Institute of Paper Science and Technology
Atlanta, Georgia

IPST Technical Paper Series Number 742

NMR Analysis of Oxidative Alkaline Extraction Stage Lignins

T.M. Runge and A.J. Ragauskas

August 1998

Submitted to
Holzforschung

INSTITUTE OF PAPER SCIENCE AND TECHNOLOGY
PURPOSE AND MISSIONS

The Institute of Paper Science and Technology is an independent graduate school, research organization, and information center for science and technology mainly concerned with manufacture and uses of pulp, paper, paperboard, and other forest products and byproducts. Established in 1929, the Institute provides research and information services to the wood, fiber, and allied industries in a unique partnership between education and business. The Institute is supported by 52 North American companies. The purpose of the Institute is fulfilled through four missions, which are:

- to provide a multidisciplinary education to students who advance the science and technology of the industry and who rise into leadership positions within the industry;
- to conduct and foster research that creates knowledge to satisfy the technological needs of the industry;
- to serve as a key global resource for the acquisition, assessment, and dissemination of industry information, providing critically important information to decision-makers at all levels of the industry; and
- to aggressively seek out technological opportunities and facilitate the transfer and implementation of those technologies in collaboration with industry partners.

ACCREDITATION

The Institute of Paper Science and Technology is accredited by the Commission on Colleges of the Southern Association of Colleges and Schools to award the Master of Science and Doctor of Philosophy degrees.

NOTICE AND DISCLAIMER

The Institute of Paper Science and Technology (IPST) has provided a high standard of professional service and has put forth its best efforts within the time and funds available for this project. The information and conclusions are advisory and are intended only for internal use by any company who may receive this report. Each company must decide for itself the best approach to solving any problems it may have and how, or whether, this reported information should be considered in its approach.

IPST does not recommend particular products, procedures, materials, or service. These are included only in the interest of completeness within a laboratory context and budgetary constraint. Actual products, procedures, materials, and services used may differ and are peculiar to the operations of each company.

In no event shall IPST or its employees and agents have any obligation or liability for damages including, but not limited to, consequential damages arising out of or in connection with any company's use of or inability to use the reported information. IPST provides no warranty or guaranty of results.

Running Title: Analysis of Bleached Lignins

Title: NMR Analysis of Oxidative Alkaline Extraction Stage Lignins

Authors:
Troy M. Runge and Arthur J. Ragauskas
Institute of Paper Science and Technology
500 10th Street NW
Atlanta, GA 30318

Keywords:

Lignin, Bleaching, Oxidative, Alkaline extraction, Chlorine dioxide, Sodium Hydroxide, Oxygen, Hydrogen Peroxide, Quantitative NMR, ^{1}H NMR, ^{13}C NMR

Summary

Chlorine dioxide delignified pulp was subjected to various oxidative alkaline extraction stages (EAr, E, EO, EP, and EPO) from which the residual and effluent lignins were isolated and characterized by ^{1}H and ^{13}C NMR. Results of the NMR analyses indicate an increase in unconjugated carboxyl content of the lignins with the alkali treatment; a decrease in phenolic and formyl groups with oxidant reinforcement, especially oxygen; and an enrichment in methoxyl groups with increasing amount of oxidant reinforcement. The alkaline extracted pulps were further treated to a second chlorine dioxide stage from which the residual lignins were extracted and analyzed by ^{1}H NMR. Significant structural differences were noted between the various oxidative E stage and D_1 stage lignins.

Introduction

The increasing use of ECF bleaching technologies (Pyrke, 1996; Walden's Fiber and Board Report 1997) has renewed interest in the delignification and bleaching chemistry of chlorine dioxide. The fundamental bleaching chemistry of chlorine dioxide has been studied with a variety of monomeric and dimeric lignin model compounds. These studies have found that free phenolic structures are very reactive with ClO_2 and are believed to be the primary reaction site forming a variety of oxidized and chlorinated products (Lindgren 1971; Nonni and Dence 1981; Brage *et al.* 1991 a; Brage *et al.* 1991 b; McKague et al 1993; McKague *et al.* 1994; Ni *et al.* 1994; Dence 1996). The formation of biphenyl type products has also been observed and this has been attributed to chlorine dioxide initiated radical coupling reactions. Although chlorine dioxide has been reported to react with etherified phenolic structures the rates of oxidation are significantly slower than with phenolic structures. McKague *et. al.* have shown NaOH treatment will readily saponify methyl esters, open lactone rings to muconic acids, and eliminate chlorine of ClO_2 treated lignin model compounds (McKague 1995).

Lindstom and Osterberg performed an extensive study on the high molecular mass material in spent bleach liquors from a D_0 stage and from its subsequent alkaline extraction stage (Lindstrom and Osteberg 1984; Osteberg and Lindstrom 1985). The D_0 effluents contained chlorinated material, whereas the DE effluents were significantly reduced in organic chlorine content, supporting proposed chlorine elimination reactions that are hypothesized to occur during an alkaline extraction stage. NMR analysis of these effluents indicated the presence of both aliphatic and conjugated carboxylic acids. The latter signals were attributed to the presence of muconic acid type structures (Osteberg and Lindstrom 1985).

Gellerstedt *et al.* have found that the residual lignin isolated from a OD(EOP) bleached softwood kraft pulp had not undergone dramatic modifications (Gellerstedt *et al.* 1991; Gellerstedt and Lindfors 1991). The major differences between an unbleached residual lignin and a OD(EOP) residual lignin were a lower content of aromatic ring carbons, a lower content of methoxyl groups, and a higher content of carboxylic acid groups. Studies by Sun and Argyropoulos (Sun and Argyropoulos 1996) indicated that at low charges of chlorine dioxide, guaiacyl phenolic hydroxyl groups are rapidly eliminated from lignin but at higher charges, this phenolic elimination levels off. This effect was interpreted to be due to the possible formation of phenolic groups by the scission of aryl ether linkages by elemental chlorine. The same chemical consumption trends were noted for condensed phenolic structures and this attributed to the enrichment of unreactive condensed lignin structures and possibly the formation of condensed phenolic groups by radical coupling reactions.

Hanna *et al.* and Ragauskas *et al.* (Hanna *et al.* 1998; Raguaskas *et al.* 1997; Ragauskas *et al.* 1998) have shown that pulp bleachability for a typical D(EO) sequence can be influenced by the extent of delignification and the type of pulping technology employed. Residual lignin studies suggested that the key lignin parameters influencing D(EO) bleachability are due to the presence of uncondensed and condensed phenolics and the content of β-O aryl ethers in the residual lignin.

