK pulps, resulting in a slightly lower overall chemical requirement for EMCC[®]. The residual lignin reactivity experiments suggested that the EMCC[®] pulp residual lignin was slightly more reactive than the CK residual lignin, which is consistent with the bleachability result.

1.5 PROJECT OBJECTIVES: The goals of this program were to establish the important structures in pulp that influence ClO₂ pulp bleachability as it applies to D(EO) pulp delignification and to employ the results to improve the relevant pulping and bleaching technologies. The work plan encompassed the following tasks:

- Prepare wood chips and perform kraft cooks
- Isolate and characterize lignin from kraft pulps
- Bleach kraft pulps by D₀, rapid D₀, & vapor-phase ClO₂
- Characterize bleached pulps and effluents
- Perform EO extractions of ClO₂ bleached pulp
- Isolate and characterize residual lignin from D₀, rapid D₀ and vapor phase ClO₂ pulps
- Analyze data and develop hypothesis for improved ClO₂ delignification
- Isolate and characterize residual lignin from EO pulps
- Characterize concentration of hexenuronic acids in kraft pulps
- Develop optimal acid treatment conditions to hydrolyze hexenuronic acid groups
- ClO₂ bleach hexenuronic acid free pulps.

1.6 REFERENCES:

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¹¹ SUN, Y.P., "Kraft bleach plant ECF conversion: comparison of sequences involving enzymes, chlorine dioxide, oxygen and hydrogen peroxide", *Appita J.*, **52**(1), 45 (1999).

¹² "U.S. bleached pulp mills going ECF", *Pulp Paper Project Report*, **19**(8), 1 (1999).

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2.0 PARAMETERS THAT INFLUENCE THE ClO₂ BLEACHABILITY OF SW KRAFT PULPS

2.1 INTRODUCTION:

As reviewed in the introduction section, the bleachability of kraft pulps appears to be influenced by a variety of factors including the structure of residual lignin. Lignin is a complex polymer in wood that contributes approximately 25-30% of the mass of wood. During pulping this polymer is selectively degraded; near the end of a kraft cook the selectivity of alkaline degradation between pulp carbohydrates and lignin decreases dramatically, and the cook must be halted to prevent loss of carbohydrates. At the completion of the kraft pulping process for bleachable grades, typically 3-5% lignin remains. For SW kraft pulps residual lignin consists of several lignin functional groups derived from guaiacyl units; Table 2.1 summarizes some of the predominant functional groups known to be present.

Table 2.1. Description of predominant functional groups present in SW kraft residual lignin.

Lignin Functional Unit	Structure
Noncondensed C5 phenoxy groups	
Noncondensed C5 phenoxy groups	
Methoxy groups	Ph-Ome
β-O-aryl ether	
Enol Ether	
Carboxyl groups	RCO ₂ H

Advances in pulping technology have continued unabated for the last decade in response to environmental and market pressures. The ability to lower the content of lignin in kraft pulps prior to bleaching 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.^{1,2,3} 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 employing lower cooking 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 residual lignin structure. To address this issue, several researchers have begun to characterize the nature of residual lignin in kraft pulps.^{6,7,8,9,10,11} 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 type of pulping process employed.¹² In this study, we examined the fundamental changes in lignin structure that occur when loblolly pine is cooked under conventional and simulated Lo-Solids[®] kraft pulping conditions. Lo-Solids[®] is representative of the next generation of extended modified continuous cooking technologies and can be readily retrofitted to EMCC[™] kraft digesters. A description of the SW furnishes employed and cooking parameters used is presented in the experimental section (2.4) of this report.

Prior research studies by Froass et al.¹² certainly suggested that the extent of delignification and kraft cooking technology could influence bleachability. Although these results were supported by literature results, it was unanticipated that pulp bleachability of a D(EO) treatment would not be directly related to the amounts of phenoxy groups present in the lignin. This result was significant since most bleaching textbooks¹³ assert that the ClO₂ bleaching chemistry occurs primarily via phenoxy groups and that this unit in lignin controls pulp bleachability. To define the influence of kraft pulping on ClO₂ bleaching of SW kraft pulps, a series of conventional and extended modified continuous kraft pulps were prepared, analyzed, and bleached via D(EO). The changes in lignin structure after pulping and bleaching were evaluated to determine if lignin structure contributed to pulp bleachability.

2.2 RESULTS AND DISCUSSION:

2.21 Cooking Results

To minimize experimental variations due to the wood source, a single wood sample was used for all the studies described in this paper. To fully explore the dependency of lignin structure on kraft pulping process type, we elected to prepare a series of conventional (CK) and Lo-Solids[®] (LS) kraft pulps covering a kappa number range of 39.3-11.0. Table 2.2 provides a brief description of the physical properties of these kraft pulps. These data

clearly demonstrate that extended modified continuous cooking procedures can attain lower lignin content pulps while retaining higher viscosity values.

Table 2.2. Physical properties and sample abbreviations for SW kraft pulps.

Conventional Kraft Pulps			Lo-Solids [®] Kraft Pulps		
Sample #	Kappa #	Viscosity mPa	Sample #	Kappa #	Viscosity mPa
CK33	33.0	32.6	LS29	29.3	43.4
CK28	28.3	24.8	LS26	26.1	36.1
CK21	21.3	22.6	LS19	19.1	25.5
CK20	20.4	22.4	LS17	17.1	21.1
CK18	18.1	18.5	LS16	16.0	19.2
CK15	14.7	13.3	LS11	11.0	12.1
CK13	13.3	13.1			

2.12 Kraft Pulps - Analyzed by ¹H NMR

Our interest in these pulps was twofold. First, we were interested in determining if pulps of differing lignin contents and kraft cooking technologies would have differing types of lignin structures. Second, we wished to determine if the lignin structures present in the LK and CK pulps would also impact pulp bleachability. To examine these issues, the residual lignin from kraft pulps CK33-13 and LS29-11 were isolated and characterized by NMR. Following literature methods, residual lignin was extracted from each of these pulps 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 quantitative ¹H NMR methods that have been developed by Lundquist.²⁶ Figure 2.1 provides a representative spectrum of a lignin sample analyzed by proton NMR.

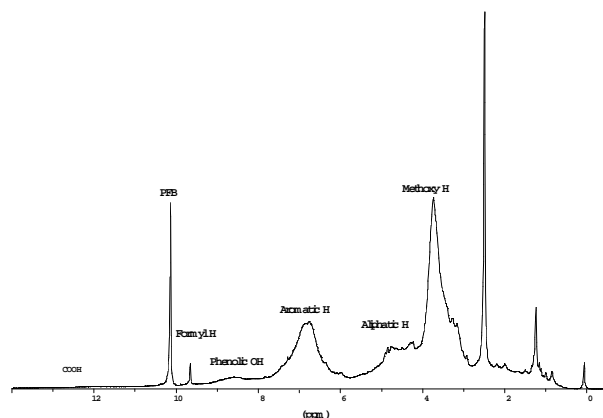


Figure 2.1. Quantitative ¹H NMR spectrum of lignin samples.

The analysis of lignin structure by NMR is well described in the literature and provides a facile means for characterizing a variety of functional groups of lignin, including acid groups, methoxyl, phenoxy, and aliphatic units. The results of these analyses for the 13 pulps studied in this paper are summarized in Figures 2.2-2.5.

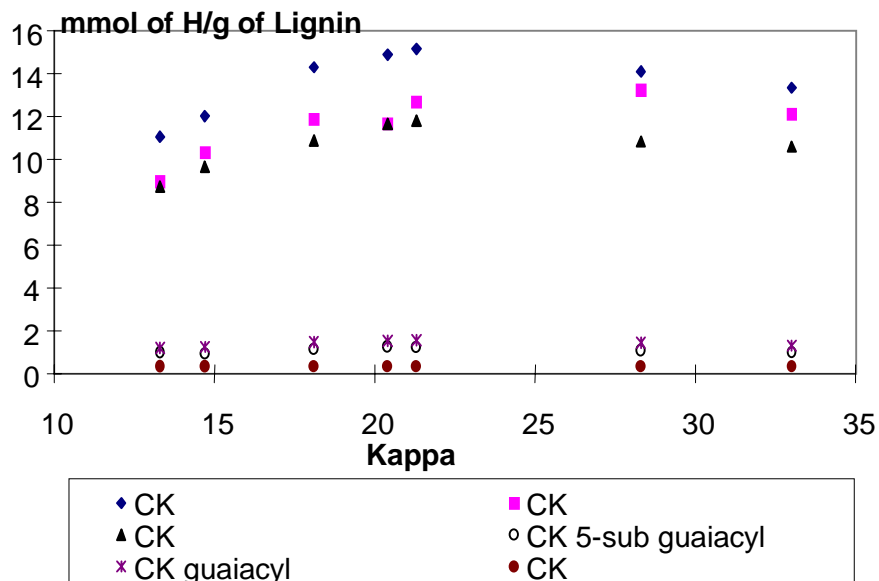


Figure 2.2. Content of different structural moieties in lignin samples isolated from CK pulps as determined by ^1H NMR.

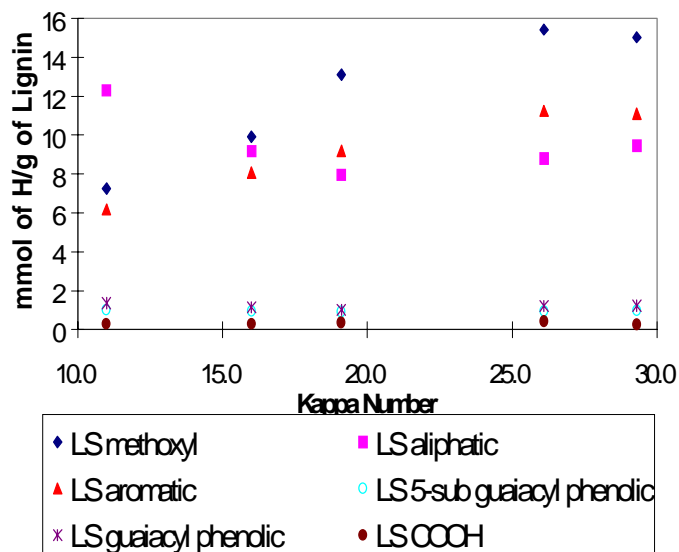


Figure 2.3. Content of different structural moieties in lignin samples isolated from LS pulps as determined by ^1H NMR.

It is clear from these studies that for both conventional (CK) and modified (LS) kraft pulps the content of methoxyl and aromatic hydrogens in residual lignin decreases as the extent of delignification is increased. 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 LS17 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.

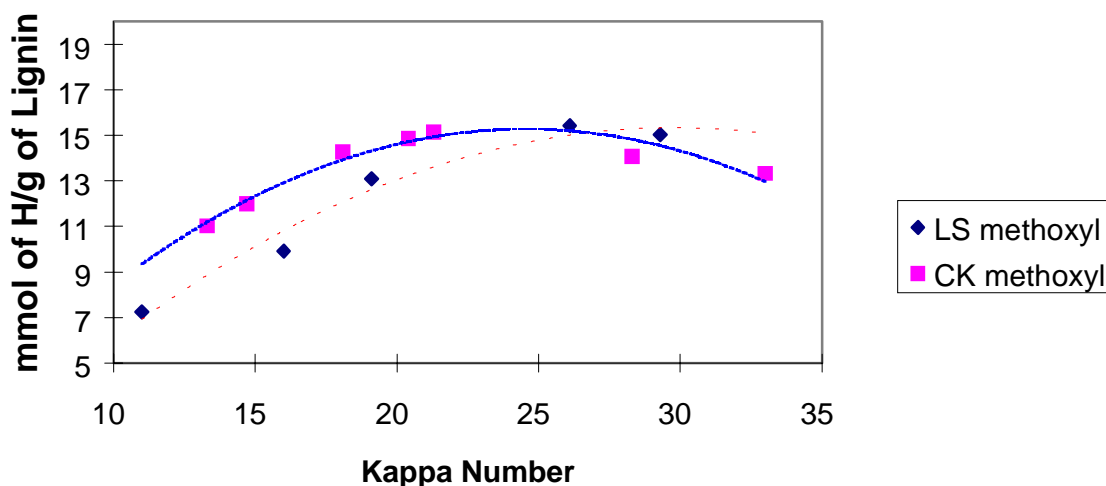


Figure 2.4. Changes in methoxyl content of residual lignin samples isolated from LS and CK pulps as determined by ^1H NMR.

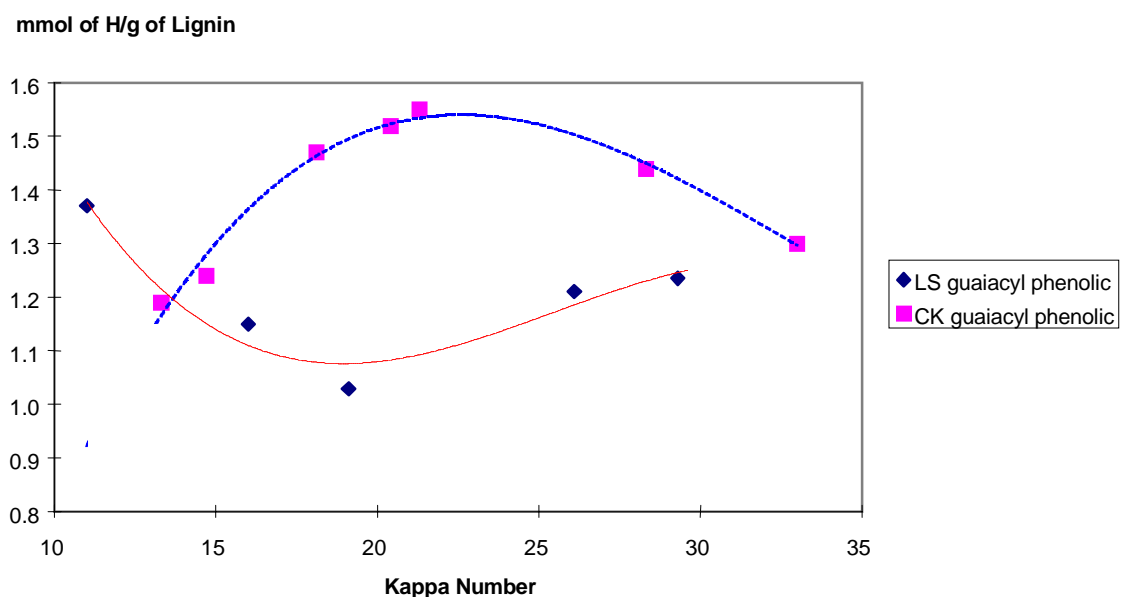


Figure 2.5. Changes in guaiacyl content of residual lignin samples isolated from LS and CK pulps as determined by ^1H NMR.

As shown in Figure 2.4, the content of methoxyl 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 (see Fig. 2.5) exhibited a more complex pattern. At high kappa values, both the conventional and modified kraft pulps (ca. 30 kappa number) have comparable levels of phenoxy groups, but as delignification is extended, the LS pulps exhibit a decrease in free phenols whereas the conventional have an increase. Finally, at low kappa levels (<15), the extended modified pulps appear to have higher contents of free phenols. We have previously noted¹² a comparable pattern of residual lignin when comparing a conventional kraft pulp with an EMCC pulp. These differences in lignin structure were attributed to differing amounts of β -O-aryl ethers present in the pulp as delignification proceeds due to the differences in pulping.

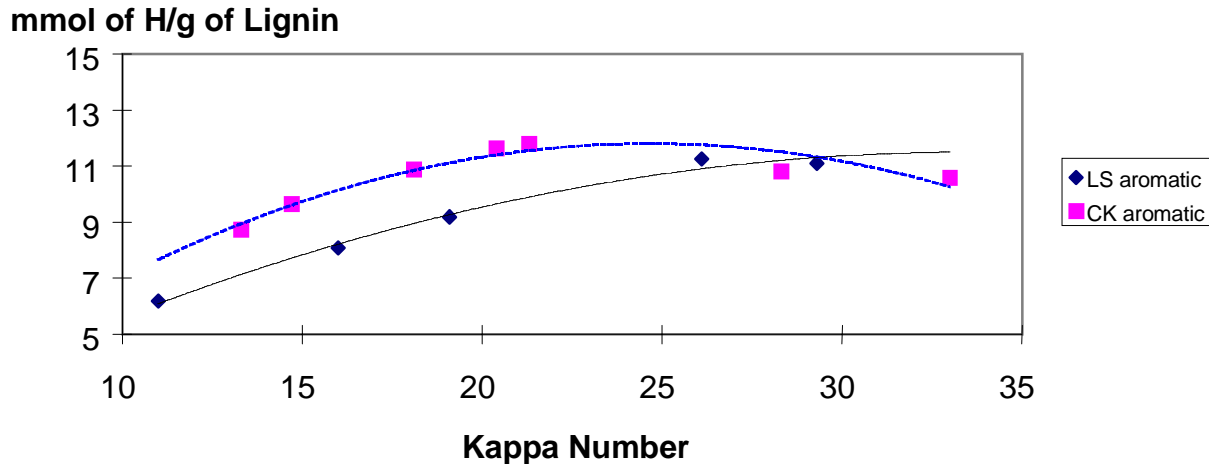


Figure 2.6. Changes in aromatic proton content of residual lignin samples isolated from LS and CK pulps as determined by ^1H NMR.

Figure 2.6 shows that there is a decrease in aromatic proton character in residual lignin as delignification is increased from the kappa ~30 pulps to kappa 11 pulps. Furthermore, as previously noted, the extended modified 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.¹²

2.13 Kraft Pulps - Analyzed by ^{31}P NMR

The characterization of lignin by derivatization with 2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane (see Eq. 1) followed by analysis by ^{31}P NMR allows for facile analysis of the hydroxy groups present in lignin.

