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Breaking the Oxygen Delignification Barrier: Lignin Reactivity  
and Inactivity

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# **Breaking The Oxygen Delignification Barrier: Lignin Reactivity And Inactivity**

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Low kappa factors (0.05 KF) of chlorine and chlorine dioxide were employed to chemically pretreat softwood kraft pulp and associated residual lignin before an oxygen delignification stage. Quasi-pretreatments using nitrogen dioxide were performed in parallel and all results were compared to high kappa factor treatments (KF = 0.20) of pulp and lignin to exaggerate and examine the lignin structural changes contributing to the pulp delignification response during an oxygen stage. The principal spectroscopic method chosen to investigate the chemical changes in lignin was  $^{31}\text{P}$  NMR. One of the most significant results arising from these studies was the relatively constant content (< 30% change) of the condensed phenolics despite the efficacy of the chemical pretreatment stage for the lignins. Interestingly, the free phenolics were not appreciably consumed, strongly suggesting that these moieties should be the focus of any future attempts to maximize the performance of an oxygen stage.

The issue of overcoming the limits to oxygen delignification has received increased research attention recently. Since oxygen provides significant environmental and economic benefits, reportedly being able to increase yield, successfully reduce lignin levels and thus provide bleaching cost savings while maintaining compatibility with recovery operations, increased delignification without compromising yield or pulp properties is a very desirable goal [1-10]. One promising avenue for enhanced delignification that has witnessed considerable research attention is the use of pretreatments to improve the bleaching response of pulp in an oxygen stage [11-13]. Pretreatments may be defined as low kappa factor (KF, low molecular chlorine multiples/kappa of pulp) pulp bleaching stages that follow pulping to increase pulp bleachability without adversely affecting pulp properties.

The current research was conducted to elucidate the chemical basis for the limits in oxygen delignification through an analysis of various significant functional groups in lignin. These groups were analyzed after chemical treatments that employed low and high kappa factors of chlorine and chlorine dioxide in addition to an intermediate kappa factor of nitrogen dioxide. Gierer and others have provided the fundamental chemical underpinnings for the structural changes imparted to lignin during oxygen delignification [14-16]. Highly reactive hydroxyl radicals, for example, can react with aromatic and aliphatic lignin structures to generate organic radicals which are purportedly susceptible to attack by superoxide. Superoxide has been suggested to be involved in the scission of aromatic, conjugated, and aliphatic (side chains) lignin structures. Ring opening and side chain elimination reactions can induce carboxylic acid formation and enhance lignin solubility in alkaline conditions. The resistance of lignin removal after 50% delignification during an oxygen stage has been extensively studied and has in part been attributed to carbon-carbon bond structures that are recalcitrant to degradation. For example, dimeric arylpropane units containing saturated side chains such as bireosol display a reduced reactivity in oxygen systems [17]. In addition, while Lai reports that diphenylmethane lignin units are notoriously stable, he contends that condensed phenolic lignin structures are unstable, while Argyropoulos has maintained that condensed phenolic structures are the major factor limiting oxygen delignification [18-24]. Much of the work that remains to be done in this area requires an increased understanding of the role and fate of the lignin structures that are activated or that remain inert during an oxygen stage.

Herein, we report the structural changes that occur to the residual kraft lignin of two mill pulps, manufactured by EMCC® (extended modified kraft cooking) and CC (conventional cooking) technologies, after both chemical pretreatments (using varying kappa factor charges of chlorine, chlorine dioxide, and nitrogen dioxide) and followed by oxygen delignification. Specifically we have correlated the chemical structural changes of the lignin to the delignification efficiency observed for the two industrial pulps. We have obtained quantitative  $^{31}\text{P}$  NMR spectra and elemental analyses of all lignins in an effort to identify the structural factors responsible for the inactivity and reactivity of lignin during oxygen delignification.