Although further studies are needed into the bleaching chemistry of chlorine dioxide, an under-investigated aspect of ECF bleaching is the fundamental chemistry associated with an oxidative alkaline extraction stage. A variety of researchers have documented the improved delignification performance of an (EO), (EP), or (EOP) stage versus an E-stage after the D delignification stage (Meng *et al.* 1984; Althouse 1988; Klein *et al.* 1994; Van Lierop *et al.* 1994; Clark and Johansson 1995; Berry 1996). Sun and Argyropoloulos have examined the bleaching chemistry of an EOP stage and concluded similar reactions occur in an EOP stage as an O_2 delignification stage, although to a lesser extent (Sun and Argyropoulos 1995). The main reactions found in these stages were the formation of carboxylic acids and the degradation of phenolic components. Studies by Runge *et al.* investigated the influence of the type of oxidative reinforcement in an E stage was examined (Runge *et al.* 1997; Runge *et al.* 1998). These study also found the major effects of that oxidant reinforcement to be an enrichment in carboxylic acids and the degradation of phenolic components. Additionally, apparent molecular weight distribution of the dissolved lignins were shown to decrease with increased oxidant reinforcement, clearly suggesting that the oxidants are capable of significantly degrading lignin in this stage.

In this study, we further examined the chemical changes imparted in an E-stage when reinforced with an oxidant. ^{1}H and ^{13}C NMR are employed as spectroscopic tools to determine functional changes caused by a chlorine dioxide stage, following the oxidative alkaline extraction stage, performed with various oxidant reinforcements.

Materials and Methods

Materials

Chemicals were used as received from Aldrich, Acros, and VWR, except for the p-dioxane, which was distilled in the presence of $NaBH_4$. NMR solvents were purchased anhydrous and dried over 4A molecular sieves prior to use. Filtered nanopure deionized (DI) water was used where water was required. 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.

Pulps

The kraft pulp was prepared from a single loblolly pine (*Pinus taeda*) approximately 30 years in age and free from disease. The wood was debarked, chipped, screened, and conventionally cooked in a laboratory scale digester. The pulping was performed at 18.8% active alkali, 30% sulfidity, 1500 H-factor, 4:1 liquor:wood ratio, and a cooking temperature of 172°C. The brownstock was screened, washed, and then submitted to a typical chlorine dioxide (D_0) delignification stage (0.20 kappa factor) in a Quantum reactor at 10% consistency for 45 minutes at 45°C (Reeve 1996). The bleached pulp was then filtered, washed with water, and characterized.

Alkaline Extraction Conditions

The chlorine dioxide delignified pulp was added to a continuously stirred pressure reactor, and the consistency was adjusted to 10%. The pulp was then warmed to 70°C, bleaching chemicals were added, and the mixture was stirred for 75 minutes (Berry 1996). Table 1 summarizes the chemicals and charges employed during the alkaline extraction stage. Upon completion of the extraction, the pulp was removed from the reactor, filtered, and thoroughly washed. The alkaline extracted pulps were characterized in terms of kappa number, acid insoluble lignin %, and pulp viscosity.

Pulp Characterization

The pulp's lignin content was measured using a 1/4 kappa test (TAPPI Useful Method UM-246) and a modified acid insoluble lignin test method (TAPPI Test Method T 222 om–88). The acid insoluble lignin method was modified to use an autoclave to speed up the sulfuric acid hydrolysis of the carbohydrates in the pulp (Karr *et al.* 1991). The remaining lignin was filtered, dried, and weighed to give an acid-insoluble weight percentage. Percent delignification was calculated from the kappa number and acid insoluble lignin content using the brownstock lignin as a reference. Carbohydrate degradation was measured indirectly by solvating the pulp in cupriethylenediamine and measuring these solutions' viscosities with a capillary viscometer (TAPPI Test Method T 230 om–94). The D_1 stage pulps were also measured for delignification by acid insoluble lignin content, CED viscosity, and ISO Brightness. The selectivity of the bleach stages was determined by the quotient of Δ kappa/Δ viscosity.

Ninety-five percent confidence intervals (CI) on the delignification % and CED viscosity data were calculated using a pooled variance obtained from three complete replicates on the D, DE, and D(EP) pulps. The variance value was obtained from 3 replicates for the D, DE, and D(EP) pulps for kappa (3 tests/sub-sample), acid insoluble lignin (3 tests/sub-sample), and CED viscosity (2 tests/sub-sample). Confidence intervals on the ISO brightness data were calculated using a pooled variance obtained from three complete replicates on the DED pulps (4 tests/sub-sample). The 95% CI are shown with the characterization data in the Results and Discussion section.

Lignin Isolation

The bleached pulps' residual lignin was isolated using an acidic p-dioxane hydrolysis procedure modified from the literature (Pepper *et al.* 1959; Gellerstedt and Lindfors 1991; Gellerstedt *et al.* 1994; Froass *et al.* 1996). The procedure placed the dried pulps in a round-bottom flask with a solution of 0.10 M HCl 9:1 dioxane:water to achieve a final consistency of 8%. The pulp slurry was refluxed for 2 hr under argon before filtering through celite and a medium glass-fritted funnel. The celite was washed with additional 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 1N 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.

Dissolved lignins in the various alkaline extraction stage effluents were also isolated. The collected effluents were filtered through celite, neutralized with 1N HCl, and concentrated. The concentrated effluent samples were freeze-dried and vacuum-dried to complete dryness. A portion of the dried effluent was measured for ash content. The majority of the effluent was resuspended in water, acid precipitated, coalesced by freezing/thawing, centrifuged, and decanted. The remaining solid was washed in this manner 3 times before freeze-drying to obtain the final purified lignin. The yield was calculated by the ratio of the purified weight to the initial weight after correction for the ash content.

^{1}H NMR Spectroscopy

Quantitative ^{1}H NMR spectra were acquired on underivatized lignins in DMSO-d_6 using trimethyl silyl propionate-d_4 (TSP) as the internal standard (Li and Lundquist 1994; Ragauskas *et al.* 1997; Ragauskas *et al.* 1998; Moe *et al.* 1998). ^{1}H NMR conditions included a 90 degree pulse, a TD of 32k, a 15s 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 the 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. A typical ^{1}H NMR spectrum is shown in Figure 1.

^{13}C NMR Spectroscopy

Quantitative ^{13}C NMR spectra were recorded with an inverse gated 90 degree pulse sequence, an 11s delay, a TD of 32k, and a sweep width of 330 ppm (Robert 1992; Ralph *et al.* 1996). The NMR experiments were performed at 50°C on samples containing 300-400 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 (Robert 1992). A typical ^{13}C NMR spectra is shown in Figure 2.

NMR Error Analysis

The error analysis was performed by bleaching, isolating, and analyzing the residual lignin of a DE sequence three separate times and comparing the results. The standard deviations were used along with a student t value to obtain a least significant difference (LSD) value at a 95 % confidence interval. The calculated LSD values for the functional groups obtained by ^1H and ^{13}C NMR are shown in Table 2 and Table 3, respectively. The ^1H NMR data show relatively small variation with the notable exception of the methoxyl and aliphatic protons. The overlap of these groups makes integration difficult.

Results and Discussion

Pulp Characterization

The chemistry of an alkaline extraction stage was explored by preparing a SW kraft pulp with a kappa number of 30.4 (viscosity of 30.3 cP). This pulp was then bleached under standard Do conditions with a kappa factor of 0.20, at 10% consistency for 45 min at 45°C. The bleached pulp was then washed and extracted under various alkaline extraction conditions. The results of the alkaline extraction stages are summarized in Table 4. An examination of the delignification trends indicated that all extraction stages reinforced with an oxidant, including a typical E-stage (containing dissolved ambient oxygen) out-performed the lignin extraction properties of an (EAr) stage. The application of additional oxidant (either O and/or P) enhanced the delignification properties of the alkaline extraction stage. The CED viscosity measurements suggested that the addition of an oxidant in the alkaline extraction stage did not significantly degrade the pulp carbohydrates.