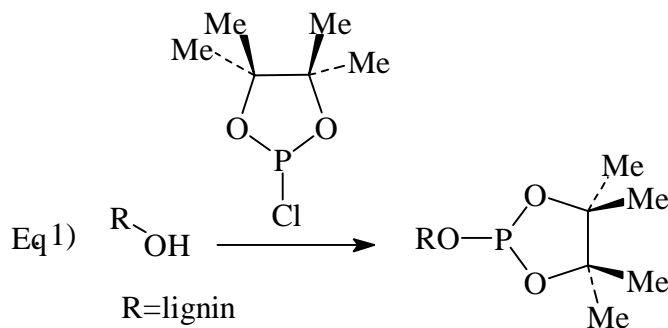


Fig. 2.7 provides typical ^{31}P NMR spectral data acquired from residual lignin. This approach facilitates the measurement of aliphatic, condensed, and noncondensed phenolics and

carboxylic acid groups. Figures 2.8-2.11 summarize the changes in lignin structure between conventional and Lo-Solids[®] kraft softwood pulps at varying levels of lignin content.

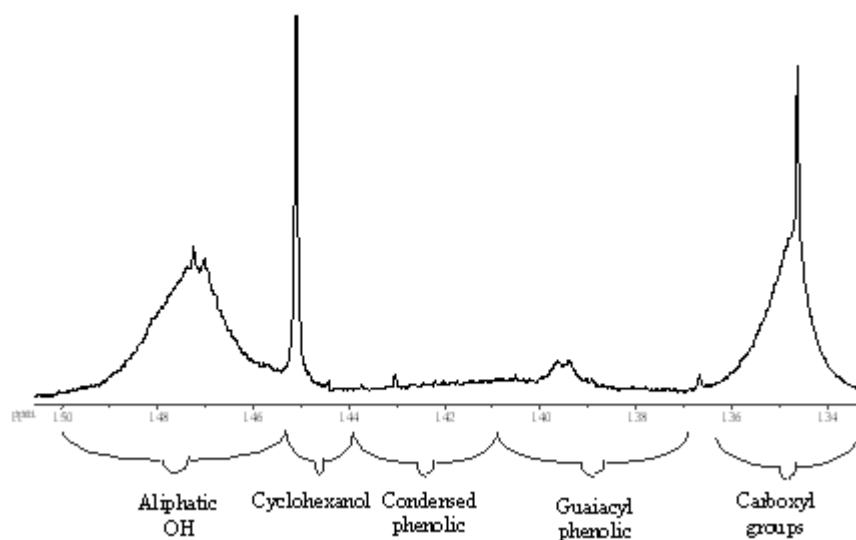


Figure 2.7. ^{31}P NMR spectral data for phosphitylated residual lignin.

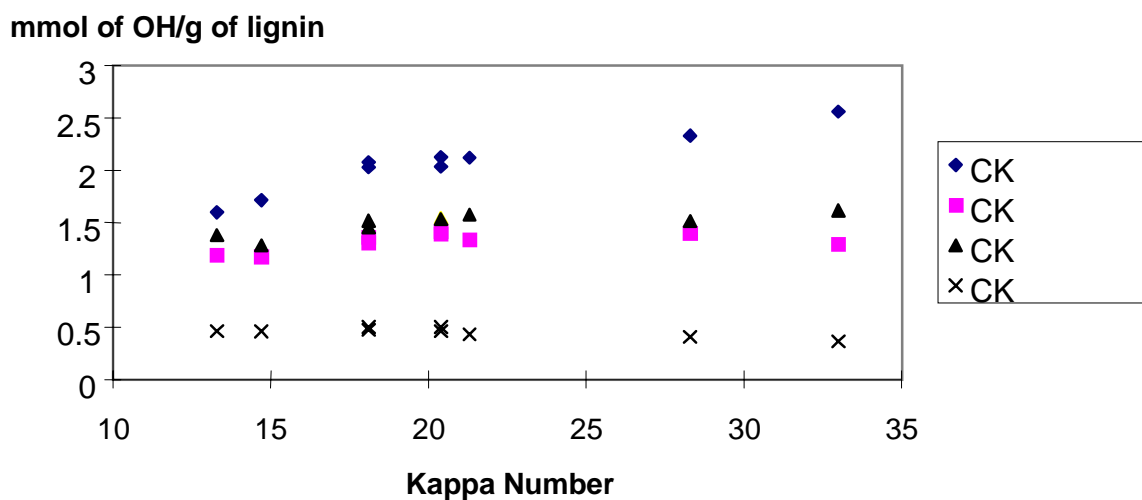


Figure 2.8. Content of aliphatic, guaiacyl, condensed guaiacyl, and carboxylic hydroxy groups in lignin samples isolated from CK pulps as determined by ^{31}P NMR.

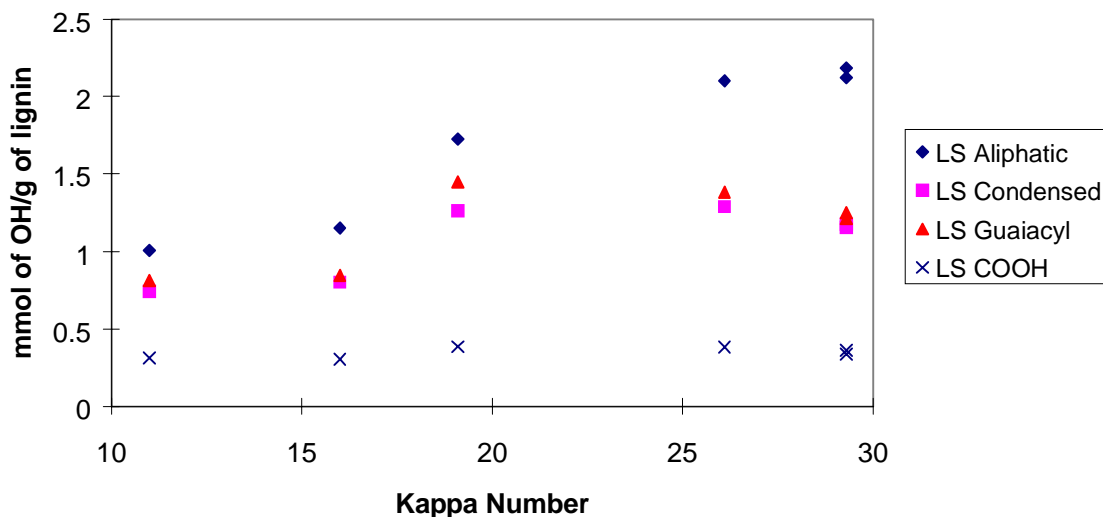


Figure 2.9. Content of aliphatic, guaiacyl, condensed guaiacyl and carboxylic hydroxy groups in lignin samples isolated from LS pulps as determined by ^{31}P NMR.

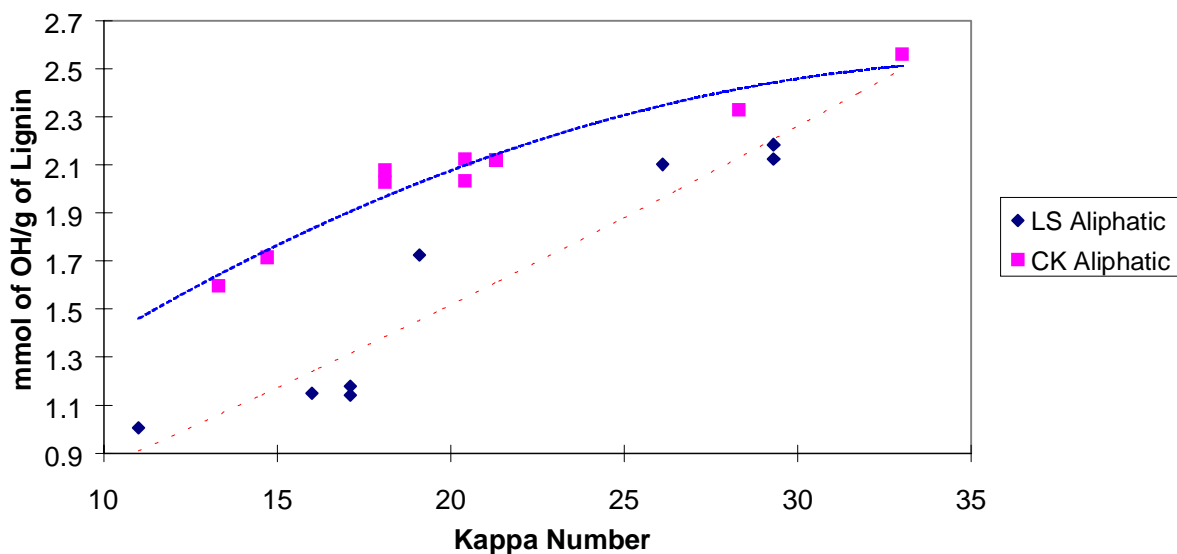
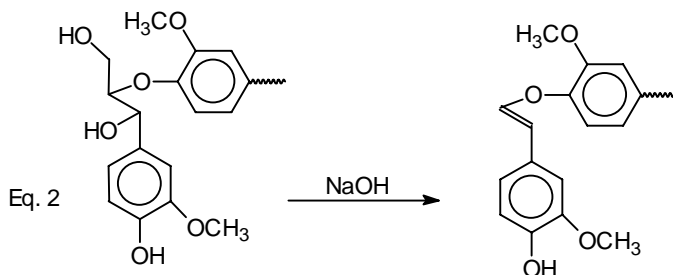


Figure 2.10. Changes in aliphatic hydroxy content of residual lignin samples isolated from LS and CK pulps as determined by ^{31}P NMR.

As shown in Figure 2.10, both conventional and Lo-Solids[®] pulps exhibit a loss in aliphatic signals as the amount of residual lignin is decreased. The principal mechanism for loss of aliphatic hydroxy groups is by loss of formaldehyde (see Eq. 2). Certainly, it is to be expected that this reaction would occur more frequently as delignification proceeds and this is exactly

what is observed in Fig. 2.10. Interestingly, the Lo-Solids[®] pulps exhibit slightly less aliphatic character, suggesting that this chemistry is occurring more frequently in the extended modified kraft cooking process.



The changes in acid groups for the CK and LS residual lignin samples are summarized in Figure 2.11.

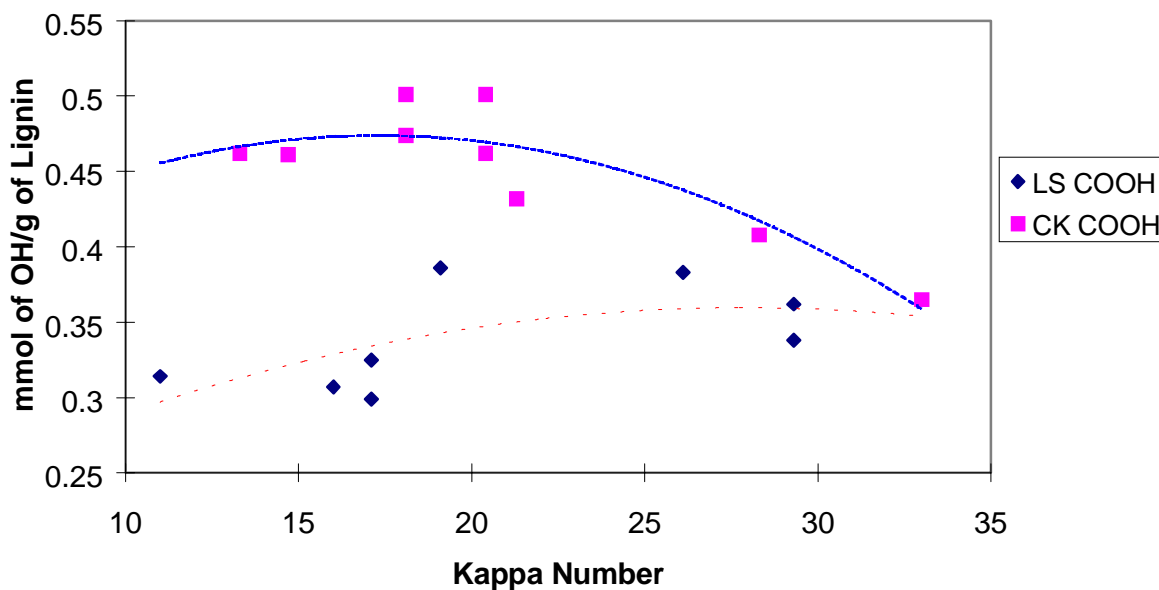


Figure 2.11. Changes in acid group content of residual lignin samples isolated from LS and CK pulps as determined by ³¹P NMR.

As previously reported,¹³ conventional pulps exhibit an increase in acid character as delignification proceeds. To date, we have interpreted the presence of acid groups to be due to an enrichment of carboxylic acid groups in residual lignin and not due to an oxidative process. Based on this assumption, it appears that the Lo-Solids[®] pulping

process does not lead to as significant an accumulation of acid groups as observed in conventional pulping.

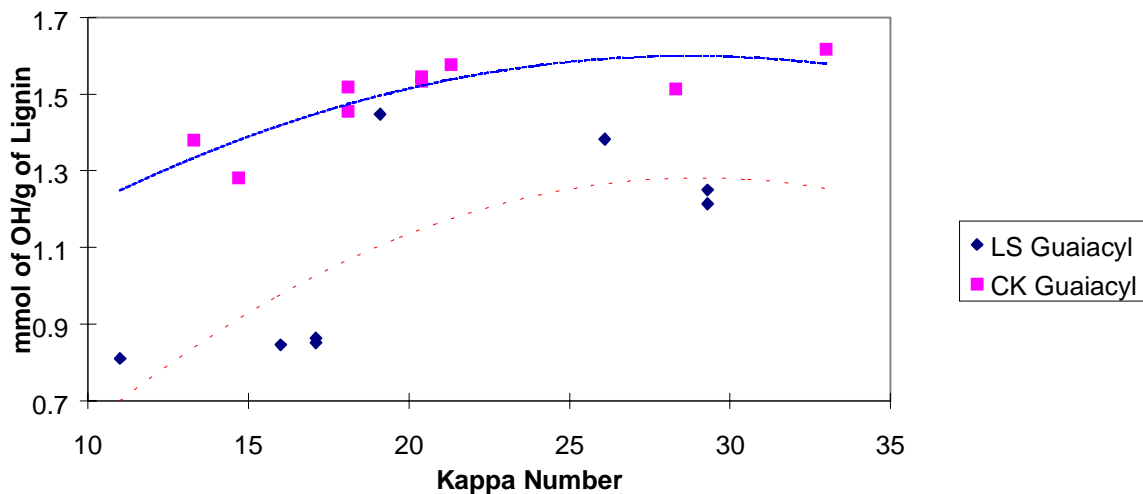


Figure 2.12. Changes in guaiacyl phenoxy content of residual lignin samples isolated from LS and CK pulps as determined by ^{31}P NMR.

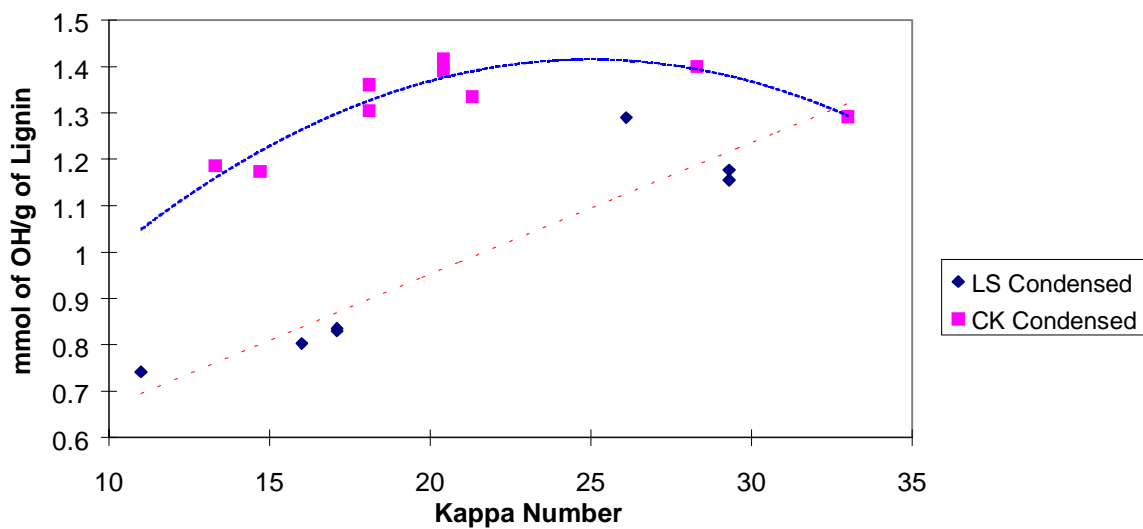


Figure 2.13. Changes in condensed guaiacyl phenoxy content of residual lignin samples isolated from LS and CK pulps as determined by ^{31}P NMR.

Figures 2.12 and 2.13 summarize the analysis of phenoxy groups present in the residual lignin. Although the results do not exactly mirror the analysis by ^1H NMR and we did not expect the results to be identical, it is clear that the trends in each analysis are comparable. The most important observation to come out of this analysis is that the Lo-Solids[®] pulps exhibit a lower amount of free phenolics (both condensed and noncondensed) than conventional pulps. This result is very significant given the accepted mechanisms by which chlorine dioxide degrades lignin via free phenolics.

Based on the ^{31}P and ^1H NMR studies it appears that the Lo-Solids[®] pulping process yields lignin with less condensed phenolic lignin structure but is overall more condensed than is typically present in a conventional kraft pulp of comparable lignin content. This result is very significant since the process changes implemented in Lo-Solids[®] kraft pulping were targeted, in part, to minimize condensed lignin and yet we have noted increases in this type of lignin. The results of these studies have been discussed with Ahlstrom Machinery Corp. and other industry representatives, and they are evaluating the practical implications of these studies for improved digester design.