## Methods

**Pulping and Oxygen Delignification.** Kraft pulps were manufactured by industrial sponsors using typical EMCC® (MK) and Conventional Cooking (CK) technologies. The kappa numbers measured for the MK and CK pulps were 23.2 and 22.4, respectively.

Oxygen delignification runs were conducted on a 300-ml PARR Instruments Pressure Reactor employing the following conditions: 60 minutes, 100°C, 100 psi, 2.33% NaOH charge (relative to mass of pulp), 10% consistency (when applicable), and subject to mild (5 hz) impeller-blade stirring. The headspace in the PARR reactor was thoroughly flushed with oxygen before application of pressure. Lignin oxygen runs were done by dissolving 75 mg of each lignin into 60 mL of alkaline charged water and stirring. The starting and ending pHs for the runs ranged from 11.3 to approximately 10.. All pulps and lignins were removed after the runs and allowed to cool before either a thorough distilled water wash or acid precipitation, respectively.

**Lignin Isolation.** The residual lignins of the MK and CK pulps were isolated by a slightly modified acid hydrolysis procedure that involved a 1 hour reflux of the pulps in an 0.1 N HCl solution containing 9:1 *p*-dioxane:water for. *P*-dioxane was distilled over sodium borohydride powder for one hour immediately before use. After reflux, the supernatant was collected and the dioxane was removed under reduced pressure. The pH of the remaining water suspension was adjusted to 2.0; the

resultant lignin suspension was frozen to increase lignin coalescence, and allowed to thaw after 24 hours. The precipitate was collected by centrifugation. The preceding process was repeated in triplicate using fresh water rinses of pH = 2.0. The resultant lignin was lyophilized and collected. Product recovery yields were based on the pulp starting kappas (total lignin content) and typically ranged from approximately 40 to 60 %.

**High, Intermediate, and Low Kappa Factor Pretreatments.** The pulp pretreatments were conducted at 0.05 kappa factor using freshly prepared chlorine or chlorine dioxide. In order to amplify and more fully explain the chemical effects induced by these pretreatments, higher kappa factors of 0.20 were used, in addition to the use of an intermediate kappa factor of 0.10 for a nitrogen dioxide pretreatment. Nitrogen dioxide pretreatments were accomplished by introducing the appropriate amount of a sodium nitrite solution followed by nitric acid. All pulp pretreatments were conducted in sealed bags and were run at 70° C for 30 minutes while maintaining a final pH of approximately 2.0. All pretreatment conditions used for the pulps were applied to the residual lignins, except that the lignin was dissolved in 9:1 dioxane:water and stirred at ambient temperature in round bottom flasks. All kappa values have an experimental error of approximately 3%. Bleachability in this work will refer to a given level of delignification at constant conditions (caustic, temperature, and time of reaction).

**Recovery of Lignin from Pretreatment and Oxygen Bleaching.** Lignin pretreatment and oxygen bleaching runs were performed after the pulp runs to provide a fundamental basis for the delignification observed in the pulps through analysis of discrete lignin functional groups. Thus, the residual lignins from the MK and CK pulps were systematically isolated and investigated through <sup>31</sup>P NMR. Since our objective was to provide an accurate summary of the fate of the lignin structural subunits after pretreatment and a subsequent oxygen stage, it was necessary to recover as much of lignin as possible after pretreatment and oxygen bleaching. All lignins were therefore recovered as quantitatively as possible by exhaustive ethyl acetate extraction as described by Asgari and Argyropoulos [22]. Any remaining aqueous phase that remained after chemical reactions in either dioxane/water or alkaline water was removed under reduced pressure and DMF was added to the remaining precipitate to specifically dissolve low molecular weight lignin fragments [22]. The DMF layer was filtered to remove insoluble salts and the remaining

solution was added drop-wise to diethyl ether to precipitate the lignin. Lignins were lyophilized and vacuum-oven dried before NMR analyses. Recovery yields for the lignins after both pretreatment and oxygen bleaching runs typically ranged from 55-75%.