Oxidative reinforcement of the alkaline extraction stage has a profound effect on increasing the brightness values after the D_1 stage, as shown by the D_1 pulp properties in Table 4. Although higher brightness values are expected for pulps with reduced lignin contents, it is interesting to note that the D(EP)D pulps yielded a higher brightness value than the D(EO)D pulps, despite the fact that the D(EP)D pulps had greater amounts of lignin. These results emphasize the significance of chromophore removal in oxidative alkaline extraction stages for subsequent brightness development.

NMR Findings

The structure of residual and effluent lignin throughout the first three stages of a bleaching sequence were characterized by well-established quantitative ^{1}H and ^{13}C NMR methods. Analyzing lignins by NMR provides for a facile and rigorous characterization of numerous functional groups. Residual lignins were isolated for NMR analysis from the characterized bleached pulps using an acid hydrolysis procedure. The yields of the residual lignins, shown in Table 5, are typical for kraft pulps with the notable exception of the D_1 residual lignins. Two possibilities for these lignins' low yields are hypothesized. The first reason may be due to an overestimation of the lignin content, as it is difficult to measure acid insoluble lignin in samples with this low amount of lignin. Kappa number determinations were not possible, as the lignin content was too low. The second reason for the low yields of D_1 lignins may be that these lignins are highly oxidized and are difficult to precipitate when using the acid hydrolysis procedure. Table 5 also includes the calculated yields of dissolved lignins isolated from the effluent of the various alkaline extraction stages.

Carboxylic Acid Content

One of the most significant functional group changes that occurred with all of the alkaline extraction stages examined was the substantial increase in carboxylic acid group content for the residual and effluent lignin. This can be seen in the carboxylic acid ^{1}H NMR data shown in Table 6. The carboxyl group increase appears to be independent of oxidant reinforcement, suggesting it is due to the alkali. The analysis of the carboxyl moiety was further explored using ^{13}C NMR to discern between the carbon atoms of conjugated and unconjugated carboxyl groups also shown in Table 6 (Robert 1992). The data show the increase in carboxyl groups for the alkaline extraction stage to be comprised entirely of unconjugated COOH groups.

This previously unreported effect was attributed to be due, in part, to muconic acid methyl ester (MAME) saponification, as shown in Figure 3. Both the original MAME and the formed muconic acid are shown with their equilibrium closed lactone form. It is interesting to note that the lactone form represents the unconjugated COOH form, which is the component that increases during the alkaline extraction. This indicates that either the alkaline extraction conditions or the isolation procedure causes an equilibrium shift from the muconic acid to the lactone structures.

Further proof of the MAME saponification reaction occurring during the alkaline extraction can be seen from the stacked carbon plot shown in Figure 4. The plot shows D residual lignin and E stage residual and effluent lignin. A peak at 52 ppm (Evtuguin and Robert 1997) corresponding to the methyl ester carbon can be clearly seen in the D_0 stage residual lignin spectra, but is eliminated from both the E stage's residual and effluent lignins.

Phenolic Content

Unsubstituted and C5-substituted phenolic content of the isolated lignins were measured by ^{1}H NMR. The results are shown in Table 7. In general, the phenolic content decreased for lignins isolated from alkaline extraction stages with oxidant reinforcement, especially the stages with oxygen reinforcement, namely, the (EO) and (EPO) stages. The decrease in unsubstituted phenolic groups was more predominant than the decrease in C5-substituted phenolic groups. This suggests that C5-substituted units are less reactive to oxygen oxidation than unsubstituted phenolic units. Other researchers have noted this trend of substituted phenolic groups being more difficult to oxidize (Gellerstedt et al 1986; Sun and Argyropoulos 1995).

Methoxyl Content

The methoxyl content of alkaline extracted lignin was measured with ^{13}C NMR. The methoxyl data, shown in Table 8, indicates a slight increase in methoxyl content with increasing oxidative treatment. This is believed to be due to an enrichment of lignin containing methoxyl groups relative to the aromatic content. The inclusion of oxygen in an alkaline extraction stage leads to a selective oxidation of phenolic units. The oxidation is capable of destroying the aromatic nature of the phenolic group. Hence, after an oxygen reinforced alkaline extraction stage, the lignin is enriched with aromatic methoxylated lignin. Since ^{13}C NMR uses the aromatic region as the quantitative reference, it displays an enrichment of methoxyl content in both the residual and effluent lignins.

Formyl Content

The formyl content of the isolated lignins was measured with ^{1}H NMR, shown in Table 9. The data reveals a decrease of the lignin's formyl content during alkaline extraction stages reinforced with oxygen. It is possible that the formyl groups are being oxidized to carboxyl groups by the oxygen, although no additional increase in COOH groups was noted for the oxygen reinforced lignins. The negligible change in the formyl content indicates that this is a relatively minor reaction if it does occur.

Unaltered ^{13}C Functional Groups in the E Stage*

Although, ^{13}C NMR provides a valuable tool capable of characterizing many lignin functional groups, the majority of these groups were found not to be insensitive to the various alkaline extraction conditions. In the analysis of the effluent and residual lignins isolated in this study the aliphatic C-O bonds of the phenylpropane unit appeared to be relatively insensitive to the conditions used in the alkaline extraction procedure. As summarized in Table 10, the relative amounts of these units appears to increase after the D_0 stage and then not change much further. These results suggest that the oxidative chemistry of an (EP), (EO), or (EPO) stage functions primarily on the aromatic component of lignin.

Second D stage residual lignins

The five different alkaline extraction stage pulps were further treated to a second chlorine dioxide (D_1) stage. This pulp's residual lignin was isolated and examined by ^1H NMR for functional group changes. A typical spectrum of a D_1 lignin is shown in Figure 5. The plot shows the aromatic nature of this lignin diminished while the aliphatic nature increased. A comparison of the D_1 residual lignin's ^1H NMR data to each other yielded no statistical difference. This implies that differences measured in the alkaline extraction stage from the various oxidants did not carry through the D_1 stage. When the D_1 lignin ^1H NMR data were compared to the previous E* stage, considerable changes in all the structural groups were noted. To concisely report the changes, average values for the various alkaline extraction stages were compared to the average of the residual D_1 stage. These comparisons are shown in Table 11.

These results indicate that the D1 stage aggressively removes most of the residual lignin structure remaining in the pulp. The lack of correlation between residual lignin from specific DE*D stages and the brightness values reported in Table 4 suggests that the structural parameters reported in Table 13 are not principal components in determining the observed brightness values.