2.2 D(EO) SW KRAFT PULP BLEACHABILITY STUDIES:

From a mill perspective, it is well known that the bleachability of kraft pulps can vary substantially. Pulp bleachability can be influenced by a wide array of factors from process variables such as the efficiency of pulp washing¹⁴ to fundamental chemistry issues, including the structure of residual lignin¹⁵ and carbohydrates in the fiber.¹⁶

Teder and Sjoström¹⁷ have demonstrated that alkaline sulfite pulping yields pulps with significantly improved bleachability properties with respect to kraft pulps. Classical studies by Germgard¹⁸ have shown that post-oxygen delignified kraft pulps are less bleachable than pre- O_2 kraft pulps with chlorine dioxide. Recently, studies by Buchert et al.^{19, 20} have advanced our knowledge on how carbohydrates, specifically hexenuronic acids, can impact pulp bleachability.

It is also well known that the structure of residual lignin can influence pulp bleachability, especially with chlorine dioxide. This dependency is due in part to the reactivity of chlorine dioxide with phenoxy groups. Kumar et al.²¹ studied differences in pulp bleachability between RDH and conventional kraft pulps and suggested a correlation between phenoxy content of the residual lignin and bleachability. Gellerstedt and Al-Dajani²² have reported that the bleachability of softwood kraft pulps with chlorine dioxide or hydrogen peroxide was influenced by kraft cooking conditions. These differences in bleachability were attributed to differences in residual lignin content, lignin-carbohydrate complexes, and condensed carbohydrates. Froass et al.¹² observed that for softwood kraft pulps, the kappa number of the pulp and the pulping process employed influenced bleachability. The total available chlorine (TAC) consumed per unit kappa number reduction in the D(EO) sequence was found to decrease as the kappa number decreased despite the fact that the lower kappa pulps were found to have higher amounts of phenoxy

groups. A closer examination of the residual lignin structure prior to bleaching suggested that the amounts of condensed phenolics increased as delignification was extended and it was hypothesized that these units were detrimentally influencing pulp bleachability.

In this project, we further examine the relationship between pulp bleachability and chlorine dioxide delignification for a series of conventional pulps and pulps from Lo-Solids[®] kraft cooks. The bleachability properties of these pulps were examined after D₀ and D(EO). The D₀ stage was performed using a kappa factor of 0.05 and 0.20 at 10% consistency with high shear mixing and a ClO₂ retention time of 1 min. Previous studies by Schwantes and McDonough²³ have shown that substantial delignification of kraft pulps can be accomplished with reaction times significantly less than what is employed in a typical D₀ stage. The resulting pulps were then alkaline extracted in an oxygen-reinforced stage. Pulp bleachability, measured as TAC/ Δ (kappa number), was determined after the D₀ and (EO) stage. Residual lignin was isolated before and after each stage and changes in lignin functional groups were determined employing modern NMR methods.

2.30 RESULTS AND DISCUSSION:

Bleachability of Kraft Pulps

Recent studies at IPST have shown that the rapid kinetics of chlorine dioxide delignification of kraft pulps can be utilized for bleaching provided that good uniform mixing can be accomplished. Preliminary studies reported by Schwantes²³ demonstrated that most of the delignification of a D₀ stage is accomplished within the first 1-2 minutes of bleaching, provided that the bleaching chemical is uniformly distributed throughout the bleaching reactor. This type of very short bleaching stage, referred to as Rapid D₀, reduces AOX formation and offers significant savings in bleach plant capital equipment. This report examines the results of applying this process in the delignification of a series of softwood kraft pulps manufactured under conventional conditions and conditions that correspond to Lo-Solids[®] cooking. This was of interest because the short retention time is expected to yield bleached pulps having lignins whose structural features are unaffected by secondary reactions.

The results summarized in Table 2.3 indicate that the conventional pulps exhibited only slightly improved bleachability at higher lignin contents when the ClO₂ retention time is kept short. The LS pulps were equally bleachable at high and low lignin contents under these conditions. These results differ somewhat from those of earlier studies by our group,¹² indicating that the decreased bleachability of low-kappa pulps at normal D₀ retention times is related to inhibition of reactions that occur after the initial phase.

Table 2.3. Bleachability of CK and LS pulps towards Rapid D₀ and EO.

Pulp	k.f.	TAC	Δ Kappa	TAC/ Δ Kappa
CK-32.4	0.05	1.62	D - 5.9 EO-13.6	0.274 0.119
CK-32.4	0.20	6.48	D - 15.3 EO-24.3	0.423 0.267
CK-21.3	0.20	4.26	D - 9.2 EO-15.3	0.463 0.278
CK-14.7	0.20	2.94	D - 6.5 EO-10.6	0.452 0.277
LS-29.3	0.05	1.46	D - 5.1 EO-13.0	0.286 0.112
LS-29.3	0.20	5.86	D - 13.7 EO-22.2	0.428 0.264
LS-19.1	0.20	3.82	D - 8.8 EO-14.6	0.434 0.262
LS-15.6	0.20	3.12	D - 6.9 EO-11.8	0.452 0.264

The LS pulps were modestly easier to delignify than the conventional pulps, requiring a ClO₂ charge that was an average of 4% lower than in the case of CK for a given kappa number reduction measured after the (EO) stage. The TAC/ Δ kappa values were larger than normally observed at normal retention times in the D₀ stage because no credit was taken for the unutilized residual remaining after only one minute. In order to limit the D₀ reaction time to exactly one minute, it was necessary to stop the reaction by injection of sulfite, which destroyed the residual and precluded its measurement. It is for this reason that, in practical applications, low kappa factors are recommended for Rapid D₀.

2.31 Residual Lignin Analysis

The difference in bleachability between the CK and LS pulps suggests that it may be possible to tailor pulp properties to a bleaching chemical. However, before such a strategy can be rationally designed, the fundamental principles involved in bleachability must be determined. Several researchers have begun elucidating how process changes in the kraft pulping can moderate the structure of residual lignin. Studies by Hortling et al.²⁴ have compared the differences in residual lignin that occur between Superbatch and conventional kraft pulps. Gellerstedt¹¹ has reported differences in bleachability of Scandinavian softwood kraft pulps dependent upon how they are cooked. Jiang and Argyropoulos²⁵ have found that residual lignin from modified continuous kraft pulping procedures has lower amounts of condensed phenolic units and higher amounts of carboxylic acids as compared to lignin isolated from conventional kraft pulps. Froass et

al. have shown that pulps prepared under simulated conventional and EMCC[®] conditions exhibited differences in residual lignin structure and bleachability.¹² It was hypothesized in these latter studies that condensed phenoxy groups and β -O-aryl ether groups may influence chlorine dioxide bleachability of kraft pulps. This report further examined the relationship between pulp bleachability and residual lignin structure.

In section, 2.12 and 2.13 we examined the structure of the residual lignin present in the CK and LS pulps and demonstrated clear differences in residual lignin structure. The results of these studies suggested the CK and LS pulps had comparable lignin functional groups at kappa numbers of approximately 30. As delignification was extended, the CK pulps were found to have higher amounts of phenolics and methoxyl groups than the LS pulps. To further explore the relationship between bleachability and residual lignin structure, we isolated residual lignin structure after the Rapid D₀ and (EO) stages employed in the current study. These samples were then analyzed employing ¹H NMR according to the method of Li and Lundquist.²⁶ This procedure provides a convenient method of determining the concentration of phenolic units, carboxylic acids, and methoxyl groups in residual lignin. The changes in methoxyl content for the unbleached and bleached pulps is summarized in Figure 2.14

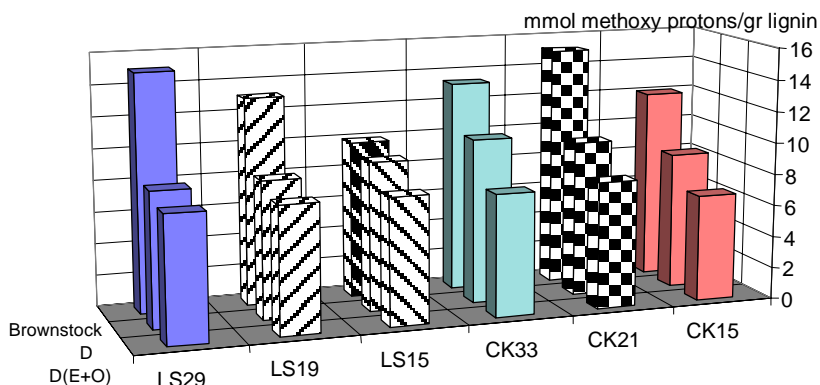


Figure 2.14. Methoxyl proton content for residual lignin from brownstock, D, and D(EO) CK and LS pulps as determined by ¹H NMR.

The decrease in methoxyl content from the brownstock to the Rapid D₀ bleached pulps is a result of the demethoxylation chemistry associated with chlorine species in the D₀ stage. The additional decrease in methoxyl content measured after the (EO) stage can be attributed, in part, to the hydrolysis of muconic acid methyl esters during alkaline extraction. Nonetheless, the largest loss in methoxyl content occurred during the Rapid D₀ stage.

Another group of significant interest in chlorine dioxide bleaching is the phenolic unit. The use of proton NMR provides a method of monitoring the changes in the concentration of this functional group as pulping and bleaching proceeds. The results of this analysis for the LS and CK pulps are summarized in Figure 2.15.

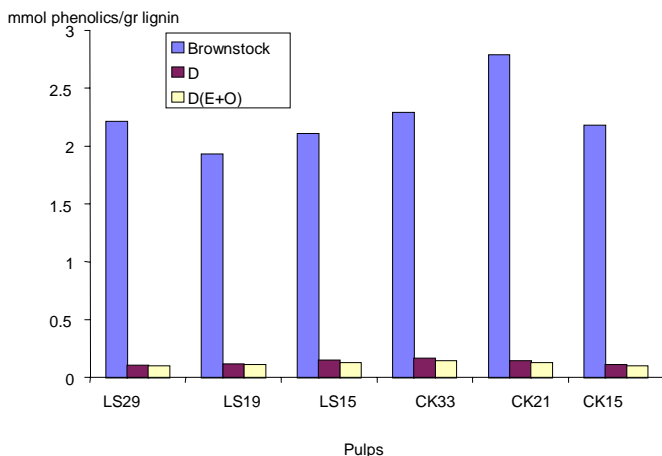


Figure 2.15. Phenoxy proton content for residual lignin from brownstock, D, and D(EO) CK and LS pulps as determined by ^1H NMR.

The results of this analysis suggested that the Rapid D_0 stage was efficient at removing most of the phenolics from the residual lignin isolated for these studies.

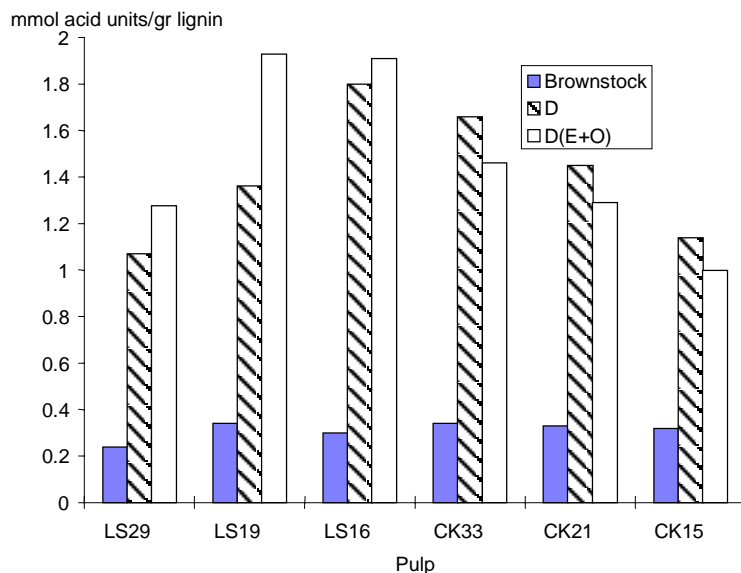


Figure 2.16. Carboxylic acid proton content for residual lignin from brownstock, D, and D(EO) CK and LS pulps as determined by ^1H NMR.

As expected, the extensive oxidation of lignin yielded a residual lignin that contained a significant enrichment of acid groups, as summarized in Figure 2.16.

In light of these substantial structural changes in the residual lignin, the parameters contributing to differences in bleachability become more difficult to elucidate. Nonetheless, a close inspection of the residual lignin components of the starting pulps did suggest a possible contributing factor. The CK pulps studied in this report have both higher noncondensed and condensed phenoxy structures. Perhaps most notable is the increased amount of condensed phenolics.

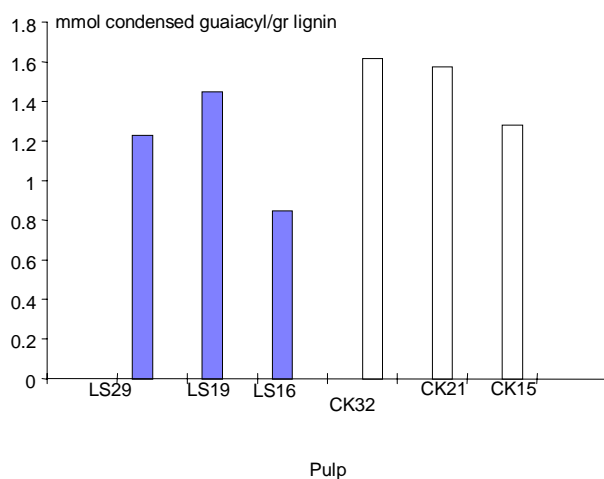


Figure 2.17. Condensed guaiacyl proton content for residual lignin for CK and LS pulps as determined by ^{31}P NMR.

The results of the ^{31}P NMR analysis of the phosphitylated residual lignin samples suggests that the conventional pulps have higher amounts of condensed lignin than the EK pulps. Hence, the CK pulps, despite having higher total phenolic concentration, are less reactive to chlorine dioxide due possibly to the increased amounts of condensed phenolics.

It is interesting to compare the results of this analysis with our prior studies on conventional and EMCC[®] pulps. The results of pulp bleachability studies for these latter pulps and the phenolic content of the residual lignins are summarized in Table 2.4.

Table 2.4. Kraft residual lignin structure and bleachability of EMCC[®] (E) and conventional softwood kraft pulps bleached via D₀(E+O).

Pulp ¹	TAC ² /Δ Kappa	mmol total phenolics/gr lignin ³	mmol condensed phenolics/gr lignin
E:29	0.21	2.07	0.91
E:18	0.22	2.15	0.94
C:28	0.21	2.07	0.89
C:18	0.23	2.29	0.99

¹E pulps were prepared via simulated EMCC[®] conditions, C pulps were prepared under simulated conventional kraft conditions; kappa number of the unbleached softwood kraft pulp is given after the letter; ²pulps were bleached under conventional D₀ (0.20 k.f.) (E+O) stages (see Froass et al.¹² for experimental further details); ³lignin isolated in the same manner as employed in this paper.

Our results with the CK pulps mirror the previous published results summarized in Table 2.4. As the kappa number of our CK or C pulp was lowered from the 30s to the mid-20s the phenoxy content increased and bleachability decreased. In each case, this can be attributed to the increase in condensed phenolic lignin units. The LS pulps do not have the same profile of condensed lignin, and presumably this explains the differences in bleachability between the LS pulps and the E pulps in Table 2.4.

Along with the residual lignin samples selected, bleach effluents were isolated and characterized. The combined effluents from the CK33 pulp bleached D(EO) were collected along with the effluents from replacing (EO) with E, EOP. Replacing the sequence D(EO) by DE decreased delignification efficiency by 7%, whereas the addition of 0.5% P in the (EOP) stage improved delignification by 6%. The residual lignin from the D(EO), DE, D(EOP) bleached pulps and effluents were collected and analyzed by ³¹P NMR. The results of this analysis are summarized below in Figure 2.18 and these measurements must be viewed in a semi-quantitative manner since the recovery of this highly oxidized lignin was typically less than 25%.

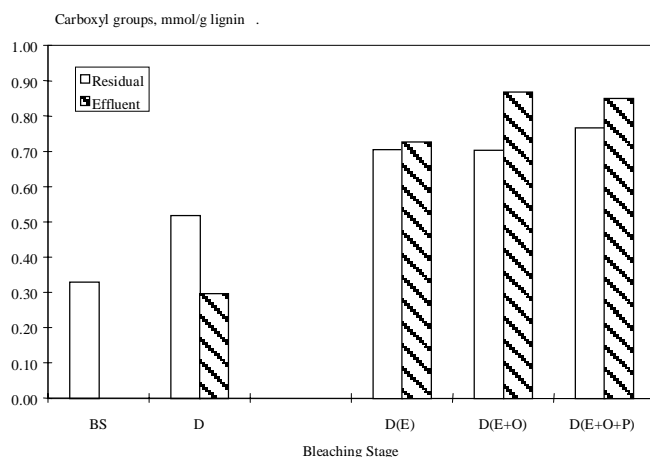


Figure 2.18. Carboxyl groups of residual lignin from CK33 brownstock and after D₀, DE, D(EO), and D(EOP) treatments along with effluents.

2.4 EXPERIMENTAL PROCEDURES:

Materials

All reagents and solvents were commercially purchased and used as received, except for the p-dioxane, which was distilled in the presence of NaBH_4 . NMR solvents were purchased anhydrous and stored over 4Å molecular sieves. Deionized water was used for all operations except the lignin isolation procedure. Filtered nanopure deionized water was used for the lignin isolation procedure. Chlorine dioxide was generated from the reduction of sodium chlorate with oxalic acid employing 9 N sulfuric acid. The small amount of chlorine that was generated by this process was measured and converted to chlorine dioxide by the stoichiometric addition of sodium chlorite.

