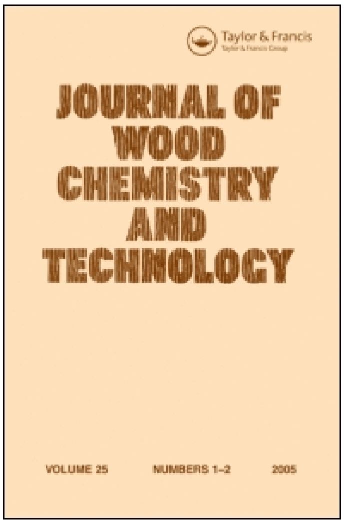

Journal of Wood Chemistry and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597282

# New Insights into Lignin Modification during Chlorine Dioxide Bleaching Sequences (III): The Impact of Modifications in the (EO) versus E Stage on the $D_1$ Stage

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**To cite this Article** Brogdon, Brian N. and Lucia, Lucian A.(2005) 'New Insights into Lignin Modification during Chlorine Dioxide Bleaching Sequences (III): The Impact of Modifications in the (EO) versus E Stage on the $D_1$ Stage', Journal of Wood Chemistry and Technology, 25: 3, 133 — 147
**To link to this Article: DOI:** 10.1080/02773810500191690
**URL:** http://dx.doi.org/10.1080/02773810500191690

Journal of Wood Chemistry and Technology, 25: 133–147, 2005
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ISSN 0277-3813 print/1532-2319 online
DOI: 10.1080/02773810500191690

# New Insights into Lignin Modification during Chlorine Dioxide Bleaching Sequences (III): The Impact of Modifications in the (EO) versus E Stage on the $D_1$ Stage

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**Abstract:** Chlorine dioxide delignification ($D_0$) modifies kraft residual lignin by oxidizing phenolic groups to *both* quinone and muconic acid structures. Alkaline extraction (E), in addition to removing solubilized lignin, converts quinone moieties to polyphenols. These polyphenols are easily oxidized by oxygen in an (EO) stage or by $ClO_2$ in a $D_1$ stage to hydroxyquinones (~1.8 mmol/g lignin). Pulps treated by $D_0E$ consume considerably more $ClO_2$ in the $D_1$ than $D_0$(EO), and have lower bleachability, as was quantified by a simple bleaching model. Both $D_0E$ and $D_0$(EO) pulps approach a common brightness ceiling (~83 ISO) when excess $ClO_2$ is applied. Examination of the post-$D_1$ b* values indicates that $D_0E$ and $D_0$(EO) also have similar asymptotic b* values (~6), indicating that both pulps have similar

Dedicated to Drs. Donald R. Dimmel and Thomas J. McDonough on their retirement from the Institute of Paper Science and Technology.

The authors thank Mark Turner of the Institute of Paper Science and Technology (IPST) at Georgia Tech for his assistance with the laboratory digester cooks of the black spruce employed in this study. Portions of this work were presented at the 2003 International Symposium of Wood and Pulping Chemistry in Madison, Wisconsin and the 2003 TAPPI Fall Technical Conference in Chicago, Illinois.

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residual chromophores. Hydroxyquinone structures appear to be eliminated in the $D_1$ stage for $D_0$(EO) pulps, and at high $ClO_2$ levels for $D_0$E pulps.

**Keywords:** Chlorine dioxide delignification, extraction, lignin modification, alkali reactions, kappa number, klason lignin, kraft pulps, bleaching, bleachability, bleaching sequences, quinones, muconic acids, phenolics, oxygen

## INTRODUCTION

Bleaching is performed to increase the brightness and cleanliness of unbleached pulps. This task is accomplished by removing the remaining vestiges of lignin and chromophores that are contained within the chemical pulp without adversely affecting its carbohydrate integrity. On the industrial scale, this goal is achieved by employing multistage bleaching processes, whereby the first stages delignify and the final stages brighten the pulp.[1] Various oxidants such as oxygen (O), chlorine dioxide (D), and ozone (Z), are utilized in the initial stages to modify and fragment the residual lignin. Subsequently, this modified lignin is solubilized and removed in an extraction stage (E), where other oxidants, such as oxygen and/or hydrogen peroxide may be applied. (e.g., (EO), (EP), or (EOP)). It is known that future brightness development and limitations of a pulp (i.e., bleachability) can be greatly influenced by its previous pulping and bleaching delignification history.[1–9]