Conclusions

The results of these studies suggest that the bulk of the oxidative degradation in a DE* treatment occurs during the D_0 stage. The use of the oxygen-free (EAr) stage provided an effective tool to study the effects of ambient oxygen dissolved in an E stage. Reinforcement of an E stage with either oxygen and/or peroxide resulted in additional removal of free phenolics from lignin primarily by oxidation of uncondensed structures. The role of condensed (C5-substituted) lignin in influencing the reactivity of lignin is especially important and is consistent with the results of several other researchers studying pulp bleachability. Along with the changes in phenoxy content, the oxidative reinforcement of an E-stage leads to the formation of additional carboxyl groups. A large portion of the increase in acid groups in E* lignin is due to the saponification of muconic methyl esters. The loss of methoxyl content and aromatic content is consistent with the theorized ClO_2-lignin reactions described in the literature. Presumably some of the methoxyl groups in lignin are demethylated by chlorine during the chlorine dioxide stage forming phenolics groups that are reactive towards oxidative degradation.

The D_1 stage is very effective in oxidizing the majority of the remaining phenolics and aromatic units. Perhaps of greater significance for ECF bleaching is the apparent loss of structural differences in residual lignin after the various DE*D stages, and the lack of correlation between the lignin structures studied and overall brightness values. In hindsight this may be expected since the structural features studied do not directly contribute to the color of the pulp and therefore should not correlate to brightness. Clearly, as the role of bleaching changes from delignification to brightening different structures in pulp influence bleaching. The role of chromophores in pulp bleachability is a more challenging issue to study and one that will require the use of new tools before the relationship is fully understood.

Acknowledgments

The authors wish to thank Drs. T.J. McDonough and D.R. Dimmel for valuable discussions and constructive suggestions, and the Institute of Paper Science and Technology and its Member Companies for supporting this research. The authors would like to specifically thank Union Camp Corporation for the donation of the Loblolly Pine log, and Potlatch Corporation for the pulping of the chips. Portions of this work were used by T.M.R. as partial fulfillment of the requirements for the Ph.D. degree at IPST.

References

Althouse, E.B. 1988. Hydrogen Peroxide Addition to E(O) Bleaching Stages is Beneficial. Pulp and Paper 62(6). pp. 68-70.

Berry, R. 1996. (Oxidative) Alkaline Extraction. Pulp Bleaching: Principles and Practice. Eds. Dence, C., Reeve, D. TAPPI Press, Atlanta. pp. 291-320.

Brage, C., Eriksson, T., and Gierer, G. 1991. Reactions of Chlorine Dioxide with Lignins in Unbleached Pulps. Part I. Holzforschung 45(1). pp. 23-30.

Brage, C., Eriksson, T., and Gierer, G. 1991. Reactions of Chlorine Dioxide with Lignins in Unbleached Pulps. Part II. Holzforschung 45(2). pp. 147-152.

Clark, F.M., and Johansson, N.G. 1995. Alkaline Extraction, E+P and P Stages. 1995. 1995 Bleach-Plant Operations Short Course: Course Notes, TAPPI Press, Session 4, Paper no. 4.

Dence, C.W. 1996. Chemistry of Chemical Pulp Bleaching. Pulp Bleaching: Principles and Practice. Eds. Dence, C., Reeve, D. TAPPI Press, Atlanta. pp. 125-159.

Evtuguin, D.V.; Robert, D. 1997. The Detection of Muconic Acid Type Structures in Oxidized Lignins by ^{13}C NMR Spectroscopy. Wood Science and Technology. 31. pp. 423-431.

Froass, P., Ragauskas, A., McDonough, T., and Jiang, J. 1996. Chemical Structure of Residual Lignin from Kraft Pulp. Journal of Wood Chemistry and Technology. 16(4). pp. 347-365.

Gellerstedt, G., and Lindfors, E. 1991. On the Structure and Reactivity of Residual Lignin in Kraft Pulp Fibers. International Pulp Bleaching Conference Proceedings, Stockholm, Sweden, SPCI. pp. 73-88.

Gellerstedt, G., Gustafsson, K., and Lindfors, E.L. 1986. Structural Changes in Lignin during Oxygen Bleaching. Nordic Pulp and Paper Research Journal. 3. pp.14-17.

Gellerstedt, G., Lindfors, E.L., Pettersson, M., Sjoholm, E., and Robert, D. 1991. Chemical Aspects on Chlorine Dioxide as a Bleaching Agent for Chemical Pulps. International Symposium on Wood and Pulping Chemistry Proceedings, Appita, Parkville, Victoria, Australia, Vol.1. pp. 331.

Gellerstedt, G., Pranda, J., and Lindfors, E.-L. 1994. Structural and Molecular Properties of Residual Birch Kraft Lignins. Journal of Wood Chemistry and Technology. 14(4). pp. 467-482.

Hanna, R.J., Fisher, J.J., Krohn, M.J., Goyal, G.C., Packwood, R.E., and Ragauskas, A.J. 1998. Differences in Bleaching and Refining Response of Displacement Batch Hardwood and Softwood

Caused by Pulping Conditions and Structure of Residual Lignin. 1998 International Pulp Bleaching Conference, Helsinki, Finland, TAPPI Press, Atlanta. pp. 323-328.

Kaar, W.E., Cool, L.G., Merriman, M.M., and Brink, D.L. 1991. The Complete Analysis of Wood Polysaccharides Using HPLC. Journal of Wood Chemistry and Technology. 11(4). pp.447-463.

Klein, R.J., Strunk, W.G., and Vegega, A.M. 1994. Low Kappa Factor Bleaching - A Low Capital Strategy to Achieve EPA Guidelines. International Non-Chlorine Bleaching Conference Proceedings. Miller Freeman, San Francisco. Chapter 2-1.

Li, S., and Lundquist, K. 1994. A New Method for the Analysis of Phenolic Groups in Lignins by ^{1}H-NMR Spectrometry. Nordic Pulp and Paper Research Journal. 3. pp. 191-195.

Lindgren, B.O. 1971. Chlorine Dioxide and Chlorite Oxidation of Phenols Related to Lignin. Svensk Papperstidning. 74(3). pp. 57-63.

Lindstrom, K., and Osterberg, F. 1984. Characterization of High Molecular Mass Chlorinated Matter in Spent Bleach Liquors (SBL) Part 1. Alkaline SBL. Holzforschung. 38(4). pp. 201-212.

McKague, A.B., Kang, G.J., and Reeve, D.W. 1993. Reaction of a Lignin Model Dimer with Chlorine and Chlorine Dioxide. Holzforschung. 47. pp. 497-500.

McKague, A.B., Reeve, D.W., and Xi, F. 1995. Reaction of Lignin Model Compounds Sequentially with Chlorine Dioxide and Sodium Hydroxide. Nordic Pulp and Paper Research Journal. 2. pp. 114-118

McKague, A.B.; Kang, G.J.; Reeve, D.W. 1994. Reactions of Lignin Model Dimers with Chlorine Dioxide. Nordic Pulp and Paper Research Journal. 2. pp. 84-87.

Meng, T., Owens, R., and Strunk, W. 1984. Saving Energy with Hydrogen Peroxide. PIMA Magazine 66(5). pp. 38-40.