A single mature loblolly pine tree grown in the southeastern United States was employed for all pulping studies reported in this paper. The tree was debarked, chipped, and carefully screened. Figures 2.19 and 2.20 summarize the physical properties of the accept wood chips.

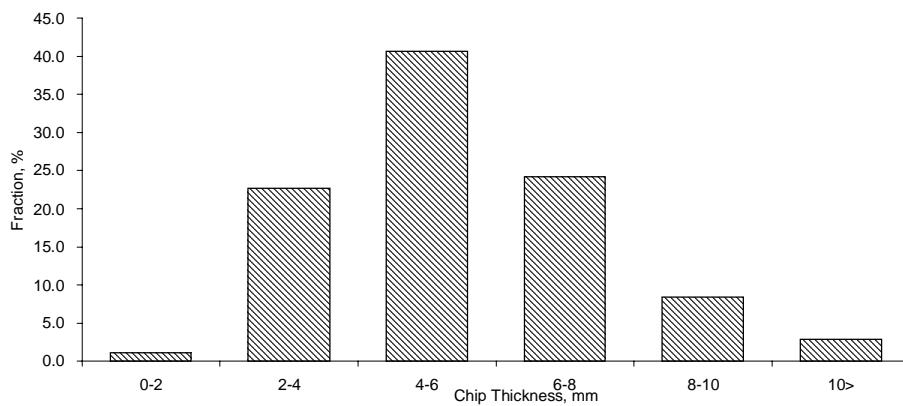


Figure 2.19. Average chip thickness, mm.

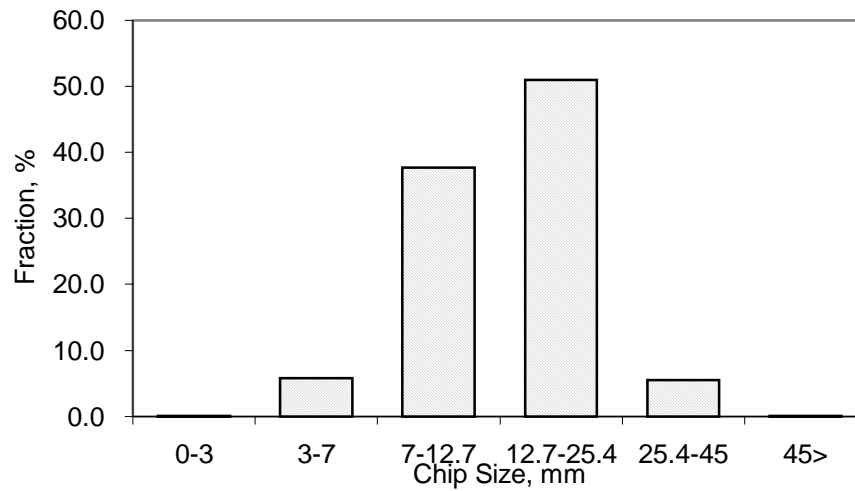


Figure 2.20. Average chip size distribution.

SW Kraft Pulping

The kraft pulping experiments were performed at Ahlstrom Machinery Corp. in Glens Falls, NY. Established procedures⁴ were used to simulate conventional and Lo-Solids® kraft cooking procedures. Table 2.5 summarizes the cooking parameters employed for the SW kraft cooks and the physical properties of the pulps.

Table 2.5 Conventional and Lo-Solids® SW kraft pulping conditions and pulp properties from the CK and LS pulps.

	Conventional Kraft Pulps (CK)							Lo-Solids® Kraft Pulps (LS)					
Pulp	CK33	CK28	CK21	CK20	CK18	CK15	CK13	LS29	LS26	LS19	LS17	LS16	LS11
Kappa #	33.0	28.3	21.3	20.4	18.1	14.7	13.3	29.3	26.1	19.1	17.1	16.0	11.0
Total Yield % on Wood	48.6	48.1	46.6	47.4	46.8	44.7	44.0	48.3	47.8	45.6	44.9	44.2	41.8
Max. Temp	168	170	170	170	171	171	171	160	163	166	169	170	170
H-Factor	1201	1213	1999	2311	2987	3496	3499	2003	2442	3362	4126	4489	4474
Total EA Consumed % on wood NaOH	14.8	14.0	15.4	14.9	15.3	16.7	16.4	14.1	15.2	15.0	15.9	16.6	17.8

Residual Lignin Isolation and Characterization

Residual lignin was isolated from the various pulps by employing an aqueous acidic-dioxane solution following literature procedures.⁹ In brief, the procedure required an air-dried SW kraft (50-150 gr o.d.) to be placed in a flask with a solution of 0.10 M HCl 9:1 dioxane:water at 8% consistency. The pulp slurry was refluxed for 2 h under argon before filtering through celite and a medium glass-fritted funnel. The celite was washed with an additional 500 mL of p-dioxane. The filtrate was neutralized with a saturated sodium bicarbonate solution before the p-dioxane was removed under reduced pressure at 40°C. The lignin was precipitated by acidification with 1.00 N HCl. The lignin was further coalesced by freezing, thawing, and centrifuging. The supernatant was decanted to the level of the precipitated lignin. This washing procedure was performed 3 times before the lignin was freeze dried. On average, the yield of residual lignin from the CK and LK kraft was 55% (see Table 2.6).

Table 2.6. Yield of lignin recovered from lignin isolated from SW kraft brownstock pulps.

Conventional Kraft Pulp	% Lignin Recovered ^a	Lo-Solids® Kraft Pulp	% Lignin Recovered
CK33	58	LS29	52
CK28	52	LS26	49
CK21	54	LS19	48
CK20	55	LS17	53
CK18	51	LS16	55
CK15	57	LS11	45
CK13	66	-	-

^a% lignin recovered=(mass of lignin recovered)/(kappa number of pulp x oven-dry weight of pulp x 0.147%).

Table 2.7. Yield of lignin recovered from bleached SW kraft pulps.

CK Pulp	%Lignin Yield ^a	EK Pulp	%Lignin Yield
CK32.4: D ₀ (EO)	35 36	EK29.3: D ₀ (EO)	30 36
CK21.3: D ₀ (EO)	29 29	EK19.1: D ₀ (EO)	30 28
CK14.7: D ₀ (EO)	30 39	EK15.6: D ₀ (EO)	28 29

^a% lignin recovered=(mass of lignin recovered)/(kappa number of pulp x oven-dry weight of pulp x 0.15%)

Quantitative ¹H NMR analysis of the residual lignin samples was accomplished employing underivatized lignins in DMSO-d₆ using trimethyl silyl propionate-d₄ (TSP) as the internal standard. ¹H NMR measurements were accomplished following the method of Li and Lundquist²⁶ employing a Bruker 400 MHz DMX spectrometer. Operating conditions included a 90-degree pulse, a TD of 32 k, a 15 sec. delay, and a sweep width of 24 ppm. The NMR experiments were performed at 50°C on samples containing 35-50 mg

lignin/mL of DMSO- d_6 . The Fourier transformed spectra were integrated according to reported chemical shifts for lignin functional groups relative to an internal standard sodium-3-trimethylsilyl-propionate-2,2,3,3- d_4 (TSP). Using the known weight of the TSP in solution, the lignin functional group integrals were transformed into units of mmol/g isolated lignin.

Hydroxyl functional groups in isolated lignins were quantified by ^{31}P NMR spectroscopy using a slight modification of the procedure developed by Argyropoulos.²⁷ Approximately 35 mg of dried isolated lignin was weighed into a 2 mL vial. To the vial was added 280 μL pyridine containing chromium acetylacetonate (2 mg/mL) and cyclohexanol (2 mg/mL). After the lignin was completely solubilized by the pyridine solvent, 175 μL CDCl_3 was added with stirring. Fifteen minutes before NMR analysis, 75 μL 2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane was added to the lignin solution with vigorous stirring.

Quantitative ^{31}P NMR analysis was acquired under the following conditions: 25-second pulse delay, inverse-gated decoupling (Waltz-16), 30° pulse angle, a time domain of 32K with one degree of zero filling, 200 acquisition transients, and 4.0 Hz line broadening. Signal assignments and integration regions were based on literature methods.²⁷

BLEACHING STUDIES:

Rapid D_0

Employing the quantum reactor, a 3% consistency pulp mixture was heated to 45°C and the pH was adjusted to either 5.0 or 4.0 for kappa factor 0.20 and 0.05 ClO_2 bleaching experiments, respectively. ClO_2 (kappa factor of either 0.05 or 0.20) was added into the quantum reactor and the pulp was mixed for 30 sec at 15 Hz, the mixer was then stopped for 30 sec, after which a quenching solution of aqueous Na_2SO_3 (mass Na_2SO_3 added = mass applied $\text{ClO}_2 \times 4.67$) was injected. The pulp mixture was then stirred for an additional 30 sec., filtered, and characterized. Kappa number was then determined.

(EO)-Stage

The pulp from the D_0 stage was thickened to 25% consistency, without washing, thoroughly disintegrated, and added to a pin mixer. The consistency was adjusted to 10%, and the pulp was then extracted under typical (EO) conditions: NaOH charge was chosen to yield a terminal pH of 10.7-11.5. The (EO) stage was performed at 70°C for 60 min. The initial O_2 pressure was 60 psig, and this was decreased 10 psig every 5 min. At the end of the (EO) stage, the pulp consistency was adjusted to 3%, the effluents were collected, and the pulp was thoroughly washed.

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CHAPTER 3: STUDIES OF CHLORINE DIOXIDE DELIGNIFICATION: VAPOR PHASE BLEACHING OF HARDWOOD AND SOFTWOOD KRAFT PULPS

3.1 INTRODUCTION:

“Vapor phase” delignification of unbleached kraft pulp consists of contacting it, at high consistency, with a gas stream containing ClO_2 . This mode of ClO_2 application has been proposed as a means of achieving efficient delignification while simultaneously generating relatively small amounts of byproduct adsorbable organic halide (AOX).^{1,2} Our interest in this process has been as part of a study of the interdependence of delignification efficiency, bleaching conditions, and residual lignin structural changes. Accordingly, we have conducted vapor phase ClO_2 delignification experiments in the laboratory and have followed them with determinations of residual lignin structural changes and effluent AOX. The emphasis of this study was on hardwood kraft pulps made from sweetgum by laboratory simulations of both conventional and RDH kraft pulping. As a comparison, some experiments were also conducted on pulps made from southern pine by laboratory simulations of conventional kraft pulping.

3.2 RESULTS AND DISCUSSION:

Results indicative of $D_0(\text{EO})$ delignification efficiency are contained in Table 3.1 for the hardwood pulps and in Table 3.2 for the softwood pulps. As shown in Table 3.1, vapor phase delignification of the hardwood pulps was remarkably more efficient than conventional, low consistency bleaching. In spite of the fact that less ClO_2 was consumed in the vapor phase experiments, the kappa number after extraction was 50% lower. This is in agreement with Mendiratta's¹ earlier observation that delignification at high consistency with a gaseous mixture of ClO_2 , O_2 , and water vapor gave much better delignification efficiency than conventional medium consistency delignification. In the present case, hardwood pulp delignification efficiency in the $D_0(\text{EO})$ partial sequence, expressed as kappa number reduction per percent of active chlorine consumed, was 4.4-5.3 for the vapor phase D_0 stage, as compared with 3.0-3.9 for the low consistency D_0 stage.

In the case of the softwood pulps, as shown in Table 3.2, there was a much smaller improvement in delignification efficiency in going from low consistency to vapor phase bleaching. This observation differs from those made earlier by Mendiratta¹ and Reeve³, indicating that vapor phase delignification efficiency is sensitive to operating conditions and perhaps also to unbleached pulp characteristics. In this regard, it is worth noting that we made no attempt to optimize the vapor phase ClO_2 stage, either for bleaching performance or effluent quality.

Several important observations not directly related to the comparison between vapor phase and conventional bleaching may also be made with regard to the data in Tables 3.1 and 3.2. One confirms the observation, made previously in this laboratory and elsewhere, that delignification efficiency exhibits a modest decrease as unbleached kappa number is decreased. The data of Table 3.2 also reveal a very large effect of kappa factor on delignification efficiency, the efficiency being more than twice as high at kappa factor 0.05 than at 0.2.

Table 3.1. Hardwood Pulp Bleaching Data.

Experiment	Process	Unbl.Pulp		D ₀ Stage			(EO) Stage			
		Pulp Type	Kappa Number	Kappa Factor	Kappa Number	Delta Kappa/TAC	NaOH Charge, % o.d.p.	Final pH	Kappa Number	Delta Kappa/TAC
HCC1	Conventional	Conv.	11.4	0.200	6.2	2.3	2.5	12.4	4.2	3.2
HCC2			15.2	0.200	7.9	2.4	2.0	12.0	5.2	3.3
HCR1		RDH	7.8	0.200	5.6	1.4	1.7	11.9	3.1	3.0
HCR2			13.4	0.200	10.0	1.3	1.7	12.0	5.2	3.1
HCR3			22.9	0.200	13.9	2.0	1.7	11.6	5.2	3.9
HVC1	Vapor Phase	Conv.	11.4	0.181	4.2	3.5	1.7	11.8	2.3	4.4
HVC2			15.2	0.171	5.3	3.8	1.7	11.8	2.5	4.9
HVR1		RDH	7.8	0.155	3.3	3.7	1.7	11.9	1.5	5.2
HVR2			13.4	0.172	5.4	3.5	1.7	11.8	2.8	4.6
HVR3			22.9	0.167	8.2	3.8	1.7	10.6	2.6	5.3

- Notes:** 1. D₀ stage conditions: For conventional bleaching, Quantum mixer, 30 min., 45°C, 3% consistency, final pH 2.5-3.0. For vapor phase bleaching, rotating spherical glass reactor, 7-10 min., 60°C, 30% consistency, final pH 2.5-3.0.
2. (EO) stage conditions: Pin mixer, 60 min., 70°C, 10% consy., oxygen pressure initially 60 psig. and decreased by 10 psig. every 5 min.

Finally, it is apparent that there is little difference in D₀(EO) delignification efficiency between hardwood and softwood pulps, or between conventional and RDH pulps, at least over the ranges of kappa numbers investigated in this study. This suggests that the relative ease of bleaching of hardwood pulps has more to do with their lower unbleached kappa numbers than with any inherent difference in ease of lignin removal.

Information on the mechanisms of delignification and potential environmental effects was obtained by collecting and analyzing filtrates from each of the bleaching stages. The resulting data are presented in Tables 3.3 and 3.4. The yield figures shown in these tables represent the

Table 3.2. Softwood Pulp Bleaching Data.

Experiment	Process	Unbl. Pulp		D ₀ Stage			(EO) Stage			
		Pulp Type	Kappa Number	Kappa Factor	Kappa Number	Delta Kappa/TAC	NaOH Charge, % o.d.p.	Final pH	Kappa Number	Delta Kappa/TAC
SCC1	Conventional	Conv.	18.7	0.050	14.2	4.8	1.2	11.2	10.2	9.1
SCC2				0.200	8.8	2.6	1.8	11.6	3.9	4.0
SCC3			30.4	0.200	14.6	2.6	2.5	11.2	4.2	4.3
SCC4			33.0	0.200	12.0	3.2	2.6	11.2	4.6	4.3
SVC1	Vapor Phase		30.7	0.050	26.4	2.8	2.5	12.2	15.8	9.7
SVC2				0.184	15.4	2.7	2.5	11.8	4.5	4.6

- Notes:** 1. D₀ stage conditions: For SCC1 and SCC2, Quantum mixer, 30 min., 45°C, 3% consistency, final pH 2.3-2.8. For SCC3 and SCC4, Quantum mixer, 45 min., 45°C, 10% consistency, final pH 2.0. For SVC1 and SVC2, rotating spherical glass reactor, 8-10 min., 60°C, 30% consistency, final pH 2.6-2.8.
2. (EO) stage conditions: Pin mixer, 60 min., 70°C, 10% consistency, oxygen pressure initially 60 psig. and decreased by 10 psig. every 5 min.

percentages of the chlorine atoms in the ClO_2 charged that are converted to the indicated species.

Striking features of the hardwood data (Table 3.3) are the markedly higher rate of AOX generation in the vapor phase process than in the conventional one, the high levels of AOX in even the conventional process, and the decreased AOX yield when low kappa number pulps are bleached. These effects are also graphically shown in Figure 3.1. Vapor phase delignification generated AOX at more than twice the rate of the conventional process, which in turn generated more than expected on the basis of a model based on a review of the literature on softwood bleaching with mixtures of ClO_2 and Cl_2 .⁴ The latter study showed that delignification of softwoods in the (DC)E partial sequence with mixtures of ClO_2 and Cl_2 rich in ClO_2 converted about 8% of the charged Cl atoms into AOX. The corresponding figures for $\text{D}_0(\text{EO})$ delignification of hardwood pulps from the present study (averages from Table 3.3) are 14% for a low consistency D_0 stage and 33% for a vapor phase D_0 stage. Tentative conclusions are that hardwood pulps give a higher yield of AOX than softwoods, and that vapor phase delignification of hardwood pulps generates abnormally large quantities of AOX under the conditions employed in this study. The higher AOX levels in vapor phase delignification may be indicative of gas phase decomposition of ClO_2 prior to its reaction with the lignin in the pulp, which would also explain the higher delignification efficiency because of the known superiority of Cl_2 - ClO_2 mixtures in this respect. The composition of the mixture of inorganic byproducts is consistent with this explanation, since the vapor phase filtrates contained somewhat lower concentrations of chloride ion, and a greater proportion of the chloride ion produced in the vapor phase process was released in the alkaline extraction stage. Both of these changes are to be expected when substitution assumes a greater role relative to oxidation. The vapor phase filtrates also contained markedly less chlorate ion (Figure 3.2), as would be expected if ClO_2 had decomposed to Cl_2 before reacting. Regardless of the mechanism, the lower rate of chlorate production is consistent with the higher delignification efficiency of the vapor phase process.