We currently lack a complete scientific description of what occurs during bleaching and how stages in a given sequence work in concert with one another to delignify and decolorize pulps. In fact, little is known as to what occurs during extraction because it is often taken for granted as an integrated extension of the previous stage. Efforts have been made by numerous investigators to define how certain oxidants modify and fragment model lignin compounds.[8–21] However, very few studies have attempted to provide a set of well-defined chemical reactions that occur in each bleaching stage,[22–26] and in particular, how the chemistry in the preceding bleaching stage affects the subsequent stage. The overall objective of our research work is to provide a unified bleaching theory correlating what we know from various published model studies to the changes that occur to the residual lignin structure as it progresses through a bleach sequence, and how each sequence interacts with one another.[23–26] A better understanding of how residual lignin and chromophores are modified during bleaching sequences will assist us in making process modifications to enhance pulp bleachability more selectively, as well as more economically feasible.

Our studies have examined a small aspect of bleaching delignification, namely that of chlorine dioxide ($D_0$) and caustic extraction (E).[24–26] In this article, we propose how oxygen alters residual $D_0$ lignin during the (EO) stage and how it impacts the $D_1$ bleaching stage. We have employed facile *in-situ* techniques[23] to track salient functional groups in the oxidized pulp. Through the results of this work, we hope to establish some of the fundamental chemistry that occurs during the (EO) and $D_1$ stages. In a companion article,[26] we examine how peroxide affects oxidative reinforced alkaline extraction stages (e.g., (EP) and (EOP)).

## BACKGROUND ON THE FUNDAMENTAL REACTIONS FOR THE (EO) STAGE

Since the 1980s, the addition of oxygen to alkali extraction (EO) has gained wide acceptance as an integral part of kraft pulp bleach sequences due to its low capital costs and its ability to reduce bleaching cost.[27–30] The application of oxygen in the extraction stage partially evolved from some earlier observations of replacing intermediate hypochlorite stages with oxygen (e.g., (DC)EHDED with (DC)EODED).[31] The action of oxygen during the extraction of chlorinated (C) or $D_0$ pulps is known to rapidly reduce the kappa number of the pulp by 2 to 4 units versus an E stage. Generally, the reactions occur within the first few minutes when sufficient oxygen pressure [~0.21 MPa (~30 psig)] is applied.[27–30,32] This observation implies that there are groups within these oxidized lignins that are easily oxidized by oxygen. Yet, it is know that the majority of the labile moieties in the residual lignin that are susceptible to oxygen attack, such as phenolic groups,[34] have been oxidized by the $D_0$ stage.[8–10,13,35] These two observations seem to be paradoxically inconsistent with one another.

One explanation that could reconcile the earlier inconsistency may be related to some of our recent findings with bleaching delignification during the $D_0ED_1$ sequence. We have shown[23–25] that the $D_0$ stage oxidizes phenolic groups in the unbleached lignin to *both* quinonoid and muconic acid structures in ~2-to-1 ratio, respectively. Based on this data, it is estimated that ~30% of the $D_0$ residual lignin structure is composed of quinones. Alkali treatment of the $D_0$ pulp in an E stage, in addition to removing solubilized lignin, was shown to convert these quinones to polyphenols, somewhat analogous to that of hydrosulfite reduction (Y) of $D_0$ pulps. These new polyphenols in $D_0E$ and $D_0Y$ pulps were shown to be reactive again toward $ClO_2$ oxidation in the $D_1$ stage, generally forming hydroxyquinones.

The formation of polyphenols from the 1,4-reductive Michael addition of hydroxide to quinones in the E stage (Figure 1), and the ease of oxidation of polyphenols in a subsequent $D_1$ stage may provide an explanation of the reactivity of oxygen with $D_0$ lignin in an (EO) stage. Simple polyphenolic compounds are known to be easily oxidized to hydroxyquinones in the presence of oxygen in alkaline environments (Figure 1).[21,36–40] Gellerstedt and Pettersson[41] also reported that polyphenolic model lignin compounds are easily oxidized by oxygen to quinone-type compounds.