Moe, S.T., Ragauskas, A.J., and McDonough, T.J. 1998. Extended Oxygen Delignification of High-Yield Kraft Pulp. Correlation between Residual Lignin Structures and Bleachability by Oxygen and Chlorine Dioxide. 1998 International Pulp Bleaching Conference. Helsinki, Finland. TAPPI Press, Atlanta. pp. 33-40.

Ni, Y., Shen, X., and van Heiningen, A.R.P. 1994. Studies on the Reactions of Phenolic and Non-Phenolic Lignin Model Compounds with Chlorine Dioxide. Journal of Wood Chemistry and Technology. 14(2). pp. 243-262.

Nonni, A.J., and Dence, C.W. 1981. The Reactions of Creosol and Propioguaiacone with Chlorine, Chlorine Dioxide and their Combinations. Svensk Papperstidning. 84. pp. R17-R24.

Osterberg, F., and Lindstrom, K. 1985. Characterization of High Molecular Mass Chlorinated Matter in Spent Bleach Liquors (SBL) Part II. Acidic SBL. Holzforschung. 39(3). pp. 149-158.

Pepper, J., Baylis, P., and Alder, E. 1959. The Isolation and Properties of Lignins Obtained by the Acidolysis of Spruce and Aspen Woods in Dioxane-Water Medium. Canadian Journal of Chemistry. 37. pp. 1241.

Pyrke, D.C. 1996. Elemental Chlorine-Free Grows as Bleaching Method. Distribution Management. 37(5). pp. 32-34.

Ragauskas, A., Lin, W., McDonough, T., and Jiang, J. 1997. Fundamental Parameters Contributing to Residual Lignin in Kraft Pulp. 1997 Tappi Pulping Conference Proceedings. TAPPI Press, Atlanta. pp. 903-908.

Ragauskas, A.J., McDonough, T.J., and Lin, W. 1998. Fundamental Parameters Contributing to Improved ClO_2 Pulp Bleaching. 1998 International Pulp Bleaching Conference, Helsinki, Finland. TAPPI Press, Atlanta. pp. 87-94.

Ralph, S., Ralph, J. and Landucci, L. 1996. NMR Database of Lignin and Cell Wall Model Compounds. Available at URL http://www.dfrc.wisc.edu/software.html. US Forest Products Lab. Madison, WI.

Reeve, D. 1996. Chlorine Dioxide in Delignification. Pulp Bleaching: Principles and Practice. Eds. Dence, C., Reeve, D. TAPPI Press, Atlanta. pp. 263-286.

Robert, D. 1992. Carbon-13 Nuclear Magnetic Resonance Spectrometry. Methods in Lignin Chemistry. Eds. Lin, S.Y., and C.W. Dence. Springer Verlag Berlin, Heidelberg. pp. 251-273.

Runge, T.M., Ragauskas, A.J., and Froass, P.M. 1997. Advances in Understanding the Basics of the First Alkaline Extraction Stage in Bleaching. 1997 Tappi Pulping Conference Proceedings. TAPPI Press, Atlanta. pp. 603-608.

Runge, T.M., Ragauskas, A.J., and McDonough, T.J. 1998. Lignin Structural Changes by Oxidative Alkaline Extraction. 1998 Tappi Pulping Conference Proceedings. TAPPI Press, Atlanta.

Sun, Y., and Argyropoulos, D. 1995. Fundamentals of High-Pressure Oxygen and Low-Pressure Oxygen-Peroxide (Eop). Delignification of Softwood and Hardwood Kraft Pulps. Journal of Pulp and Paper Science. 21(6). pp. J185-190.

Sun, Y., and Argyropoulos, D. 1996. A Comparison of the Reactivity and Efficiency of Ozone, Chlorine Dioxide, Dimethyldioxirane and Hydrogen Peroxide with Residual Kraft Lignin. Holzforschung. 50(2). pp. 175-182.

TAPPI Test Methods 1996-1997. T 222 om-88. TAPPI Press, Atlanta.

TAPPI Test Methods 1996-1997. T 230 om-94. TAPPI Press, Atlanta.

TAPPI Useful Methods 1991. UM-246. TAPPI Press, Atlanta.

Van Lierop, B., Liebergott, N., and Fuabert, M. 1994. ECF Bleaching with Very Low ClO_2 Charges. International Non-Chlorine Bleaching Conference Proceedings. Miller Freeman, San Francisco. Paper 1.

Walden's Fiber and Board Report. 1997 ECF Pulp Reaches 50% of World Market Output. Walden's Fiber and Board Report. 19(8). pp. 3.

Table 1. Alkaline Extraction Conditions

Bleaching Stage	**Bleaching Conditions Employed**[a]
E	2.0% NaOH, performed under atmospheric pressure.
EO	2.5% NaOH, 60 psig initially, decreasing 12 psig/5 minutes, final 50 minutes were performed at atmospheric pressure.
EP	2.5% NaOH and 0.5% hydrogen peroxide.
EPO	2.5% NaOH, 0.5% hydrogen peroxide, 60 psig initially, decreasing 12 psig/5 minutes, final 50 minutes were performed at atmospheric pressure.
EAr	All oxygen was removed from the pulp and chemicals by employing a freeze-thaw cycle. 2.0% NaOH was used, and the reactor was slightly pressurized with argon (10 psig) to prevent the introduction of O_2 into the reactor.

[a] The charge of NaOH employed was selected so as to ensure that the terminal pH was > 10.5