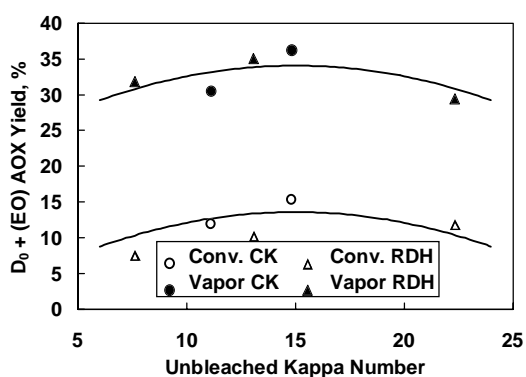


Figure 3.1. Sum of AOX yields from D_0 analyses of D_0 and (EO) stage filtrates.

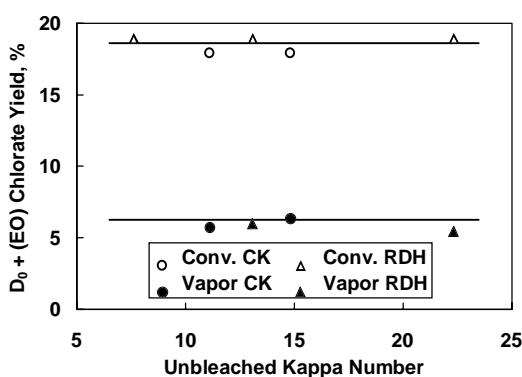


Figure 3.2. Sum of chlorate yields from analysis and (EO) stage filtrates.

Qualitatively similar observations may be made with regard to the softwood pulp data presented in Table 3.4, but the trends were generally less pronounced than in the case of the hardwood pulps. Thus, the disparity between the rates of AOX generation in the vapor phase and

conventional processes, though still great (18% vs. 10%), was smaller than in the case of hardwoods (33% vs. 14%). The AOX levels for the conventional process were only slightly greater than predicted by the model referred to earlier, and the effect of kappa number on AOX yield was either absent or too small to be apparent. The reduction in chlorate yield associated with going from the conventional process to the vapor phase process, unlike the trends just mentioned, was just as pronounced for the softwood pulps as for the hardwoods. In addition, positive effects of increasing kappa factor on the yields of both AOX and chlorate ion were observed. Figures 3.3 and 3.4 illustrate these effects.

To elucidate the mechanisms of the conventional and vapor phase ClO_2 delignification processes, residual lignin was isolated from the conventional kappa no. 15.2 hardwood pulp before bleaching, after the D_0 stage, and after the (EO) stage, for both the conventional and vapor phase bleaching processes. The residual lignin was isolated using an acidic dioxane extraction procedure that has been employed by several researchers.⁵ The resulting lignin was then purified, derivatized with 2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane, and characterized by ^{31}P NMR.⁷

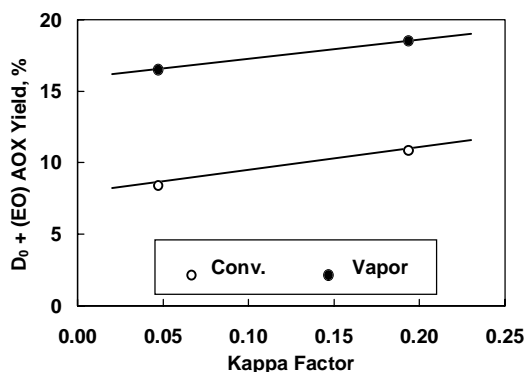


Figure 3.3. Sum of AOX yields from analyses of D_0 and (EO) stage filtrates from bleaching of softwood pulps.

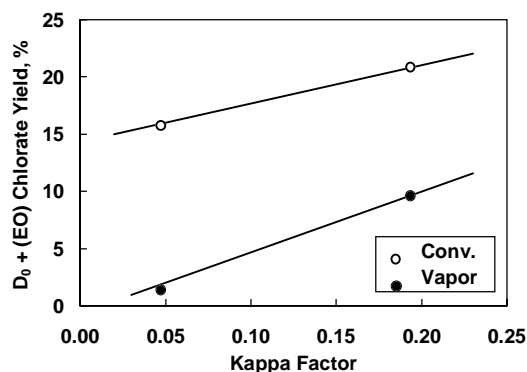


Figure 3.4. Sum of chlorate yields from analyses of D_0 and (EO) stage filtrates from bleaching of softwood pulps.

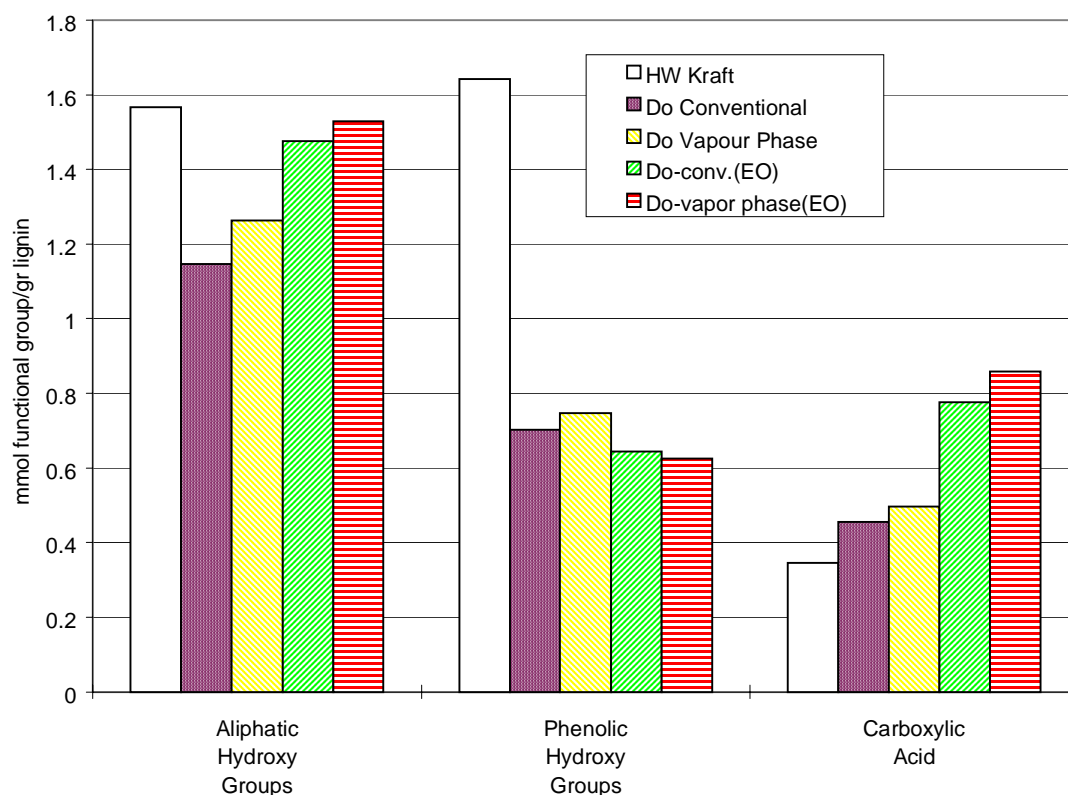


Figure 3.5. Changes in aliphatic, carboxylic, and phenolic hydroxy content for conventional hardwood kraft pulp (kappa no. 15.2) bleached D₀, 0.20 k.f., with vapor phase and conventional conditions followed by an (EO) stage.

The results of this analysis are illustrated in Figure 3.5. As expected, the residual lignin was found to be enriched in acid groups as the brownstock pulp was treated with ClO₂ and subsequently alkaline extracted in an (EO) stage. Interestingly, the residual lignin isolated from the vapor phase D₀ and D₀(EO) pulps exhibits a slight enrichment in acid groups over the conventional D₀ bleached pulp. A slight decrease in aliphatic hydroxy group content after the D₀ stage could be potentially attributed to some oxidation of the side chain of lignin. Both the conventional and vapor phase D₀ stages removed extensive amounts of phenolic groups from the residual lignin, which was expected since the phenolic group is the primary site of oxidation by chlorine dioxide.

The NMR methods employed in this study can further differentiate the phenolic groups into (a) syringyl, (b) condensed, and (c) guaiacyl and demethylated phenolics. Figure 3.6 summarizes the results of this analysis for the lignins studied in this report. Although all three types of phenolic groups are removed during the D₀ bleaching stage, it is clear that the syringyl units are the most reactive toward chlorine dioxide. Interestingly, the loss of guaiacyl and condensed types of phenolic groups appears to occur in comparable amounts. This result differs from our previous

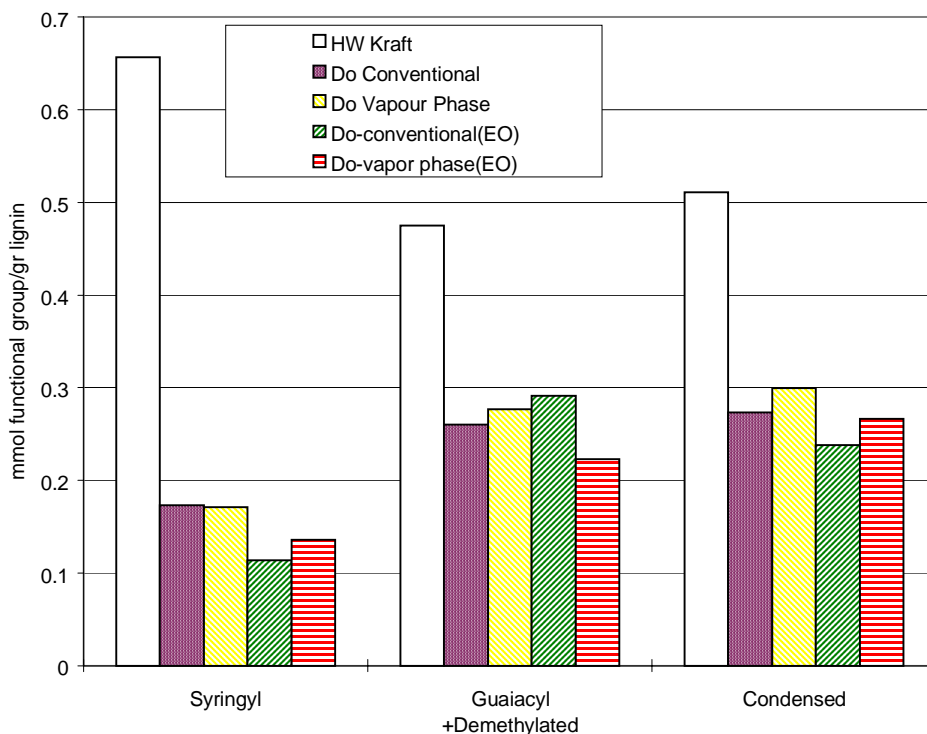


Figure 3.6. Changes in syringyl, condensed, and guaiacyl/demethylated phenolic hydroxy units for conventional hardwood kraft pulp (kappa no. 15.2) bleached D₀, 0.20 k.f., vapor phase and conventional, followed by an (EO) stage.

studies in which we noted condensed phenolic groups to be resistant to oxidative bleaching agents.⁶ The factors contributing to this trend will need to be further investigated so as to fully determine the mechanism of oxidative removal of condensed phenolics.

Table 3.3. Fate of Chlorine in Hardwood Pulp Bleaching.

Expt.	Process	Unbl. Pulp		D ₀ Stage						(EO) Stage					Total					
		Pulp Type	Kappa Number	Kappa Factor	AOX, kg/t	Yields of Cl Cpds, Mole % ClO ₂				AOX, kg/t	Yields of Cl Cpds, Mole % ClO ₂				AOX, kg/t	Yields of Cl Cpds, Mole % ClO ₂				Total Cl Recovery, %
						AOX	Cl ⁻	ClO ₃ ⁻	ClO ₂ ⁻		AOX	Cl ⁻	ClO ₃ ⁻	ClO ₂ ⁻		AOX	Cl ⁻	ClO ₃ ⁻	ClO ₂ ⁻	
HCC1	Conv.	Conv.	11.4	0.200	0.541	11.9	44	16	1	0.037	0.8	8	1	4	0.571	12.7	52	18	5	87
HCC2			15.2	0.200	0.834	13.7	47	17	1	0.136	2.2	8	1	2	0.960	16.0	55	18	3	92
HCR1		RDH	7.8	0.200	0.294	9.4	56	18	1	0.052	1.7	8	1	m.i.	0.261	11.1	64	19	m.i.	94
HCR2			13.4	0.200	0.737	13.8	51	18	1	0.142	2.7	8	1	m.i.	0.589	16.4	59	19	m.i.	94
HCR3			22.9	0.200	0.916	10.0	53	17	0	0.521	5.7	7	1	m.i.	1.152	15.7	60	19	m.i.	94
HVC1	Vapor	Conv.	11.4	0.181	1.180	28.5	43	6	0	0.092	2.2	13	0	m.i.	1.259	30.8	56	6	m.i.	93
HVC2			15.2	0.171	1.639	31.6	39	7	0	0.247	4.8	12	0	m.i.	1.867	36.3	51	7	m.i.	94
HVR1		RDH	7.8	0.155	0.705	29.3	(67)	(11)	0	0.067	2.8	19	1	m.i.	0.765	32.1	(86)	(12)	m.i.	(130)
HVR2			13.4	0.172	1.400	30.3	41	6	0	0.228	4.9	13	0	m.i.	1.612	35.3	53	6	m.i.	95
HVR3			22.9	0.167	1.445	18.9	40	6	0	0.829	10.8	11	0	m.i.	2.251	29.7	51	6	m.i.	87

Notes: 1. m.i. - Value could not be determined because of matrix interference.

2. Analytes present at concentrations below their detection limits were assumed to be present at a concentration of one-half of the detection limit.

Table 3.4. Fate of Chlorine in Softwood Pulp Bleaching.

Expt.	Process	Unbl. Pulp		D ₀ Stage						(EO) Stage					Total					
		Pulp Type	Kappa Number	Kappa Factor	AOX, kg/t	Yields of Cl Cpds, Mole % ClO ₂				AOX, kg/t	Yields of Cl Cpds, Mole % ClO ₂				AOX, kg/t	Yields of Cl Cpds, Mole % ClO ₂				Total Cl Recovery, %
						AOX	Cl ⁻	ClO ₃ ⁻	ClO ₂ ⁻		AOX	Cl ⁻	ClO ₃ ⁻	ClO ₂ ⁻		AOX	Cl ⁻	ClO ₃ ⁻	ClO ₂ ⁻	
SCC1	Conv.	Conv.	18.7	0.050	0.095	5.1	(114)	4	2	0.068	3.6	(124)	12	2	0.176	8.7	(238)	16	4	(268)
SCC2				0.200	0.656	8.8	74	18	1	0.176	2.4	15	3	1	0.772	11.1	89	21	2	123
SCC3			30.4	0.200	1.300	10.7	n.d.	n.d.	n.d.	0.130	1.1	n.d.	n.d.	n.d.	1.43	11.8	n.d.	n.d.	n.d.	n.d.
SCC4			33	0.200	1.210	9.2	n.d.	n.d.	n.d.	0.160	1.2	n.d.	n.d.	n.d.	1.37	10.4	n.d.	n.d.	n.d.	n.d.
SVC1	Vapor		30.7	0.050	0.297	9.6	75	2	1	0.216	7.0	19	0	1	0.476	16.6	94	2	2	115
SVC2				0.184	1.261	11.2	56	10	0	0.846	7.5	15	0	0	1.955	18.6	71	10	0	100

Notes: 1. n.d. - Not determined.

2. Analytes present at concentrations below their detection limits were assumed to be present at a concentration of one-half of the detection limit.

3.3 EXPERIMENTAL:

HW Kraft Pulp Bleaching

Vapor phase D₀ stage bleaching was done by passing a stream of nitrogen and chlorine dioxide through a rotating spherical flask containing fluffed pulp at 30% consistency maintained at 60°C. The gas stream was generated by stripping ClO₂ from a 6.2 g/L solution containing a negligibly small amount of Cl₂. The flask containing ClO₂ solution, initially at 4°C, was placed in a 90°C water bath, and the flow of N₂ was immediately started. An amount of ClO₂ solution containing 3 g ClO₂ was used in every case, and the amount of ClO₂ delivered to the reaction flask was controlled by controlling the N₂ flow rate and the duration of the experiment. For example, 2.92 g ClO₂ was delivered by passing N₂ through the solution for 10 min. at a flow rate of 6.5 L/min. The gas leaving the reactor was passed through 10% KI, which was subsequently titrated iodometrically to determine the amount of unreacted ClO₂. HW pulps supplied with an amount of ClO₂ corresponding to a kappa factor of 0.20 consumed 77-91% of the applied ClO₂, depending on the unbleached kappa number. Kappa no. 30.7 SW kraft pulp, when supplied with an amount of ClO₂ corresponding to a kappa factor of 0.276, consumed 67%, an amount corresponding to a kappa factor of 0.184. For all pulps, the ClO₂ was completely consumed when the amount supplied corresponded to a kappa factor of 0.05.

Conventional D₀ stage bleaching was done in a Quantum reactor at 3% consistency and 45°C for 30 min. The mixer was turned on during ClO₂ addition, for 15 sec. thereafter, and for 5 seconds every 5 min. throughout the remainder of the bleaching period. Both types of D₀ stage were followed by an (EO) stage conducted in a laboratory pin mixer at 10% consistency and 70°C for 60 min. The oxygen pressure was initially 60 psig. and was decreased by 10 psig. every 5 min. Filtrate samples were collected immediately upon termination of each bleaching stage. After vapor phase D₀ stages and (EO) stages, the pulp was diluted to 3% consistency and thoroughly mixed before filtering. Samples for AOX determination were acidified to pH 2 with concentrated HNO₃. All samples were refrigerated pending analysis. Determinations of AOX were made according to EPA method 1650. Chloride, chlorate, and chlorite were determined by capillary ion electrophoresis.