**Quantitative Lignin  $^{31}\text{P}$  NMR Analyses.** Spectral characterization of the residual lignins was accomplished on a 400 MHz Bruker DX Spectrometer employing published procedures [25]. All residual lignins were dissolved in a solution of 650  $\mu\text{L}$  of pyridine/ $\text{CDCl}_3$  (v/v 1.6/1) that contained either cyclohexanol or *endo*-N-hydroxy-5-norbornene-2,3-dicarboximide as an internal standard and chromium acetylacetonate as an internal relaxation agent. The samples were phosphitylated with 2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane. Regions for integration have been reported elsewhere [26]. The integration values have a reproducibility of approximately 95%.

## Results and Discussion

### *Pulp Studies*

The initial studies focused on determining the effect of pulp pretreatments on the delignification responses of MK and CK pulps. Shown in Figure 1 are the delignification responses of the pulps after oxygen delignification.

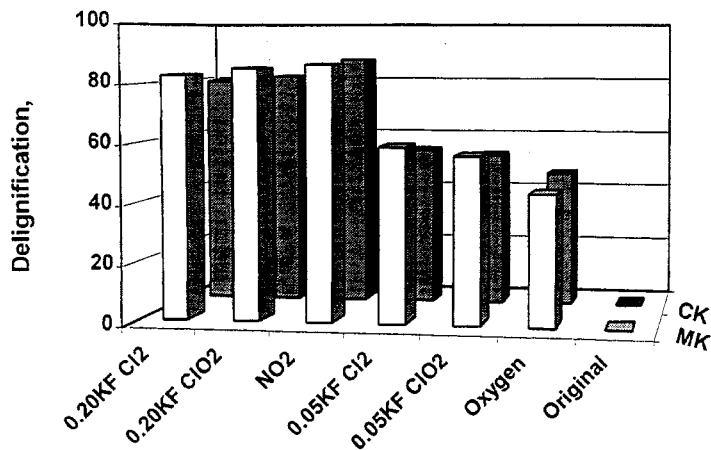


Figure 1. The levels of oxygen delignification obtained for the MK and CK pulps as a function of pretreatment.

The oxygen control level of delignification achieved for both pulps is approximately 45%. The low KF chlorine and chlorine dioxide pretreatments increase the delignification by an additional 30% over the threshold levels, and additionally the MK pulp has a better delignification response than the CK pulp by over 2 kappa units. One of the more remarkable findings in the above figure is the high delignification achievable by a relatively modest NO<sub>2</sub> pretreatment. Obviously, modest NO<sub>2</sub> treatments (KF = 0.10) tremendously boost delignification in a subsequent oxygen stage in a manner comparable to high kappa factor pretreatments using chlorine and chlorine dioxide (KF = 0.20). The enhancement of the performance of an oxygen stage by varying concentrations of NO<sub>2</sub> has been well described in the literature [27-29]. These results validate the ability of this particular treatment to predispose lignin to enhanced oxygen delignification. It is noteworthy that this data provide evidence that the MK pulps display slightly better bleachability than the CK pulps (on the order of at least 10%).

#### *Carboxylic Acid Content*

The carboxylic acid group is typically associated with a significant increase in the oxidation state of lignin. It is an important structural change that occurs in any bleaching process since it the primary way of imparting an enhanced degree of solubility to lignin and typically follows ring opening, aliphatic cleavage, or other oxidative fragmentation of lignin. Shown in Table 1 is a list of the carboxylic acid group changes for all the lignins analyzed in this study. A chlorine dioxide (D) pretreatment caused approximately 30% increase in the overall acid content of both the CK and MK lignins, not unlike what has been previously observed in D bleaching [30]. However, chlorine (C) pretreatments did not induce the generation of similar acid levels.