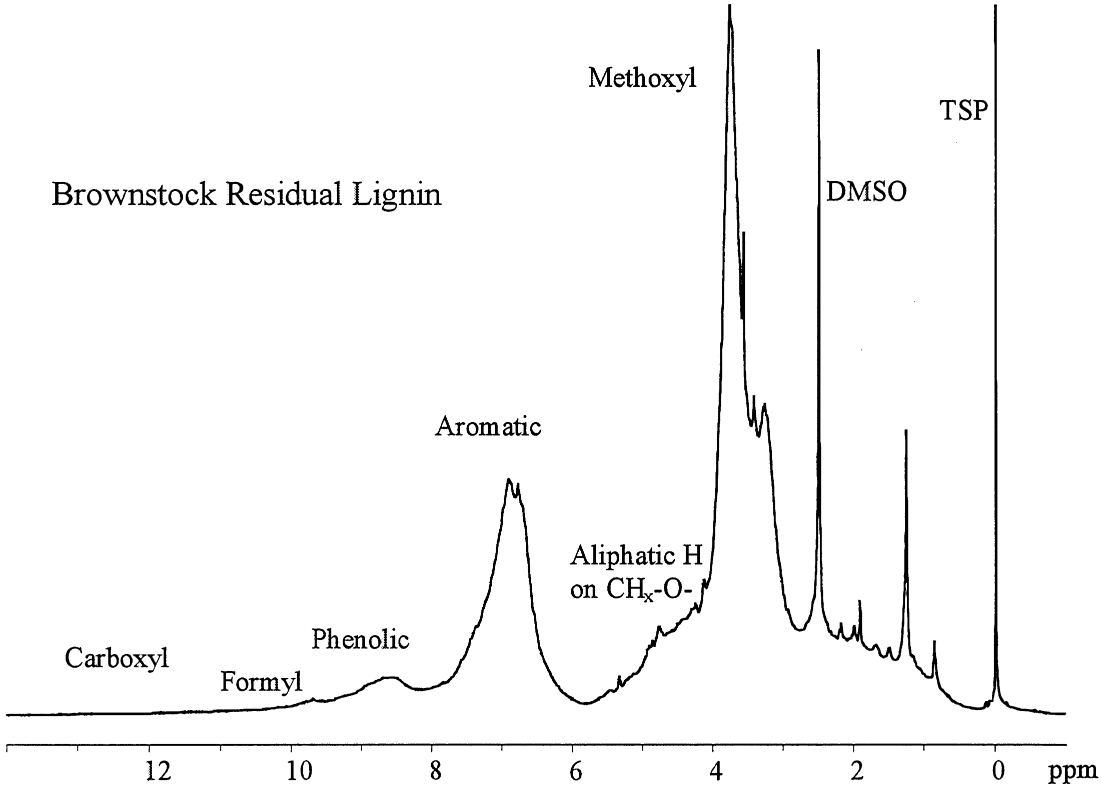

Figure 1. Typical ^{1}H NMR Spectrum (Brownstock Residual Lignin)

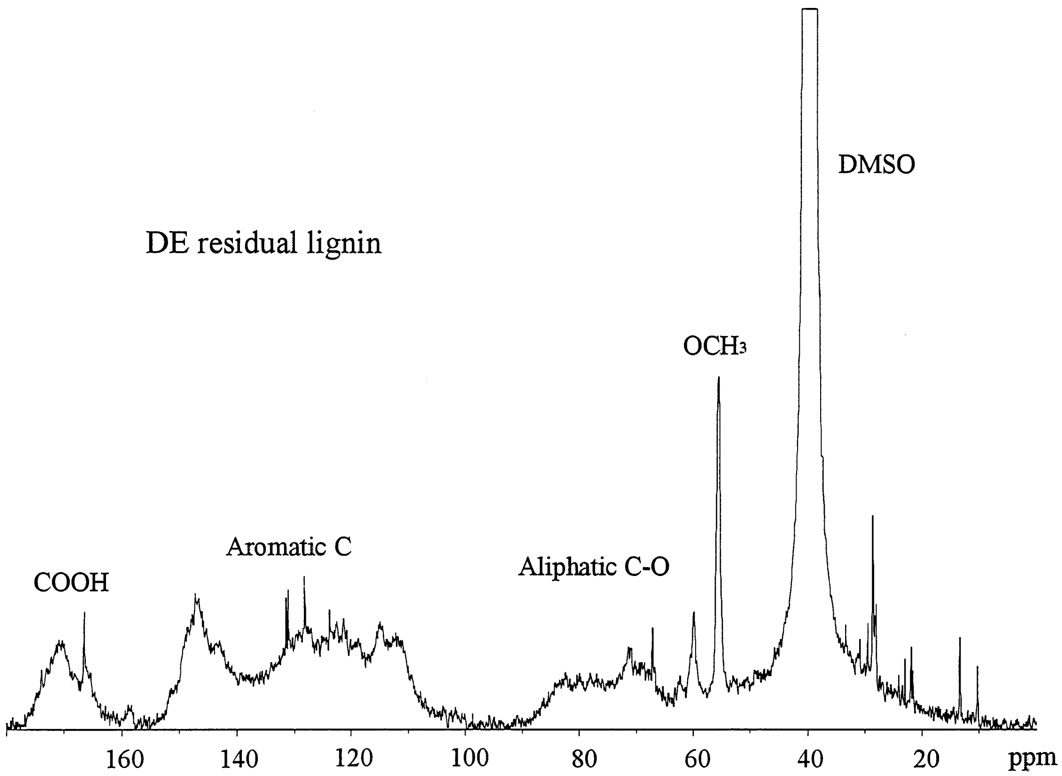

Figure 2. Typical ^{13}C NMR Spectrum (DE Residual Lignin)

Table 2. ^{1}H NMR Least Significant Difference Values

Functional Group	**Average**	**St. dev.**	**LSD**
Carboxyl H	1.84	0.027	0.159
Formyl H	0.26	0.029	0.167
Unsubstituted Phenolic	0.44	0.031	0.183
C5-Substituted Phenolic	0.43	0.009	0.054
Aromatic and Vinyl H	7.09	0.137	0.800
Aliphatic H on CH_x-O-	8.99	0.437	2.551
Methoxyl H	12.04	0.656	3.831

Table 3. ^{13}C NMR Least Significant Difference Values

Functional group	Average[a]	St. dev.	LSD
Unconjugated COOH	0.84	0.016	0.095
Conjugated COOH	0.32	0.015	0.088
Aliphatic C-O bond, Cβ in β-O-4; Cα in β–5 and β–β	0.75	0.072	0.420
Aliphatic C-O bond, Cα in β-O-4	1.09	0.089	0.520
Aliphatic COR	0.44	0.061	0.356
Aliphatic C-O Cγ in β-O-4	0.43	0.039	0.230
Methoxyl OCH_3	0.69	0.017	0.097
Cβ in β–β and Cβ in β-5	0.17	0.019	0.108
Aromatic C-R (substituted)	3.82	0.027	0.158
Aromatic C-H (unsubstituted)	2.18	0.027	0.158

[a]signal intensity measured is relative to the aromatic region (δ 154 – 106 ppm)

Table 4. Pulp Properties of the Brownstock, D stage, and the Various E Stages

Bleaching Sequence	**Delignification by Kappa *(CI)*[a]**	**Delignification by Acid Insol. lignin *(CI)***	**CED Viscosity *(CI)***	**ISO brightness *(CI)***	**Selectivity (Δkappa/Δvisc.)**
D	48.9% *(± 0.89%)*	28.8% *(± 1.47%*	26.7 *(± 0.29)*	N/A	4.36
D(EAr)	23.2% *(± 1.54%*	84.2% *(± 2.55%*	25.7 *(± 0.50)*	N/A	7.60
DE	22.0% *(± 0.89%*	87.0% *(± 1.47%*	22.8 *(± 0.29)*	N/A	2.10
D(EO)	12.9% *(± 1.54%*	88.2% *(± 2.55%*	20.1 *(± 0.50)*	N/A	1.59
D(EP)	16.6% *(± 0.89%*	88.0% *(± 1.47%*	22.3 *(± 0.29)*	N/A	2.21
D(EPO)	11.6% *(± 1.54%*	90.0% *(± 2.55%*	20.4 *(± 0.50)*	N/A	1.81
D(EAr)D	N/A	94.9% *(± 2.55%*	22.2 *(± 0.50)*	73.6 *(± 0.61)*	N/A
DED	N/A	96.3% *(± 2.55%*	21.8 *(± 0.50)*	75.6 *(± 0.35)*	N/A
D(EO)D	N/A	97.1% *(± 2.55%*	18.6 *(± 0.50)*	76.5 *(± 0.61)*	N/A
D(EP)D	N/A	96.7% *(± 2.55%*	22.7 *(± 0.50)*	80.5 *(± 0.35)*	N/A
D(EPO)D	N/A	97.1% *(± 2.55%*	18.6 *(± 0.50)*	84.1 *(± 0.61)*	N/A

[a] CI describes a 95% confidence interval from a pooled variance.