The autoxidation of polyphenols in the (EO) stage to hydroxyquinones should result in a significant drop in the kappa number when compared to an

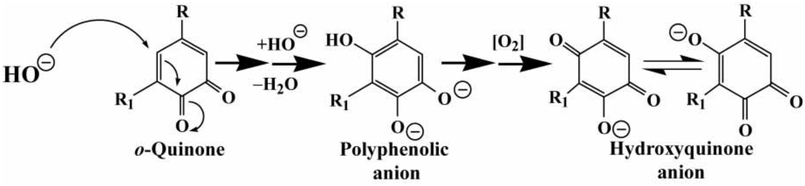

***Figure 1.*** Postulated reactions of *o*-quinones during (EO) stage treatment of $D_0$ oxidized pulps. **R** = lignin side chain and $\mathbf{R_1}$ = H or $OCH_3$.

E stage, because quinone structures have one less double bond than the aromatic polyphenolic units. Several studies have established that acidic $KMnO_4$ stoichiometrically reacts with the carbon-carbon double bonds contained in the rings of aromatic[42] and quinonoid units of model lignins.[23] Brogdon *et al.* have demonstrated that periodiate oxidized pulps, which contain significant levels of quinones (~1.8 mmol/g lignin), have much lower kappa numbers (~4 to 5 units) than unbleached pulp even though both pulps have almost similar amounts of Klason lignin.[23,24] These investigators established that $KMnO_4$ consumption during the kappa number test is directly related to the amount of carbon-carbon double bonds contained in the lignin and that quinones consume 1/3 less $KMnO_4$ than corresponding aromatic units.

In this study, we examined whether $D_0$ quinones were being converted to polyphenols by hydroxide and the subsequent structures being oxidized by oxygen in an (EO) stage. To test this hypothesis, we examined the similarities of (EO) stages performed on $D_0$ and periodate oxidized pulps, which are known to contain significant levels of *o*-quinones. We tracked the formation and elimination of quinone and hydroxyquinone structures through the analysis of kappa number and Klason lignin content of the various treatments.[23–25] In addition, we also investigated how the E and (EO) stages affect $ClO_2$ oxidation in a subsequent $D_1$ stage in terms of lignin modification and bleachability.

## RESULTS AND DISCUSSION

### Analysis of $D_0$E vs. $D_0$(EO) Residual Lignin

Samples of a black spruce kraft pulp were oxidized with either $ClO_2$ in a $D_0$ stage (0.15 KF), or with excess sodium *meta*-periodate (Table 1). The amount of residual lignin in these pulps was determined directly by Klason lignin analysis and indirectly by the kappa number test. We examined the change in the $KMnO_4$ consumption per unit of lignin for these oxidized pulps. As has been observed in our previous studies,[23–25] $ClO_2$ and periodate oxidation caused the lignin/kappa ratio to shift from 0.15 to 0.18. This shift in the ratio has been correlated to the amount of quinones contained in the

*Table 1.* Analysis of residual lignin in kraft pulps after various oxidative, alkaline, and reductive treatments

| Pulp[a] | Kappa number | Klason lignin (%) | Lignin/ Kappa ratio | mL 0.1*N* $KMnO_4$/g lignin | mmol quinones/g lignin |
|---|---|---|---|---|---|
| Unbleached | 24.0 | 3.6 | 0.15 | 670 | Non-detectable |
| $D_0$ (0.15 KF) | 17.6 | 3.2 | 0.18 | 550 | 1.9 |
| $D_0$E | 11.3 | 1.7 | 0.15 | 670 | Non-detectable |
| $D_0$(EO) | 8.9 | 1.6 | 0.18 | 560 | 1.8 |
| $D_0$(EO)Y | 8.4 | 1.3 | 0.15 | 650 | Non-detectable |
| Periodate | 18.8 | 3.4 | 0.18 | 550 | 1.9 |
| Periodate-E | 16.6 | 2.5 | 0.15 | 660 | Non-detectable |
| Periodate-(EO) | 13.6 | 2.4 | 0.18 | 570 | 1.5 |
| Periodate-(EO)Y | 14.0 | 2.2 | 0.16 | 640 | Non-detectable |

[a] Y denotes hydrosulfite reduction: KF denotes Kappa Factor charge of $ClO_2$ in $D_0$ stage.