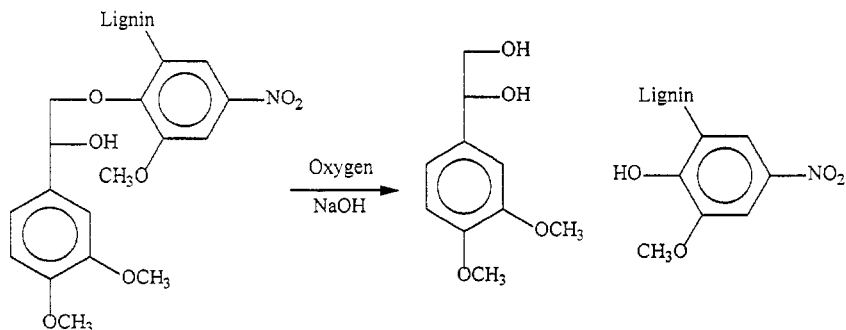


Table 1. The carboxylic acid content for pretreated and post-oxygen (expressed as pretreatment/KF/O) treatment residual MK and CK lignins expressed in mmoles/gram of lignin. The recovery yields for these lignins ranged between 55 and 75% of the original lignin mass.

CARBOXYLIC ACID CONTENT (mmoles/g lignin)	MK	CK
Brown Stock	0.30	0.31
<i>Oxygen Control</i>	0.76	0.90
Cl <sub>2</sub> /0.05	0.24	0.26
Cl <sub>2</sub> /0.05/O	0.70	0.80
ClO <sub>2</sub> /0.05	0.41	0.43
ClO <sub>2</sub> /0.05/O	1.04	1.01
NO <sub>2</sub> /0.10	0.24	0.22
NO <sub>2</sub> /0.10/O	0.76	0.58
Cl <sub>2</sub> /0.20	0.21	0.25
Cl <sub>2</sub> /0.20/O	0.51	0.54
ClO <sub>2</sub> /0.20	0.72	0.65
ClO <sub>2</sub> /0.20/O	1.39	1.09

We found from elemental analysis, however, that there was a heavy incorporation of chlorine, up to 15% in the lignins, which partially offset the introduction of acid groups. Also, it was found by Lachenal et al. that at low KFs of chlorine, acid level increases are not as appreciable as for a D pretreatment [31]. In fact, the generation of carbon dioxide and carbonate have been found to be significant pathways during chlorinations of pulp [31]. Interestingly, carboxylic acid generation was not found to be as significant in NO<sub>2</sub> pretreatments. Again, this was not surprising since significant incorporation of nitrogen (approximately 5-10%) was found and a previously described mechanism of NO<sub>2</sub> reactions with lignin as shown in Figure 2 provides a partial explanation [29]. NO<sub>2</sub> has been postulated by Walding et al. to induce significant depolymerization through nitration reactions. In fact, Samuelson has found that the tendency to delignify from such treatments owes not so much to

increased hydrophilicity by acid incorporation, as to extensive lignin degradation into fragments smaller than found in ordinary bleaching sequences.



*Figure 2. The hydrolysis of nitrated lignin during an oxygen stage that follows a  $\text{NO}_2$  pretreatment as described in Walding's work is shown above. It is expected to be facile since the highly electronegative nitrated lignin subunit can be displaced by the  $\alpha$ -hydroxyl group under alkaline conditions.*

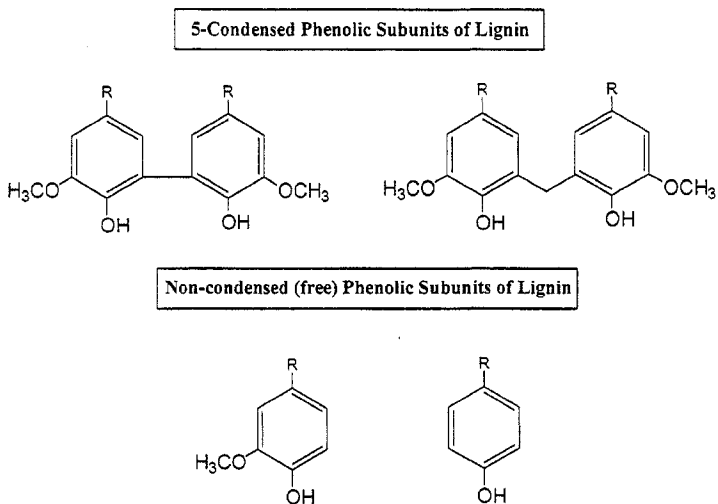
The discrepancy between the levels of acid between CK and MK (higher for MK, opposed to trends shown in Table 1) after an oxygen stage can be explained by the greater abundance of aliphatic hydroxyls in MK over CK by more than 10%. The  $\alpha$ -hydroxyls can participate in a base-induced intramolecular expulsion of an adjoining  $\beta$ -nitrated ring leaving a vicinal diol that can further oxidize to a terminal acid during oxygen delignification