The unbleached pulps were prepared in the laboratory by standard methods. All of the HW kraft pulps were prepared from fresh sweetgum chips at the laboratories of Beloit Corp. A SW pulp of 18.7 kappa number was prepared at IPST. The remaining softwood pulps were provided through the courtesy of J. Jiang and K. Crofut of Ahlstrom Machinery Inc., who prepared them from southern pine chips supplied by IPST (see Chapter 2).

Lignin isolation

The isolation of lignin from the kraft pulps was accomplished employing standard literature methods.⁵ In brief, air-dried pulp (60 g oven-dry weight) was added to an aqueous 0.1 N HCl (146 ml 1 N HCl), p-dioxane (1300 ml freshly distilled) solution, and this mixture was then refluxed for 2 hr. under an argon atmosphere. The mixture was then filtered, and the filtrate was filtered through celite. The solution was neutralized with sodium bicarbonate and concentrated

under reduced pressure. After the filtrate was vacuum distilled to less than 10% of the original volume, water was added (3 x 200 mL) and the mixture was reconcentrated under reduced pressure. The aqueous solution was then acidified pH to 2.5 with an aqueous 1 N HCl solution. The resulting precipitate was collected, washed several times with distilled water, and freeze-dried.

Lignin NMR studies.

NMR data were acquired with a DMX 400 MHz Bruker spectrometer. Quantitative ^{31}P -NMR experiments were performed following standard literature methods.⁷

3.4 CONCLUSIONS:

Vapor phase ClO_2 delignification of hardwood kraft pulps made from sweetgum is remarkably more efficient than conventional low consistency ClO_2 delignification. At 0.2 kappa factor, delignification efficiency in the $\text{D}_0(\text{EO})$ partial sequence, expressed as kappa number reduction per percent of active chlorine consumed, was 4.4-5.3 for the vapor phase D_0 stage, as compared to 3.0-3.9 for the low consistency D_0 stage.

In the case of southern pine kraft pulps, there was a much smaller improvement in delignification efficiency in going from low consistency to vapor phase bleaching. This observation differs from those made earlier by others, indicating that vapor phase delignification efficiency is sensitive to operating conditions.

Vapor phase delignification of hardwood kraft pulps generated abnormally large quantities of AOX under the conditions employed in this study, and conventional ClO_2 delignification of hardwood pulps generated more AOX than expected on the basis of softwood bleaching data. AOX yields in $\text{D}_0(\text{EO})$ delignification of hardwood pulps from the present study are 14% for a low consistency D_0 stage and 33% for a vapor phase D_0 stage. These figures may be compared with the 8% to be expected on the basis of earlier softwood pulp bleaching data.

Vapor phase filtrates contained somewhat lower concentrations of chloride ion, and a greater proportion of the chloride ion produced in the vapor phase process was released in the alkaline extraction stage. The vapor phase filtrates also contained markedly less chlorate ion. These observations, as well as the observations of improved delignification efficiency and higher AOX yields, are consistent with the hypothesis that ClO_2 partially decomposes in the vapor phase before reacting with the pulp.

Qualitatively similar observations were made in the vapor phase $\text{D}_0(\text{EO})$ delignification of softwood kraft pulps, but the trends were generally less pronounced than in the case of the hardwood pulps. Under the conditions used in this study, vapor phase delignification produced an AOX yield of approximately 18%, as compared with approximately 10% in conventional low consistency ClO_2 delignification. Positive effects of increasing kappa factor on the yields of both AOX and chlorate ion were also observed.

Differences in the structure of residual lignin after conventional and vapor phase bleaching were slight. This may indicate that the superior bleaching efficiency of the vapor phase process is due to the diminished importance of reactions that occur between active chlorine compounds and dissolved organic byproducts. The absence of such reactions would leave no evidence in the residual lignin structure. This explanation is also consistent with the elevated AOX levels resulting from vapor phase bleaching if it is assumed that part of the dissolved organic material that consumes active chlorine in the liquid phase is chlorine substituted.

3.5 REFERENCES:

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CHAPTER 4: IMPROVING THE BLEACHABILITY OF HARDWOOD KRAFT PULPS

4.1 INTRODUCTION:

Pulp bleachability is an issue of critical fundamental and practical interest in the pulp and paper industry. The ability to tailor a bleaching sequence to yield target brightness values with minimal use of bleaching chemicals and/or new capital equipment has obvious potential for savings in operating and capital costs. Our previous studies¹ have shown that the bleachability of SW kraft pulps is largely influenced by the bleaching chemistry of lignin. The factors controlling bleachability of HW kraft pulps are more complicated since both carbohydrates and lignin contribute to the apparent kappa number of HW kraft pulps. The interaction of these two components in controlling pulp bleachability is poorly understood since no reported studies have examined how both components simultaneously influence bleaching chemistry.

The formation of hexenuronic acids during pulping (see Figure 4.1) is currently a very active research area that has been shown to have practical mill considerations. Early studies by Clayton² examined the behavior of 4-O-methyl- α -D-glucuronoxylans from poplar, white birch, and white elm with alkali at 170°C and found indirect evidence for the formation of hexenuronic acids.¹

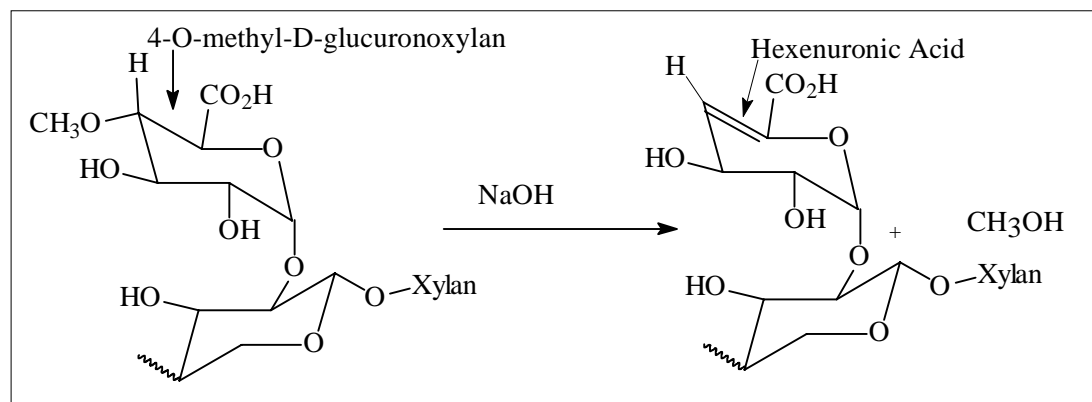


Figure 4.1 Alkali-catalyzed formation of hexenuronic acids.

Subsequent studies by Johansson and Samuelson³ and Simkovic et al.⁴ provided additional experimental evidence supporting the formation of hexenuronic acids from 4-O-methyl- α -D-glucuronoxylans. Finally, Teleman et al.⁵ isolated and characterized hexenuronic acids from an enzymatically hydrolyzed unbleached kraft pulp.

Studies by Vuorinen et al.⁶ and Buchert et al.⁷ further explored the chemistry of hexenuronic acids in kraft pulps. They demonstrated that hexenuronic acids contribute approximately 50% to the kappa number of several northern Scandinavian kraft pulps. Furthermore, these unsaturated sugars were shown to readily consume electrophilic bleaching chemicals such as chlorine dioxide and ozone. A series of well-designed acid hydrolysis studies identified reaction

conditions under which hexenuronic acids could be removed from kraft pulps (see Figure 4.2) without significantly impacting their physical properties.

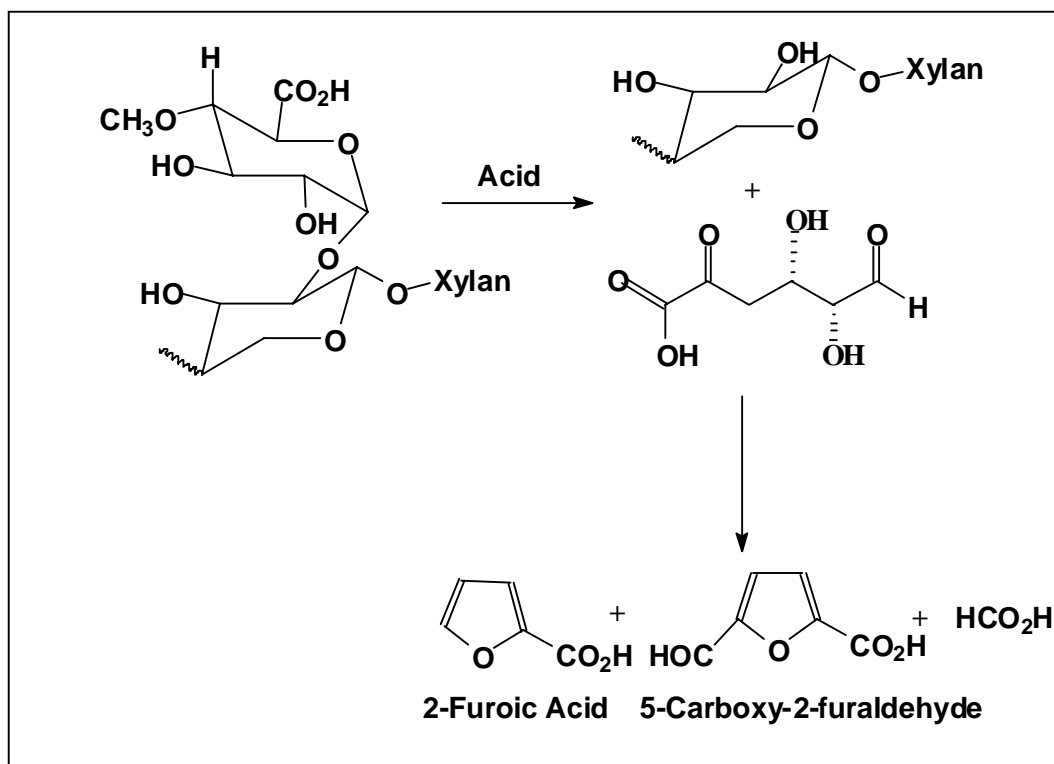


Figure 4.2. Proposed acid hydrolysis pathway for hexenuronic acid.⁵

Following these reports, several investigators began to explore the impact of hexenuronic acids on pulp bleaching operations. Li and Gellerstedt⁸ have examined the contribution of hexenuronic acids to a pulp's kappa number. Roberts⁹ and da Silva Filho et al.¹⁰ have reported that the presence of hexenuronic acids is a principal factor controlling the affinity of pulp fibers for nonprocess elements. Senior et al.¹¹ reported that the use of AQ in a kraft cook could influence the amount of hexenuronic acids present in HW kraft pulps. Nilvebrant and Reimann¹² have shown that hexenuronic acids can contribute to oxalic acid formation from a Z-stage. Lachenal and Chirat¹³ have demonstrated that the differing rates of reaction for chlorine dioxide with lignin and hexenuronic acid can be employed to improve HW kraft bleaching operations. Vuorinen et al.¹⁴ have studied the impact of hexenuronic acids in ECF and TCF bleaching operations.

Despite this significant body of work, few reported studies had examined the presence of hexenuronic acids from commercial North American kraft pulping operations prior to the studies in this report. This phase of the research program studied several parameters:

- Examined the concentration of hexenuronic acids in commercial SW and HW kraft pulps from U.S. operations.
- Evaluated how pulping parameters influence the formation of hexenuronic acids.
- Examined the importance of the role of lignin and hexenuronic acids in controlling HW pulp bleachability.
- Developed low-cost hexenuronic acid removal technologies.
- Evaluated full-sequence bleaching consequences of hexenuronic acids.
- Evaluated the role of lignin structure in pulp bleachability of HW kraft pulps.

4.2 RESULTS AND DISCUSSION:

Evaluating the Role of Hexenuronic Acids in U.S. Kraft Pulps.

Although the presence of hexenuronic acids has been well documented for Northern European⁶⁻⁸ kraft pulps, the presence of these unsaturated sugars in North American fiber sources has not been as extensively studied. To examine this issue, we acquired pulp samples from several mills in the U.S. Each pulp sample was exhaustively washed and analyzed for kappa number and viscosity. The pulps were then refluxed at 3% consistency in a pH 3 buffered solution for 2 and 5 hours. Under these conditions, hexenuronic acids are released from the hemicellulose chains and are converted to 5-carboxy-2-furaldehyde and 2-furoic acid. As shown in Figure 4.3, all the commercial HW kraft pulps exhibited a significant reduction in kappa number after acid hydrolysis ranging in value from 22% to 53%. Interestingly, the ease of acid-catalyzed removal of hexenuronic acids from kraft pulp was found to vary substantially for some pulps. For most of the HW kraft pulps examined, a two-hour acidic treatment significantly reduced the kappa number of the pulp. For the pulp from Mill B, a five-hour acid stage was required to maximize the drop in kappa number. The factors contributing to this diversity in response to a hot acid stage are unknown.

Acid hydrolysis of commercial softwood kraft pulps was not as effective at reducing the kappa number of the pulps, as shown in Figure 4.4. Repeating the acid stage with a series of laboratory-prepared loblolly pine continuous extended modified kraft pulps yielded comparable results as summarized in Figure 4.5. The results from acid hydrolysis of SW mill and lab kraft cooks suggest that only a small proportion of the pulp kappa number can be attributed to acid-sensitive hexenuronic acid groups. These results suggest that the minor presence of hexenuronic acids is further reduced as delignification of SW kraft pulps is extended from kappa number 30 to a kappa number of 20.

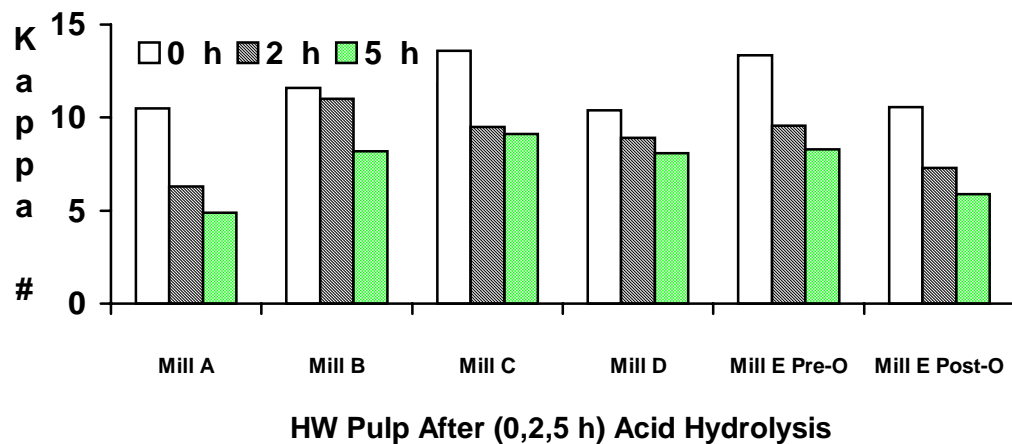


Figure 4.3. Kappa number of commercial HW kraft pulps before and after refluxing in pH 3 aqueous buffer solution for 2 and 5 h.

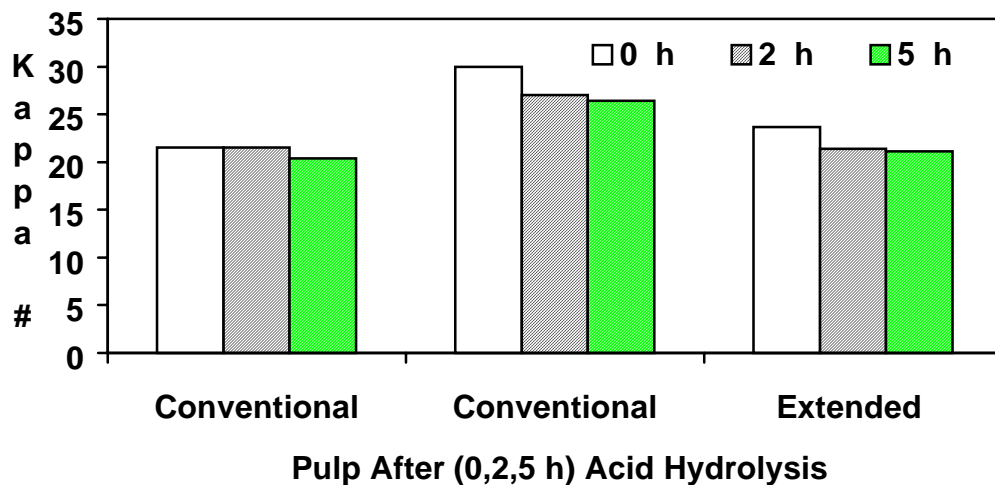


Figure 4.4. Kappa number of commercial SW kraft pulps before and after refluxing in an pH 3 aqueous buffer solution for 2 and 5 h.