$D_0$ or periodate pulps.[23–25] The level of quinones was estimated from this shift based on the weighted averages of $KMnO_4$ consumption for aromatic (11.6 equiv./mol lignin) and quinone moieties (~7.6 equiv./mol lignin) in the modified residual lignin. The results from this analysis indicated that the $D_0$ and periodate pulps contained ~1.9 mmol quinones/g residual lignin. These values also closely correspond to the ~1.6 mmol/g lignin reduction of methoxyl group content we measured in spruce kraft lignin after oxidation with $ClO_2$ or periodate. Demethoxylation is an indirect indicator of *o*-quinone formation.[24]

The $D_0$ and periodate pulps in Table 1 were subjected to either caustic extraction (E) or oxygen-reinforced extraction (EO). The E stage caused the lignin/kappa number ratio of $D_0$ and periodate pulps to return to 0.15, comparable to that of the unbleached lignin. This is consistent with our earlier reports for an E stage,[25] and is analogous to the effect of hydrosulfite reduction of $D_0$ and periodates pulps. The change in $KMnO_4$ consumption by the alkali-modified $D_0$ lignin indicates that the quinones are converted to polyphenolic structures, which contain an extra carbon-carbon double bond, which consumes additional $KMnO_4$ during the kappa number determination.

We postulate that what is occurring in the (EO) is depicted in Figure 1. In this scheme, the quinones from the $D_0$ and periodate oxidized lignin are reacting with hydroxide anions to form polyphenolic structures, which are in turn being oxidized by the oxygen to hydroxyquinones. As noted earlier, polyphenolic structures are known to rapidly react with oxygen under alkaline conditions to form hydroxyquinones.[21,36–42] Such hydroquinone structures in (EO) lignin should consume less $KMnO_4$ during the kappa number test, just like the quinones in $D_0$ and periodate oxidized lignin.

The (EO) stage treatment, unlike the above E stage, did not cause the lignin/kappa ratio of the $D_0$ and periodate oxidized pulps to return to 0.15. Instead, the ratio remained at 0.18 (Table 1). It is interesting to note that the (EO) stage did not result in additional lignin removal in both $D_0$ and periodate pulps, as noted by the Klason lignin, when compared to the E stage. The lower kappa numbers of the (EO) stage versus the E stage pulps indicates that the (EO) stage residual lignin is either more oxidized or contains fewer carbon-carbon double bonds than the E stage residual lignin.

To test the hypothesis, we treated both the $D_0$(EO) and periodate-(EO) pulps with hydrosulfite (Y). Hydrosulfite reacts with quinonoid structures to form polyphenols.[10,23] This reduction results in the formation of a carbon-carbon double bond, and in the aromatization of the quinone moiety. This action should cause the modified lignin to consume similar amounts of $KMnO_4$ as the unbleached residual lignin.[23–25] This was the observed result when the (EO) pulps were reduced by hydrosulfite, which implies that the $KMnO_4$ consumption analysis is detecting quinonoid structures. The oxidation of the polyphenols arising from the alkaline reactions of quinones during the (EO) stage should significantly affect the subsequent $D_1$ stage versus the E stage.

## Impact of (EO) vs. E stage on $D_1$ Lignin Modification

The $D_0$E and $D_0$(EO) pulps in Table 1 were bleached with various levels of $ClO_2$ in the $D_1$ stage. It should be noted that the amount of lignin in these pulps is much higher than what is considered optimum for $D_1$ brightening. The higher lignin content, however, allowed us to study how the $D_1$ stage modifies the (EO) and E stages' residual lignin. The data from our Klason lignin and kappa number analyses for selected $D_1$ pulps are given in Table 2.