Table 5. Yields of Isolated Lignin

Pulp Description	Yield of Lignin from Acid Hydrolysis[a]	Yield of Lignin from Effluent Precipitation[b]
Brownstock	65.7%	N/A
D	65.0%	N/A
D(EAr)	76.1%	39.2%
DE	77.5%	28.9%
D(EO)	57.3%	27.7%
D(EP)	60.0%	21.5%
D(EPO)	60.6%	18.8%
D(EAr)D	22.9%	N/A
DED	18.7%	N/A
D(EO)D	17.9%	N/A
D(EP)D	13.0%	N/A
D(EPO)D	13.7%	N/A

[a] yield of isolated residual lignins were based on theoretical yield of acid insoluble lignin

[b] yield of isolated dissolved lignins were based on original weight corrected for carbohydrate and ash content.

Table 6. Carboxylic acid content of lignins by NMR

Bleach Stage	^{1}H NMR – COOH (mmol/g isolated lignin)		^{13}C NMR - Unconjugated COOH (mol/aromatic ring)		^{13}C NMR - Conjugated COOH (mol/aromatic ring)	
	Residual	*Effluent*	*Residual*	*Effluent*	*Residual*	*Effluent*
Brownstock	0.68	N/A	0.15	N/A	0.01	N/A
D	1.00	N/A	0.57	N/A	0.38	N/A
D(EAr)	1.83	1.93	0.95	0.86	0.32	0.29
DE	1.87	2.33	0.84	0.84	0.32	0.31
D(EO)	2.00	2.32	0.77	0.82	0.29	0.33
D(EP)	1.78	2.04	0.99	0.96	0.37	0.38
D(EPO)	1.81	1.87	0.84	0.93	0.33	0.39

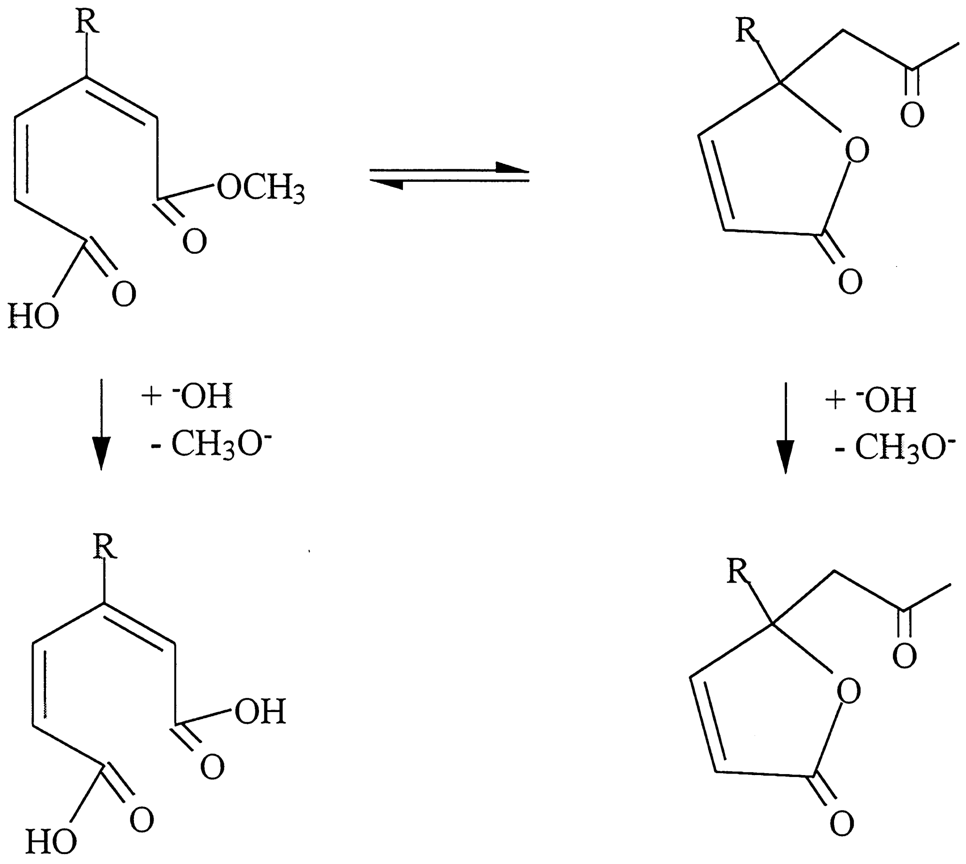

Figure 3. Muconic Acid Methyl Ester Saponification

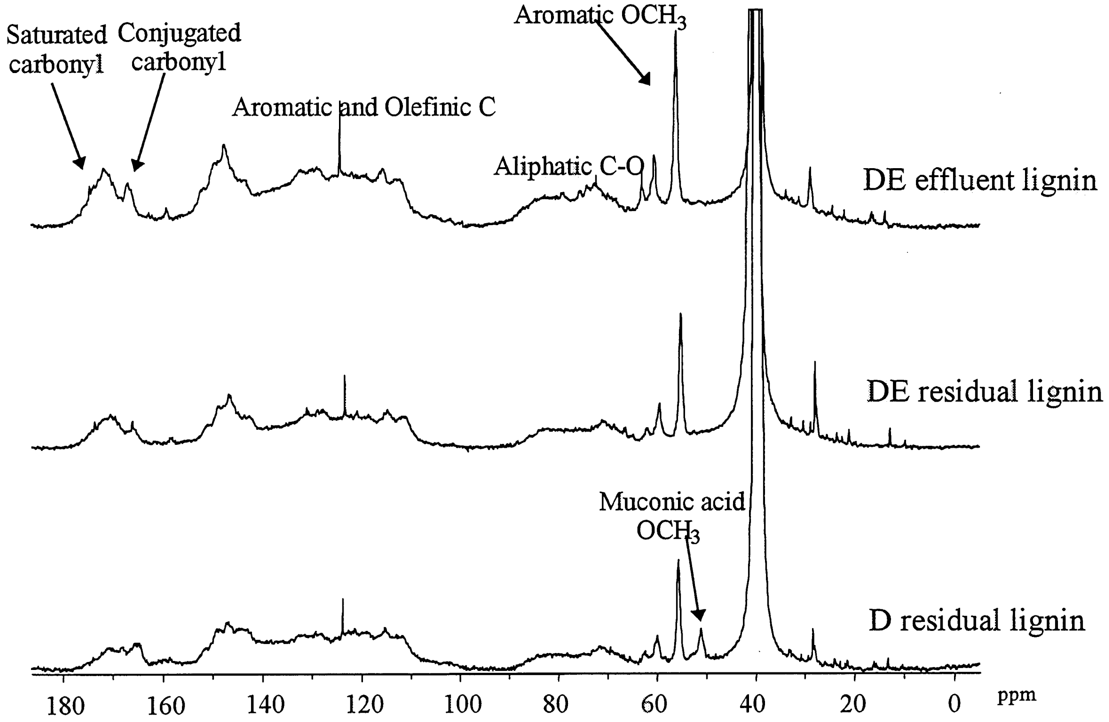

Figure 4. Stacked ^{13}C NMR Plot around an E Bleaching Stage

Table 7. Phenolic content of lignins by ^{1}H NMR

Bleach Stage	**Unsubstituted Phenolic (mmol/g isolated lignin)**		**C5-Substituted Phenolic (mmol/g isolated lignin)**	
	Residual	***Effluent***	***Residual***	***Effluent***
Brownstock	1.97	N/A	1.18	N/A
D	0.76	N/A	0.62	N/A
D(EAr)	0.63	0.48	0.51	0.38
DE	0.56	0.31	0.54	0.29
D(EO)	0.28	0.21	0.39	0.22
D(EP)	0.48	0.28	0.45	0.29
D(EPO)	0.24	0.21	0.29	0.35