The control oxygen lignins demonstrated a 2-3-fold increase in acid levels and the CK lignin had approximately 15% higher levels. The D pretreated MK lignin shows an enhanced carboxylic acid content beyond what is observed for the oxygen control that is consistent with the slightly better bleachability of its associated pulp (see Figure 1). Employing a high KF pretreatment before oxygen exaggerates the acid differences between the starting and oxygen treated lignins consistent with the pulp data. An important difference in lignin structure to account for the slightly better bleachability of the MK over CK are the higher levels of condensed phenolics and aliphatic hydroxyls of the MK lignin. The phenolics are primary sites

of reactivity for chlorine dioxide and the increased levels in the MK may explain the increased delignification response of the MK pulp.

### *Phenolic Content*

Lignin contains both condensed and non-condensed (free) phenolic lignin structures which have tremendous importance in the overall response of lignin to oxidants. Several of the structures of these important functionalities which comprise the focus of our NMR investigations are shown in Figure 3. The salient difference between condensed and non-condensed structures is the substitution pattern at the 5-position of two arylpropanoid units.



*Figure 3. The structures of some typical condensed and non-condensed (free) phenolic units in residual kraft lignins are displayed. Notice that the salient differences occur in the substitution pattern at the 5-carbon of the lignin aromatic subunits, where condensed structures have C-C bonds, whereas non-condensed have C-H bonds.*

Remarkably, although C pretreatments (both high and low KFs) did not increase carboxylic acid levels, they nonetheless tended to afford higher levels of condensed phenolics. Shown in Figure 4 are the actual levels of the condensed phenolics for the pretreated lignins. Table 2

provides a comparative analysis of the phenolic levels of all of the lignins. The levels of condensed phenolics in the C pretreatment are more significant than observed in the D pretreatment. This suggests that one of the potential side reactions of a C pretreatment is the formation of coupling products by radical reactions [31, 32]. Nonetheless, this pretreatment does not prevent the delignification efficiency associated with a subsequent oxygen stage.

Table 2. The non-condensed and 5-condensed phenolic content for the pretreated and post-oxygen (italics) residual MK and CK lignins expressed in mmoles/gram of lignin.

PHENOLIC CONTENT (mmoles/g lignin)	MK		CK	
	Non-Condensed	Condensed	Non-Condensed	Condensed
Brown Stock	0.93	0.89	0.93	0.82
<i>Oxygen Control</i>	0.60	0.64	0.69	0.68
Cl <sub>2</sub> /0.05	0.67	0.90	0.64	0.86
<i>Cl<sub>2</sub>/0.05/Oxygen</i>	0.44	0.63	0.46	0.69
ClO <sub>2</sub> /0.05	0.68	0.69	0.73	0.70
<i>ClO<sub>2</sub>/0.05/Oxygen</i>	0.53	0.58	0.56	0.67
NO <sub>2</sub> /0.10	0.20	0.43	0.19	0.44
<i>NO<sub>2</sub>/0.10/Oxygen</i>	0.30	0.52	0.24	0.46
Cl <sub>2</sub> /0.20	0.29	0.69	0.28	0.77
<i>Cl<sub>2</sub>/0.20/Oxygen</i>	0.27	0.58	0.30	0.67
ClO <sub>2</sub> /0.20	0.36	0.54	0.28	0.51
<i>ClO<sub>2</sub>/0.20/Oxygen</i>	0.34	0.46	0.40	0.35