Low dosages of $ClO_2$ resulted in significant reductions in both kappa number and Klason lignin for both $D_0$E and $D_0$(EO) pulps. For a given $ClO_2$ level, more Klason lignin was removed from the $D_0$(EO) versus the $D_0$E. To reach a given Klason lignin level, the $D_0$(EO) pulp required roughly one-half the amount of $ClO_2$ consumed by the $D_0$E pulp. The lignin/kappa ratio for the $D_0$(EO) pulp decreased from 0.18 to 0.15, whereas the ratio for the $D_0$E increased from 0.15 to 0.18 over the 0 to 1% $ClO_2$ range. The amount of quinones formed from during the 0.75 to 1.00% $ClO_2$ oxidation of the $D_0$E pulp was ~1.2 to 1.6 mmol/g lignin, which is consistent with our previous $D_1$ studies with $D_0$E pulps.[25] The basic oxidation reaction of the hydroxyquinones by $ClO_2$ is shown in Figure 2,[18,19] and is likely the reason why the $D_0$E pulp consumes more $ClO_2$ versus the $D_0$(EO) pulp. Increasing the $ClO_2$ treatment above 1.0% for the $D_0$E pulps caused lignin/kappa ratio to decrease from 0.18, analogous to the $D_0$(EO) stocks.

To further explore the differences of E versus (EO) on the $D_1$ stage, we treated the extracted periodate pulps of Table 1 with a $D_1$ stage (Table 2).

***Table 2.*** Analysis of $D_1$ residual lignin from $D_0E$, $D_0(EO)$, periodate-E, and periodate-(EO) pulps

| Pulp | Kappa number | Klason lignin (%) | Lignin/ Kappa ratio | mL 0.1*N* $KMnO_4$/g lignin | mmol quinones/g lignin |
|---|---|---|---|---|---|
| $D_0E$ | 11.3 | 1.7 | 0.15 | 670 | Non-detectable |
| $D_0ED_1$ | | | | | |
| 0.25% $ClO_2$ | 8.6 | 1.2 | 0.14 | 720 | Non-detectable |
| 0.50% $ClO_2$ | 6.6 | 0.9 | 0.14 | 720 | Non-detectable |
| 0.75% $ClO_2$ | 5.2 | 0.9 | 0.17 | 580 | 1.2 |
| 1.00% $ClO_2$ | 5.1 | 0.9 | 0.18 | 570 | 1.5 |
| 1.25% $ClO_2$ | 4.1 | 0.6 | 0.15 | 680 | Non-detectable |
| 2.00% $ClO_2$ | 3.0 | 0.4 | 0.13 | 730 | Non-detectable |
| $D_0(EO)$ | 8.9 | 1.6 | 0.18 | 560 | 1.8 |
| $D_0(EO)D_1$ | | | | | |
| 0.25% $ClO_2$ | 6.0 | 0.9 | 0.15 | 670 | Non-detectable |
| 0.50% $ClO_2$ | 4.7 | 0.7 | 0.15 | 660 | Non-detectable |
| 0.75% $ClO_2$ | 3.9 | 0.6 | 0.15 | 650 | Non-detectable |
| 1.00% $ClO_2$ | 3.8 | 0.4 | 0.11 | 950 | Non-detectable |
| Periodate-E | 16.6 | 2.5 | 0.15 | 660 | Non-detectable |
| Periodate-$ED_1$ | | | | | |
| 0.25% $ClO_2$ | 15.2 | 2.4 | 0.16 | 630 | Non-detectable |
| 1.00% $ClO_2$ | 10.7 | 1.9 | 0.18 | 560 | 1.6 |
| 2.00% $ClO_2$ | 7.0 | 1.0 | 0.14 | 740 | Non-detectable |
| 3.00% $ClO_2$ | 4.7 | 0.7 | 0.13 | 750 | Non-detectable |
| Periodate-(EO) | 13.6 | 2.4 | 0.18 | 570 | 1.5 |
| Periodate-$(EO)D_1$ | | | | | |
| 0.25% $ClO_2$ | 12.5 | 2.2 | 0.18 | 570 | 1.5 |
| 0.50% $ClO_2$ | 9.2 | 1.7 | 0.18 | 540 | 1.9 |
| 1.00% $ClO_2$ | 8.1 | 1.2 | 0.15 | 680 | Non-detectable |
| 2.00% $ClO_2$ | 4.8 | 0.6 | 0.13 | 760 | Non-detectable |