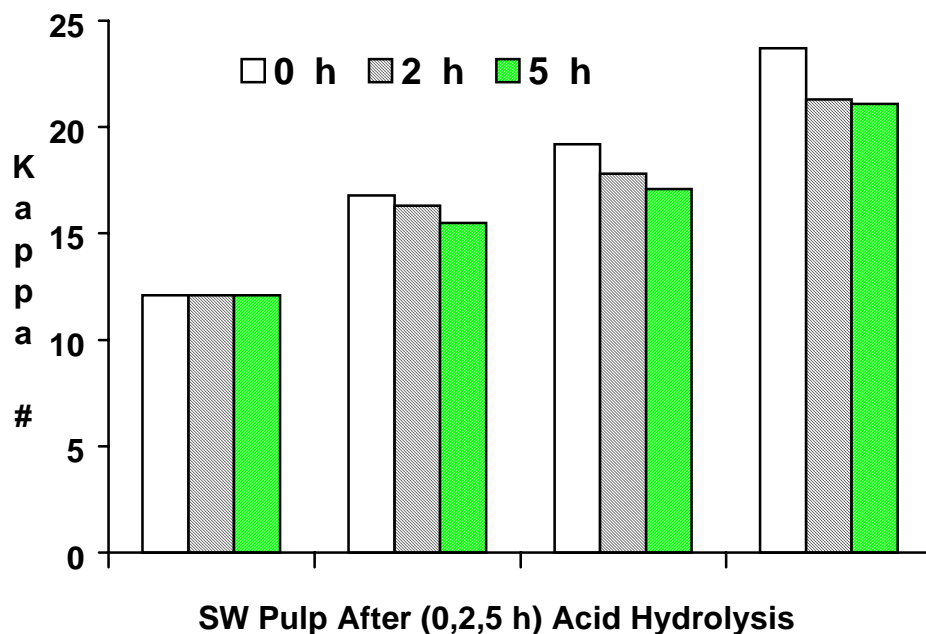


Figure 4.5. Kappa number of laboratory-prepared extended modified SW kraft pulps before and after refluxing in aqueous formic acid-sodium formate solution for 2 and 5 h.

The acid hydrolysis stage not only lowers the kappa of the kraft pulps but also reduces the pulp viscosity values. The HW kraft pulps typically incurred viscosity losses of 10 to 35% after refluxing in the hot acid stage for 5 h. For the SW kraft pulps, the acid hydrolysis resulted in 20-25% decreases in viscosity values. The acid hydrolysis conditions we employed were directed at maximizing the removal of acid-sensitive functional groups from the pulps. Based on literature considerations, the observed losses in viscosity could be minimized with additional optimization studies.¹⁵

Along with the kappa number analysis of each kraft pulp, the xylan content of each starting pulp was determined. Figure 4.6 presents the results of relating the xylan content of the kraft brownstocks to the drop in kappa number after a 5-hour acid hydrolysis treatment. These results suggest that there is a correlation between the xylan content of the starting pulp and the contribution of hexenuronic acids to the kappa number of the pulp. This result is consistent with the proposed mechanism of hexenuronic acid formation and its contribution to pulp kappa number.

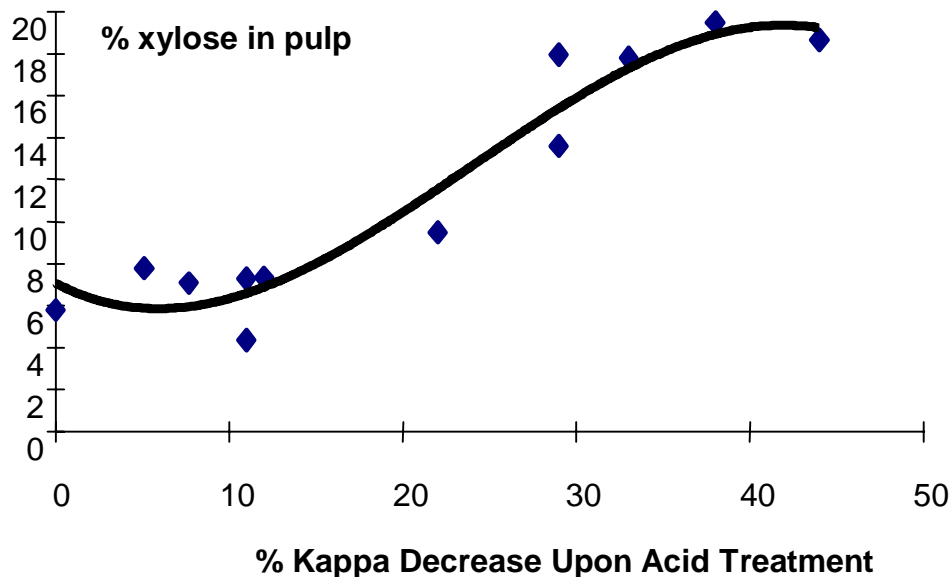


Figure 4. 6. Relationship between xylan content of SW and HW kraft pulps and the decrease of kappa number upon 5-hour acid hydrolysis stage.

In summary, the HW and SW studies reported in this section demonstrate that hexenuronic acids are a significant contributor to the kappa number of HW kraft pulps, whereas they are only a small component of the kappa number of SW kraft pulps. These results suggest that approximately 20-50% of the bleaching costs associated with HW pulp bleaching operations are due to hexenuronic acids and not lignin removal. The following section explores the relationship between kraft pulping and the content of hexenuronic acids in HW kraft pulps and the development of a low-cost hexenuronic acid removal stage.

Evaluating the Impact of Kraft pulping on Hexenuronic Acid Formation in HW Kraft Pulps

To examine how kraft-cooking technologies can influence the formation of hexenuronic acids for HW kraft pulps, we performed a series of conventional and extended modified batch cooks. These cooks were all accomplished from a common sweetgum wood source to minimize experimental variability due to the fiber source. Table 4.1 summarizes some of the important cooking and pulp parameters for these HW kraft pulps.

Table 4.1. HW Kraft pulping conditions.

H-factor	%EA charged on wood as Na₂O	Kappa #	Total Yield (%)
Conventional Kraft			
1,800	15.7	11.4	48.8
1,400	14.9	11.8	49.5
1,100	13.6	14.4	50.3
800	12.8	15.2	51.0
RDH Kraft Pulp			
1,000	NA	7.8	46.5
500	14.5	12.3	48.9
300	13.9	13.4	50.0
400	13.8	13.8	NA
250	NA	16.6	50.7
200	11.2	22.9	52.0

The conventional and RDH HW kraft pulps were refluxed in a pH 3 buffered solution for 5 hours, and the kappa number of the pulps was analyzed before and after the hot acid stage. The results of the kappa number analysis are summarized in Figure 4.7. The data suggest that differences in batch cooking do not significantly alter the formation of hexenuronic acids in kraft pulps, although there does appear to be a small reduction in the formation of hexenuronic acid groups for the RDH pulps. Of greater significance is the observed increase in kappa number that can be attributed to hexenuronic acid groups as the final pulp kappa number is reduced. The acid hydrolysis data presented in Figure 4.7 suggest that the HW kraft pulps with a kappa number of approximately 14 have the largest amount of hexenuronic acids contributing to the observed kappa number. As the delignification is extended, the pulps respond less favorably to an acid hydrolysis stage. This is presumably due to a loss of acid-sensitive hexenuronic acid groups to the kraft cooking conditions.

Along with the kappa number analysis of the acid hydrolyzed pulps, the hydrolysis effluents were analyzed by UV/Vis for the presence of 2-furoic acid. As summarized in Figure 4.2, 2-furoic acid can be used to measure the amounts of hexenuronic acids released from the pulp during a hot acid stage. The results of this analysis for the acid pulps are summarized in Figure 4.8, and the data agree with the drop in kappa number observed for the acid hydrolyzed pulps. It furthermore supports the hypothesis that for the sweetgum pulps studied, the content of hexenuronic acid groups in pulp increases as delignification is extended from kappa number 30 to approximately 14. Further depletion of hexenuronic acids was observed as delignification was

extended. This is consistent with studies⁷ that reported that the hexenuronic acids undergo a slow degradation during the latter part of a kraft cook.

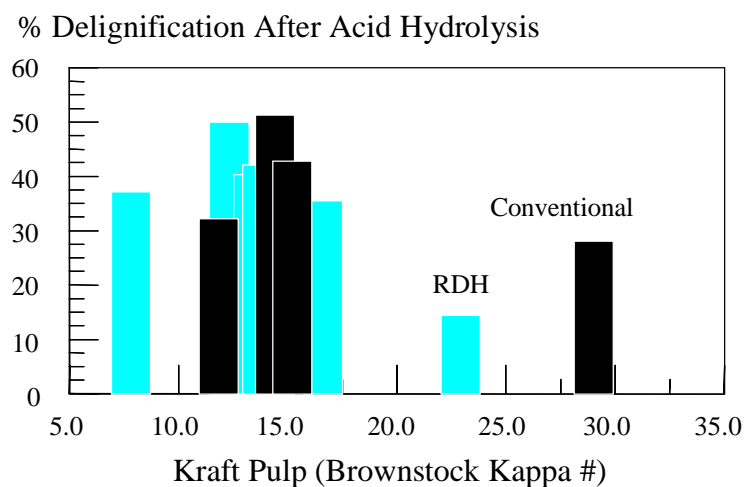


Figure 4. 7. Change in kappa number for HW kraft pulps upon acid hydrolysis (5 hour at 100°C, 3% csc, and buffer pH 3 solution) versus starting kappa number of conventional and RDH kraft pulps.

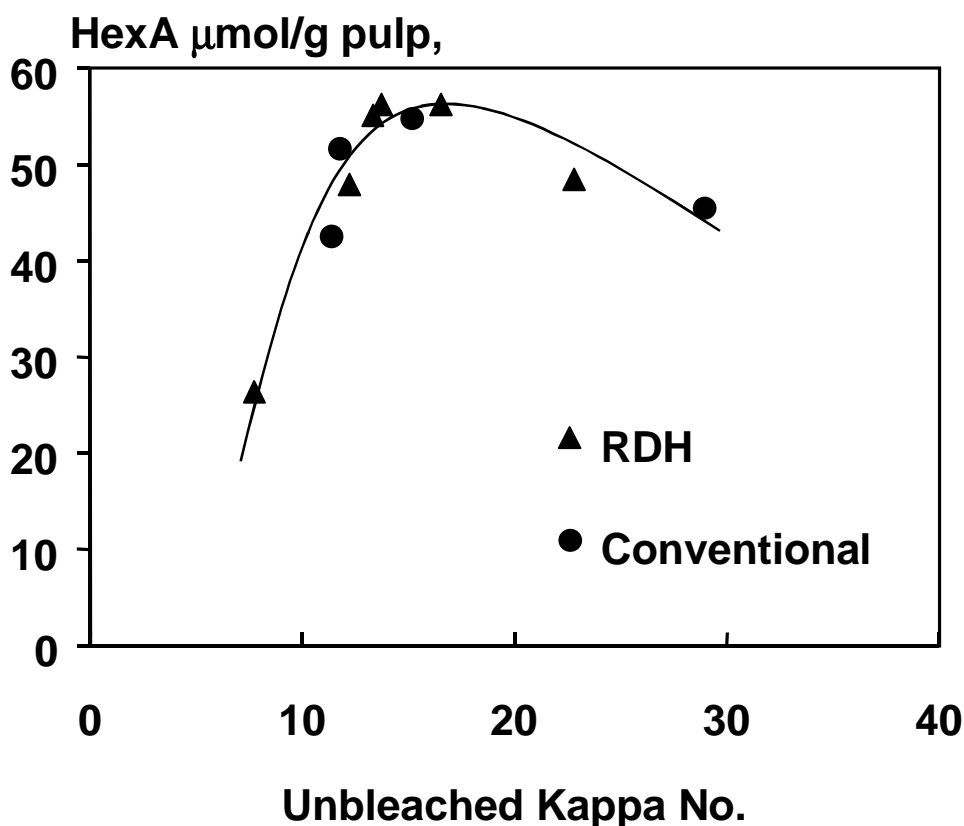


Figure 4.8. Hexenuronic acid content of unbleached RDH and conventional kraft pulps from sweetgum as determined by measuring the concentration of 2-furoic acid in the effluents from acid hydrolysis stages of the HW kraft pulps.

In summary, most U.S. HW kraft pulp bleaching operations utilize pulps that contain significant amounts of hexenuronic acids. These sugars consume approximately 20-50% of bleaching chemicals. The formation of hexenuronic acids cannot be readily precluded by changes in conventional and/or RDH cooking technologies. In the following section, development of a low-cost acid hydrolysis system is reported. The system was found to efficiently mitigate the effects of hexenuronic acids in HW kraft pulps.

Development of a low-cost acid hydrolysis-stage for HW kraft pulps.

D₀ Filtrate as Hydrolysis Medium

In their pioneering work on hexenuronic acid removal prior to bleaching, Vuorinen *et al.*⁶ used buffers (mixtures of formic acid and sodium formate) as hydrolysis media. They also used sulfuric acid, as did Siltala *et al.*¹⁶ in their mill-scale implementation of the process. Recycled filtrate from the washer following a D₀ stage may also have utility as a hydrolysis medium, replacing at least part of the required acid. Table 4.2 compares the results of mild acid hydrolysis of four sweetgum kraft pulps in D₀ filtrate with the corresponding hydrolyses in pH 3 formate buffer. It is apparent that the two media gave similar results. Kappa number reductions varied

from 16 to 52%, being higher for the pulps of lower kappa number. Apparent viscosity losses ranged from 0 to 36%. There were no significant differences in behavior between conventional and RDH pulps, nor between the two types of acid hydrolysis medium. These results demonstrate the potential usefulness of recycled D₀ stage filtrate for this application.

Effects of Hydrolysis Time and Temperature

The long retention times that have been used for complete removal of hexenuronic acid are disadvantageous. They require very large retention vessels or makeshift use of high-density storage towers, which commonly exhibit broad residence time distributions, leading to incomplete hydrolysis and poor selectivity. An alternative is to employ shorter retention times either by increasing the temperature or accepting a less-than-complete removal of hexenuronic acid that is nevertheless sufficiently large to justify the implementation of the hydrolysis stage. The data shown in Table 4.3 were obtained to address these possibilities. When the temperature was maintained in the 90-95°C range, reducing the retention time from 5 h to 1 h caused a roughly 50% reduction in the extent of hexenuronic acid removal. Reducing the time to 2 h and 3 h caused reductions in hexenuronic acid removal of 30% and 10%, respectively. It thus appears that it is possible to achieve appreciable extents of removal at retention times in the 2-3 h range.

The use of a pressurized prehydrolysis vessel to allow the temperature to be raised to 100°C or higher is another possibility. Table 4.3 shows that hydrolysis for 2 h at 100°C reduces the kappa number to the same extent as 5 h at 95°C. Increasing the temperature to 125°C allows the retention time to be shortened to 1 h with no loss in removal efficiency, or to fifteen minutes with a 20% loss in efficiency. Viscosity losses were modest under all conditions.

Table 4.2. Hydrolysis of Sweetgum Kraft Pulp by D₀ Filtrate and Formate Buffer

Unbleached Pulp			Kappa No. Reduction on Hydrolysis		Viscosity After Hydrolysis, mPa.s	
Type	Kappa No.	Viscosity, mPa.s	With		With	
			With D ₀ Filtrate ¹	Formate Buffer ²	With D ₀ Filtrate ¹	Formate Buffer ²
Conventional	29.1	60.6	6.4	4.7	40.4	38.9
	12.9	27.4	6.2	6.1	22.7	24.1
RDH	17.3	51.8	5.0	5.3	35.1	39.5
	11.8	37.8	6.1	5.7	37.8	28.7

¹Pulp acidified to pH 4 at ~2% consistency and thickened to ~25% consistency prior to dilution with D₀ filtrate to 4% consistency. Hydrolysis conditions: 95°C, 5 h. D₀ filtrate generated by bleaching sweetgum pulp (kappa no. 11.8) with ClO₂ (kappa factor 0.20) 30 min at 45°C in a Quantum mixer (final pH 2.7).

²Pulp initially at ~35% consistency diluted to 3% consistency with 10mM formate buffer followed by adjustment to pH 3.0 with H₂SO₄. Hydrolysis conditions: 100°C, 2 h.

Table 4.3. Effects of Hydrolysis Time and Temperature

Unbleached Pulp			Hydrolysis Conditions				Kappa No. Reduction on Hydrolysis	Viscosity After Hydrolysis, mPa.s
Type	Kappa No.	Viscosity, mPa.s	Consis- tency, %	Medium	Temp., °C	Time, h		
RDH	16.7	51.8	4	Filtrate ¹	90	1	2.0	47.7
						2	3.2	44.1
						5	4.6	34.6
Conv	12.0	32.9	12	Filtrate ²	95	1	3.3	28.8
						3	4.7	26.6
						5	5.2	23.3
RDH	17.3	51.8	4	Filtrate ³	95	5	5.0	35.1
				Formate ⁴	100	2	5.3	39.5
Conv.	12.0	32.9	12	H ₂ SO ₄ ⁵	95	5	5.6	24.9
					125	0.25	4.6	29.1
						1	5.9	24.4

¹Pulp initially at ~35% consistency diluted to 4% consistency with D₀ filtrate, followed adjustment to pH 3.0 with H₂SO₄. D₀ filtrate was generated by bleaching sweetgum (kappa no. 11.8) with ClO₂ (kappa factor 0.20) for 30 min at 45°C in a Quantum mixer (final pH 2.7).

²Pulp initially at ~35% consistency diluted to 12% consistency with D₀ filtrate, followed adjustment to pH 3.0 with H₂SO₄.

³Pulp acidified to pH 4 at ~2% consistency and thickened to ~25% consistency prior to dilution with D₀ filtrate to 4% consistency.

⁴Pulp initially at ~35% consistency diluted to 3% consistency with 10mM formate buffer, followed by adjustment to pH 3.0 with H₂SO₄.

⁵Pulp initially at ~35% consistency diluted to 3% consistency with dilute acid, pH 3.0. The suspension was then thickened to 12% consistency.

Effect of Hydrolysis Consistency

Most laboratory studies of hydrolysis as a bleaching pretreatment have used low consistencies for the acid treatment. On the mill scale, this is impractical because of the associated requirement for large retention vessels, high filtrate recycle rates, and high steam consumption. The data of Table 4.4 show the effect of increasing the consistency of the hydrolysis stage. The consistency can be raised to 12% with no loss in efficiency or selectivity. Higher consistencies lead to poorer selectivity and may also give slightly lower efficiency.