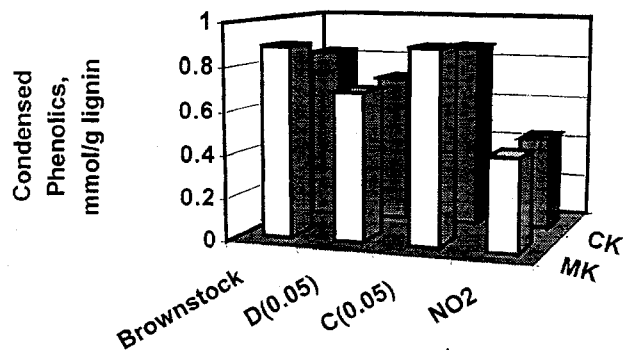


Figure 4. The content of condensed phenolics in the pretreated residual MK and CK lignins.

An experimental result that provides insight for the level of bleachability is the level of carboxylic acid for the lignins after a control oxygen stage. The CK lignin has a larger carboxylic acid content than the MK lignin, and is in fact more bleachable as a pulp. The MK lignin, however, has more condensed phenolic structures than the CK that may partially explain its diminished bleachability, a cogent argument that has been the subject of numerous investigations [20, 22, 23, 36-38]. Yet, a C/O stage appears to refute this latter argument since the MK pulp is slightly more bleachable, although it has a higher level of condensed structures. This slight increase in reactivity may well be due to other structural features such as the aliphatic hydroxyl groups (*vide infra*).

Condensed phenolic structures have received considerable attention as a major source that contribute to the inactivity of lignin during oxygen delignification. The current work has examined their role in the context of a preactivation step (pretreatments) of the lignin before oxygen and found that they remain relatively intransigent throughout the chemical bleaching/oxygen steps. Shown in Figure 5 are the levels of condensed phenolics for the lignins after an oxygen stage.

The condensed levels do not vary more than 30% throughout. *Moreover, the delignification efficiency observed in the pulps is not compromised as a result of these structural components.*

The data strongly indicate that these structures are robust and therefore stable, *and are not intrinsically the primary constituents that limit the reactivity of lignin.*

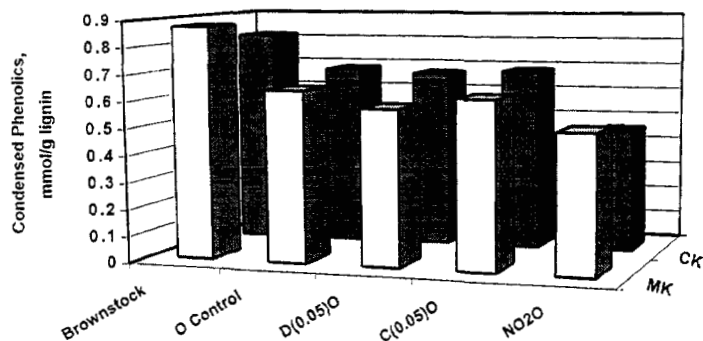


Figure 5. The content of condensed phenolics in the post-oxygen stage residual MK and CK lignins.

In fact, even high kappa factor pretreatments do not significantly affect their relative distribution with respect to total phenolics as evidenced in Figure 6. In light of the previous data, Figure 6 supports the observation that condensed phenolics are not depleted as much as free phenolics, yet, free phenolics do not change dramatically enough to account for the delignification observed in the pulps. In fact, the pretreatment phenolic ratios are quite constant, testifying to the relative robustness of both the condensed and non-condensed phenolic contents.