Table 8. Methoxyl Content of Lignins by ^{13}C NMR

Bleach Stage	**^{13}C NMR - Methoxyl (mol /aromatic ring)**	
	Residual	***Effluent***
Brownstock	0.87	N/A
D	0.57	N/A
D(EAr)	0.64	0.65
DE	0.69	0.71
D(EO)	0.71	0.77
D(EP)	0.71	0.75
D(EPO)	0.78	0.82

Table 9. Formyl Content of Lignins by ^{1}H NMR

Bleach Stage	**^{1}H NMR - Formyl (mmol/g isolated lignin)**	
	Residual	***Effluent***
Brownstock	0.78	N/A
D	0.38	N/A
D(EAr)	0.32	0.34
DE	0.42	0.30
D(EO)	0.22	0.28
D(EP)	0.33	0.31
D(EPO)	0.17	0.10

Table 10. ^{13}C NMR Functional Groups (mol/mol aromatic ring)[a]

^{13}C NMR Functional group	Brownstock	D residual	D(E*)[b] residual	D(E*) effluent
Unconjugated COOH	0.15	0.64	0.88 (0.091)	0.55 (0.061)
Conjugated COOH	0.01	0.34	0.33 (0.027)	0.23 (0.043)
Aliphatic C-O bond, Cβ in β-O-4; Cα in β-5 and β-β	0.36	0.78	0.76 (0.070	0.63 (0.058)
Aliphatic C-O bond, Cα in β-O-4	0.50	1.28	1.09 (0.088)	0.95 (0.078)
Aliphatic COR	0.23	0.88	0.43 (0.063)	0.51 (0.055)
Aliphatic C-O Cγ in β-O-4	0.27	0.43	0.43 (0.046)	0.38 (0.030)
Cβ in β-β and Cβ in β-5	0.12	0.17	0.17 (0.51)	0.16 (0.061)
Aromatic C-R (substituted)	3.78	3.86	3.80 (0.061)	3.82 (0.018)
Aromatic C-H (unsubstituted)	2.22	2.14	2.20 (0.061)	2.18 (0.018)

[a] signal intensity measured is relative to the aromatic region (δ 154 – 106 ppm)

[b] E* stands for the average of the 5 alkaline extraction conditions

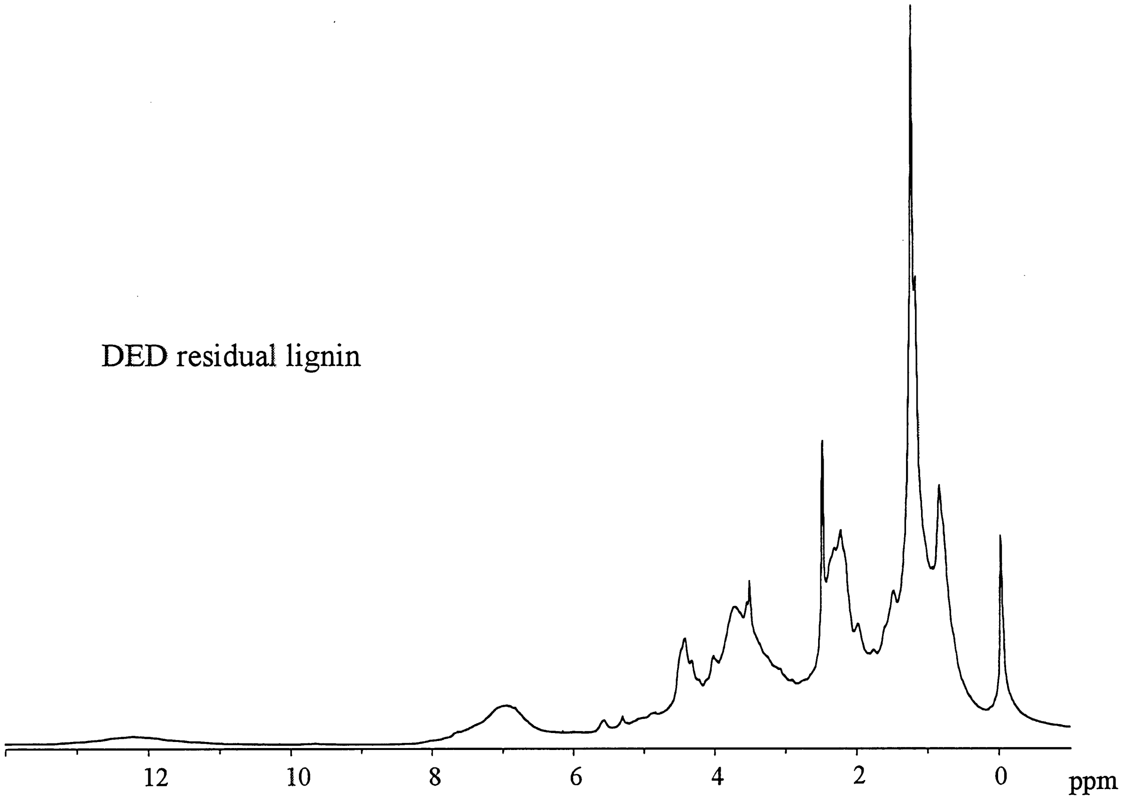

Figure 5. Typical ^{1}H NMR spectra of D_1 residual lignin (DED stage)

Table 11. Comparison of ^{1}H NMR data between D_1 and E* stage lignins

Functional group	Average E*[a] *(std. dev.)* (mmol/g isolated lignin)	Average D_1 *(std. dev.)* (mmol/g lignin)
COOH	2.0 *(0.20)*	0.91 *(0.16)*
Formyl H	0.28 *(0.09)*	0.06 *(0.03)*
Unsubstituted Phenolic	0.37 *(0.15)*	0.07 *(0.04)*
C5 Substituted Phenolic	0.37 *(0.10)*	0.16 *(0.10)*
Aromatic H	7.6 *(1.29)*	3.2 *(0.60)*
Aliphatic H	10.0 *(1.39)*	5.2 *(1.52)*
Methoxy H	13.6 *(2.40)*	5.4 *(0.85)*

[a] E* stands for the average of the 5 alkaline extraction conditions