Table 4.4. Effects of Hydrolysis Consistency

Unbleached Pulp			Consistency ¹ , %	Kappa No. Reduction on Hydrolysis	Viscosity After Hydrolysis, mPa.s
Type	Kappa No.	Viscosity, mPa.s			
Conv	12.0	32.9	4	5.4	24.4
			12	5.2	23.3
			20	4.3	19.5
			30	4.9	15.4

¹ Pulp initially at ~35% consistency diluted with D₀ filtrate, followed by adjustment to pH 3.0 with H₂SO₄. D₀ filtrate was generated as indicated in previous tables.

Effects of Prehydrolysis on Subsequent Delignification

Two conventional and three RDH sweetgum kraft pulps were delignified in the D₀(EO) partial bleaching sequence, with and without prior hydrolysis to remove hexenuronic acid. The resulting data are shown in Table 4.5.

Table 4.5. Effect of Prehydrolysis on D₀(EO) Delignification Efficiency

Unbl.Pulp		Hydrolysis Before D ₀ Stage?	D ₀ Stage ¹		(EO) Stage ²				D ₀ (EO)	
Pulp Type	Kappa Number		Kappa Number Entering	Kappa Number Leaving	NaOH Charge, % o.d.p.	Final pH	Kappa Number	Delignifi- cation, %	Delignifi- cation by D ₀ (EO), %	Delta Kappa/ TAC
Conv.	11.4	No	11.4	6.2	2.5	12.4	4.2	32	63	3.16
		Yes	7.0	4.1	1.1	11.6	2.0	51	71	3.57
	15.2	No	15.2	7.9	2.0	12.0	5.2	34	66	3.29
		Yes	9.5	5.9	1.3	11.8	2.2	63	77	3.84
RDH	7.8	No	7.8	5.6	1.7	11.9	3.1	45	60	3.01
		Yes	5.6	3.6	1.0	11.5	1.8	50	68	3.39
	13.4	No	13.4	10.0	1.7	12.0	5.2	48	61	3.06
		Yes	8.8	5.4	1.0	11.0	2.3	57	74	3.69
	22.9	No	22.9	13.9	1.7	11.6	5.2	63	77	3.86
		Yes	15.4	10.8	1	10	3	72	81	4.03

¹D₀ stage conditions: Quantum Mixer, 30 min., 45°C, 3% consistency, kappa factor 0.20, final pH 2.5-3.0.

²(EO) stage conditions: Pin mixer, 60 min., 70°C, 10% consy., oxygen pressure initially 60psig and decreased by 10 psig every 5 min.

One reason for obtaining the data shown in Table 4.5 was to verify that the reduction in kappa number achieved in the hydrolysis step does indeed result in the expected corresponding reduction in downstream bleaching chemical requirements. It is reasonable to expect, for example, that the degree of delignification achieved in subsequent D₀ and (EO) stages (expressed as a percentage of the kappa number entering the D₀ stage) should be no lower than in the absence of prehydrolysis. The data of Table 4.5 not only verify this, but also reveal additional, unexpected effects.

It is known that pulping to lower unbleached kappa numbers results in pulps that are more difficult to bleach than those having higher kappa numbers, in the sense that they consume more oxidant per unit of kappa number reduction. This phenomenon is apparent in the data of Table 4.5. Decreasing the unbleached kappa number of the conventional pulp from 15.2 to 11.4 decreased the delignification efficiency from 3.84 to 3.57 kappa units per unit of oxidant consumption. Similarly, decreasing the unbleached kappa number of the RDH pulp from 22.9 to 7.8 decreased the delignification efficiency from 3.86 to 3.01. More relevant, however, is the observation that prehydrolysis increases the efficiency of D₀(EO) delignification in spite of the fact that it decreases the kappa number of the pulp entering the D₀ stage. The result is a sharp increase in efficiency at any given entering kappa number, as illustrated in Figure 4.9.

One interpretation of this observation is that prehydrolysis conditions the residual lignin to make it more easily removable. It may be speculated that this is due to hemicellulose removal, breakage of bonds between lignin and carbohydrate, or beneficial changes in the structure of the

lignin itself. Alternatively, the improvement in efficiency may simply reflect the decrease in hexenuronic acid content, if it is assumed that hexenuronic acid is more resistant than lignin to removal by ClO_2 . This latter interpretation is, however, inconsistent with the observations by Allison et al.¹⁷ and Törngren and Gellerstedt¹⁸ that hexenuronic acid are readily removed by ClO_2 .

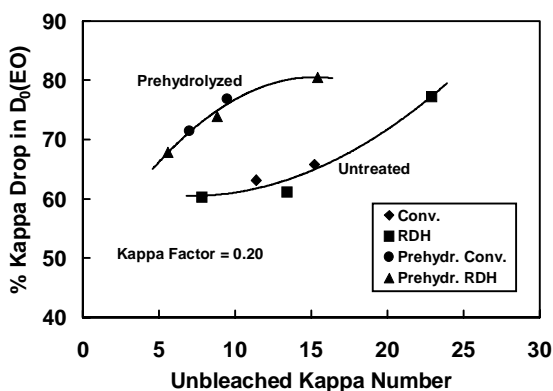


Figure 4.9. Effect of prehydrolysis on $D_0(\text{EO})$ delignification.

Full Bleaching of Prehydrolyzed Pulps

A sweetgum conventional pulp having an unbleached kappa number of 12.6 was bleached in a $D(\text{EO})\text{DD}$ sequence with and without a preceding hydrolysis step, giving the results shown in Table 4.6. In bleaching the unhydrolyzed pulp to a brightness of 88.4, the total ClO_2 consumption was 2.16%. Atmospheric prehydrolysis of the same pulp for 5 h at 95°C reduced its kappa number to 6.7, allowing a brightness of 88.4 to be reached with only 1.71% ClO_2 . A pressurized prehydrolysis for 1 h at approximately 125°C reduced the kappa number to 6.1 and allowed bleaching to 88.7 brightness with the expenditure of only 1.26% ClO_2 . Finally, the same sequence was repeated, except that the pulp was transferred directly from the prehydrolysis to the D_0 stage with no intermediate washing.

Table 4.6. D(EO)DD Bleaching After Hydrolysis

Hydro- lysis ¹ Before D ₀ Stage	D ₀ Stage ²				(EO) Stage ³			D ₁ Stage ⁴		D ₂ Stage ⁴			Summary	
	Kappa Number Enter- ing	Wash After Pre- hydro- lysis?	Visc- osity Enter- ing, mPa.s	Kappa Number Leav- ing	NaOH Charge, % o.d.p.	Kappa Number	Visc- osity, mPa.s	ClO ₂ , % o.d.	Bright- ness	ClO ₂ , % o.d.	Bright- ness	Visc- osity, mPa.s	No. of Wash- ers	Total ClO ₂ , % o.d. pulp
None	12.6	Yes	34.8	5.7	1.0	3.5	33.2	0.8	84.0	0.4	88.4	25.1	4	2.16
Atm.	6.7	Yes	22.4	3.4	1.0	1.7	21.1	0.4	84.4	0.8	88.4	16.1	5	1.71
Press.	6.1	Yes	14.6	2.3	1.0	1.5	13.7	0.4	85.7	0.4	88.7	13.3	5	1.26
Press.	6.1	No	22.1	4.4	1.3	2.2	21.2	0.8	84.8	0.6	88.7	n.d.	4	1.86

¹Hydrolysis conditions: 12% consistency; initial pH adj. to 3.0 with H₂SO₄. Atmospheric: 5 h, 95°C; Pressurized: 1 h, approx. 125°C

²D₀ stage conditions: 30 min., 45°C, 3% consistency, final pH 2.5-3.0.

³(EO) stage conditions: Pin mixer, 60 min., 75°C, 10% consy., oxygen pressure initially 60 psig and decreased by 10 psig every 5 min.

⁴D₁ and D₂ stage conditions: 180 min., 70°C, 10% consistency, final pH 3.7-4.5.

In this case, 1.86% ClO_2 was required to reach 88.7 brightness. Although no optimization was attempted in these experiments, the results demonstrate the potential for commercially viable applications of prehydrolysis in the bleaching of southern HW pulps. Significant ClO_2 savings may be realizable, especially if a washer is available for use after the prehydrolysis stage. With no washer at this point ClO_2 savings will likely be smaller, but still appreciable.

Residual Lignin Studies

The bleachability of HW kraft pulps can be influenced by both the presence of hexenuronic acids and the structure of their residual lignin. Past studies by Gellerstedt, Froass et al., Argyropoulos et al., and others^{1,23,19} have clearly established the role of lignin in influencing pulp bleachability for SW kraft pulps. To explore the relationship between bleachability, lignin structure, and pulping technology, the HW kraft pulps prepared for this study were analyzed for residual lignin structure. These structure studies were accomplished by isolating lignin from the RDH and conventional kraft pulps using an acidic dioxane lignin extraction procedure. The residual lignin samples from the kraft brownstocks were then analyzed by quantitative ^{13}C NMR methods. This procedure provides a facile means of determining the relative amounts of various lignin structural components including diphenyl methane units, methoxyl groups, β -O-aryl ether units, and acid groups. Figures 4.10- 4.13 summarize the results.

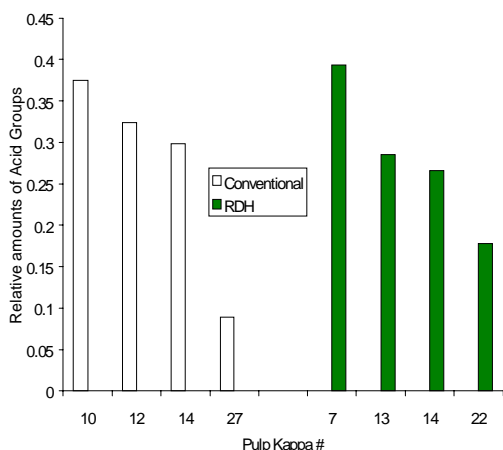


Figure 4.10. Residual lignin acid group content for series of conventional and RDH pulps. (Note: acid group content is relative to signal intensity of aromatic signal).

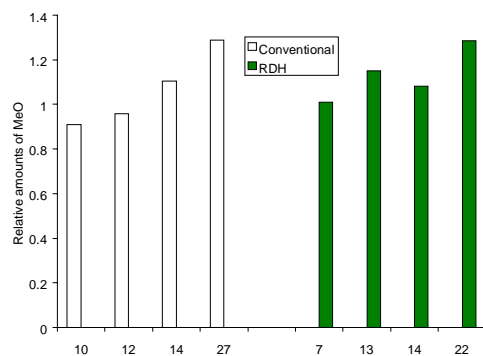


Figure 4.11. Residual lignin methoxyl group content for series of conventional and RDH pulps. (Note: MeO content is relative to signal intensity of aromatic signal).

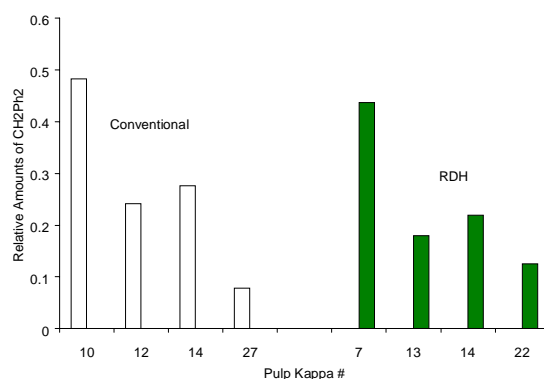


Figure 4.12. Residual lignin diphenyl methane group content for series of conventional and RDH pulps. (Note: Ph₂C content is relative to signal intensity of aromatic signal).

In general, the results are consistent with modern theories of pulping chemistry. They indicate that the lignin suffers a depletion of β -O-aryl ether units and methoxyl units as the kappa number of the pulp is reduced from 27 to 7. In addition, as the kraft cook is extended, the residual lignin in the pulp becomes enriched in acid groups and condensed lignin structures. Of greater significance in the context of the present study is the very close structural resemblance between the RDH and conventional kraft pulps. This similarity exists in spite of the differences between the two batch cooking technologies (RDH and conventional) employed in the study. It suggests that lignin structure is unlikely to result in differences in bleachability at a given kappa number.

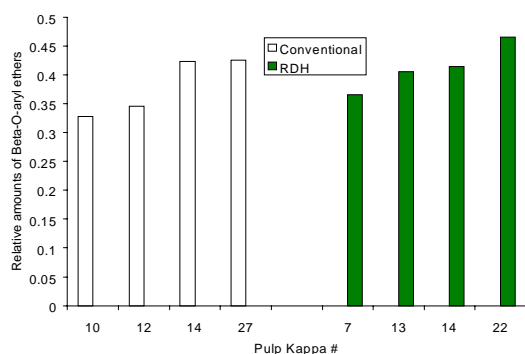


Figure 4.13 Residual lignin β -O-aryl ether group content for series of conventional and RDH pulps. (Note: β -O-aryl ether content is relative to signal intensity of aromatic signal).

4.3 CONCLUSIONS:

D₀ stage filtrate, pH 3 formate buffer, and sulfuric acid give similar results when used as media in acid hydrolysis to reduce the kappa number of HW kraft pulps. There are no significant differences between conventional and simulated RDH pulps with respect to their response to hydrolysis.

Under atmospheric conditions, complete hydrolysis, as indicated by kappa number reduction, requires a retention time of approximately 5-hours. On the other hand, it is possible to achieve appreciable extents of removal at retention times in the 2-3 h range.

Pressurized hydrolysis for 2 h at 100°C reduces the kappa number of HW pulps to the same extent as atmospheric hydrolysis for 5 h at 95°C. Increasing the temperature to 125°C allows the retention time to be shortened to 1 h with no loss in removal efficiency, or to fifteen minutes with a 20% loss in efficiency. Viscosity losses were modest under all conditions.

In atmospheric hydrolysis, the consistency can be raised to 12% with no loss in efficiency or selectivity. Higher consistencies lead to poorer selectivity and may also give slightly lower efficiency. Prehydrolysis of HW kraft pulps increases the efficiency of subsequent D₀(EO) delignification in spite of the fact that it decreases the kappa number of the pulp entering the D₀ stage. The result is a sharp increase in efficiency at any given entering kappa number. The potential exists for commercially viable applications of prehydrolysis in the bleaching of southern HW pulps. Significant ClO₂ savings may be realizable, especially if a washer is available for use after the prehydrolysis stage. With no washer at this point, ClO₂ savings will likely be smaller, but still appreciable.

Residual lignins in pulps prepared in the laboratory by conventional batch kraft cooking and simulated RDH cooking are structurally very similar. This observation is consistent with their similar response to D(EO) delignification.

4.4 EXPERIMENTAL:

Materials

All chemical reagents were commercially purchased and used as received. Commercial HW and SW kraft pulps were acquired from several mills, principally in the US southeast. In addition, a series of SW and HW batch and extended modified kraft cooks were performed in the laboratory. The SW kraft laboratory cooks were described in chapter 2 of this report and originated from a sole loblolly pine wood source. All pulps employed for hexenuronic acid analysis were extensively washed until the effluents were pH neutral and colorless.

HW Kraft Pulping

All kraft cooks were performed using a common supply of sweetgum from a 20–25 year-old tree. The wood was visually free of disease and compression wood. After debarking and chipping, the chips were screened and stored at 4°C until used. Conventional HW kraft cooking trials²⁰ were performed at a 4:1 liquor/wood ratio using 30% white liquor sulfidity (active alkali basis). Chips and cooking liquor were heated to 165°C for 90 minutes and kept at that temperature until the desired H-factor was reached.

Rapid Displacement Heating (RDH) kraft cooking trials²¹ were performed using a fully automated control system employing white liquor with 30% sulfidity (active alkali basis) and a cooking temperature of 165°C. White liquor addition was split into warm and hot black liquor pretreatments. The wood chips were pretreated with warm and hot black liquors before cooking with white liquor. At the end of the cook, hot cooking liquor inside the digester was displaced back to the hot and the warm black liquor accumulators using washer filtrate from a brownstock washing system. Table 4.1 summarizes some of the important HW kraft cooking parameters and pulp properties.

Bleaching

Conditions for each bleaching stage are given in footnotes to the bleaching data tables. Washing was omitted after the hydrolysis stages. Otherwise, pulps were well washed after each stage. General descriptions of the individual stages are given below. Hydrolysis stages were done in plastic bags placed either in a temperature-controlled water bath or in a glass beaker over water in an autoclave. Initial chlorine dioxide (D_0) stages were done in a Quantum mixer or in plastic bags. Simple extraction (E_2) stages as well as D_1 and D_2 stages were done in sealed plastic bags in a temperature-controlled water bath. Oxygen-reinforced extraction (EO) stages were done in a pressurized pin mixer with electric heating.

Pulp Testing

All pulp testing was done according to TAPPI Test Methods.

Xylan Analysis of Pulps

The xylan content of selected kraft pulps was determined following literature methods.²²

Residual Lignin Isolation and Analysis

Isolation of residual lignin from the HW kraft pulps was accomplished by employing standard literature methods.^{1,23,24} In brief, air-dried pulp (40 g oven dry weight) was added to an aqueous 1.00 N HCl (100 ml), p-dioxane (900 mL) solution and this mixture was refluxed for 2 hr under an argon atmosphere. The mixture was then filtered, pH adjusted to 5 with a saturated NaHCO_3 aqueous solution, and vacuum concentrated to 10% of its initial volume. The solution was then pH adjusted to 2.0 with 1N HCl, and the precipitated lignin was isolated by centrifugation. The lignin was then washed and vacuum dried. This procedure afforded, on average, a 40-55% yield of residual lignin in the pulp.

^{13}C NMR Analysis of Residual Lignin

Quantitative ^{13}C NMR spectra were recorded with an inverse gated 90° pulse sequence, a 14 s delay, a TD of 32k, and a sweep width of 230 ppm.²⁵ The NMR experiments were performed at 50°C on samples containing 200-400 mg lignin/mL of DMSO-d_6 . The Fourier transformed spectra were integrated according to reported chemical shifts for lignin functional groups. The integrals were normalized to the aromatic signals, which were assumed to have 6 carbons.

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