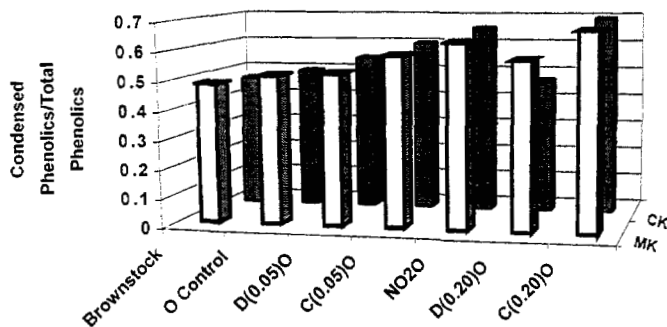


Figure 6. The ratio of condensed phenolics content to total phenolic content in the post-oxygen stage residual MK and CK lignins.

Again, the consumption of the non-condensed phenolics is surprisingly inefficient. Most work strongly indicates that these are the primary reactive sites for D and O stages [32, 33]. As shown in Table 2 (*vide supra*), the relative change in the non-condensed phenolics as part of a pretreatment is not appreciable with regard to the bleachability results for the pulps. This result suggests that the phenolic sites are not being consumed as would be expected to account for the decrease in lignin content and that alternative explanations may account for these drops. Perhaps lignin exhibits phenolic sites of differing reactivity based on their electrochemical potentials and environmental constraints and sites that contribute to increased oxidation/solubilization are activated by a pretreatment.

### *Aliphatics*

As shown in Figure 7, the aliphatic levels for the pretreated lignins diminish slightly, but this is not unusual considering that most of the pretreatments do not attack the aliphatic side chains appreciably. Chlorine, however, is known to attack side chains and efficiently deplete this functionality which is demonstrated in the pretreatment. Interestingly, although MK has a greater proportion of condensed structures, suggesting that its bleachability is hindered, it is nevertheless more bleachable than CK, perhaps as a result of the disparity in aliphatic levels between the two lignins. An exaggerated high kappa factor C pretreatment, moreover, extensively consumes the aliphatics, further supporting the latter argument for the heightened bleachability of MK versus CK pulps.

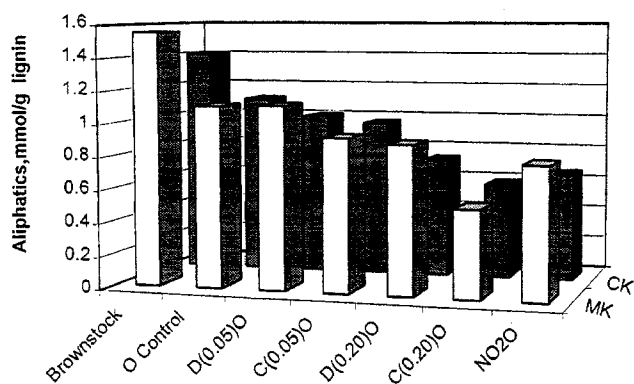


Figure 7. The content of aliphatic hydroxyl functionalities in the pretreated and post-oxygen stage residual MK and CK lignins.

## Conclusions

The free phenolics of residual lignin are surprisingly not appreciably consumed in an oxygen bleaching stage following a pretreatment stage of chlorine, chlorine dioxide, or nitrogen dioxide despite the enhanced bleachability of pretreated pulps. The NMR data strongly imply that more than 50% of these units are resistant to oxidation, while the concentration of condensed phenolics remain relatively constant. The major difference between the MK and CK lignins are the higher levels of condensed phenolics in the MK lignin which may partially assist during lignin oxidation for the C and D pretreatments. The MK pulps are slightly easier to bleach and the NO<sub>2</sub> pretreatment was extremely effective in promoting the bleachability of the pulps, which may be a consequence of its ability to fragment lignin efficiently via nitration. Condensed phenolics are nonetheless quite resistant to degradation and appear to remain in the lignin samples despite the pretreatments. Their relative robustness does not, however, appear to be the main rationale for the inactivity of lignin toward oxygen delignification, but serves to suggest that the nature and reactivity of the free phenolics deserve increasing scrutiny.

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