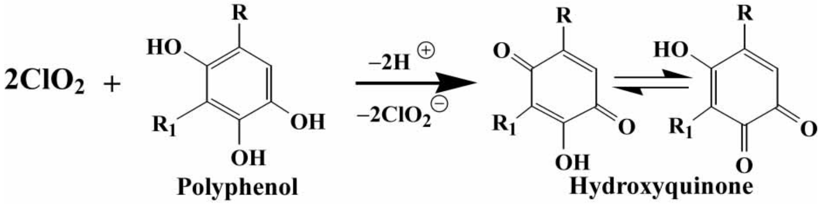

***Figure 2.*** Postulated reactions of $ClO_2$ with polyphenolic structures during the $D_1$ stage treatment of $D_0E$ pulps.[18,19] **R** = lignin side chain and $\mathbf{R_1}$ = H or $OCH_3$.

Low dosages of $ClO_2$ (i.e., 0.25%) in the $D_1$ did not affect the lignin/kappa ratio. Higher levels of $ClO_2$ (i.e., 1.0%) resulted in the periodate-E lignin/kappa ratio increasing from 0.15 to 0.18, and the periodate-(EO) lignin/kappa ratio decreased from 0.18 to 0.15. At very high levels of $ClO_2$ ($\geq$2%), the lignin/kappa ratio of the periodate-E pulp started to decrease from 0.18 to 0.13. These results mirror the previous behavior of $D_0$E and $D_0$(EO) pulps in the $D_1$ stage. This shift downward in the lignin/kappa ratio values below 0.15 at very high $ClO_2$ values in the $D_1$ for $D_0$E, $D_0$(EO), periodate-E and periodate-(EO) may reflect the complete ring rupture and fragmentation of the polyphenolics or corresponding hydroxyquinones.[26]

## Impact of (EO) vs. E stage on $D_1$ Bleachability

The $D_0$E and $D_0$(EO) pulps were bleached with various levels of $ClO_2$ in the $D_1$ stage to examine how the extraction stage conditions impact $D_1$ stage bleachability. The initial brightness of the $D_0$E and $D_0$(EO) stocks, as well as their CIE color coordinates values (i.e., L, a*, and b*) are given in Table 3. The addition of oxygen in the (EO) stage boosted the brightness by ~7 points when compared to the E stage. It is interesting that the $D_0$ stage caused an increase in the b* value, which indicates the pulp contains more yellow chromophores.

Figure 3 shows the brightening responses of the pulp in the $D_1$ stage. The data in Figure 3 were fitted to a simple brightening model that has been used to quantify pulp bleachability:[2,3]

$$B = b_0 + b_1(1 - e^{-b_2 x}) \tag{1}$$

where $B$ is the predicted pulp brightness, $x$ is the consumed amount of $ClO_2$, $b_0$ is the entering pulp brightness, and $b_1$ is the brightness gain across the $D_1$ stage. The sum $(b_0 + b_1)$ represents the asymptotic brightness limit of the $D_1$ stage, and the last parameter, $b_2$, denotes the relative rate at which this asymptotic limit is approached.

***Table 3.*** Influence of $D_0$E and $D_0$(EO) stages on brightness and CIE color coordinates (i.e., L, a* and b*) prior to $D_1$ stage

| Pulp | Kappa number | Klason lignin (%) | ISO brightness (%) | L | a* | b* |
|---|---|---|---|---|---|---|
| Unbleached | 24.0 | 3.6 | 33.0 | 75.1 | 3.2 | 19.3 |
| $D_0$ (0.15 KF) | 17.6 | 3.2 | 32.7 | 77.3 | 3.0 | 24.0 |
| $D_0$E | 11.3 | 1.7 | 38.3 | 80.1 | 2.0 | 21.3 |
| $D_0$(EO) | 8.9 | 1.6 | 45.2 | 84.3 | 1.4 | 20.1 |

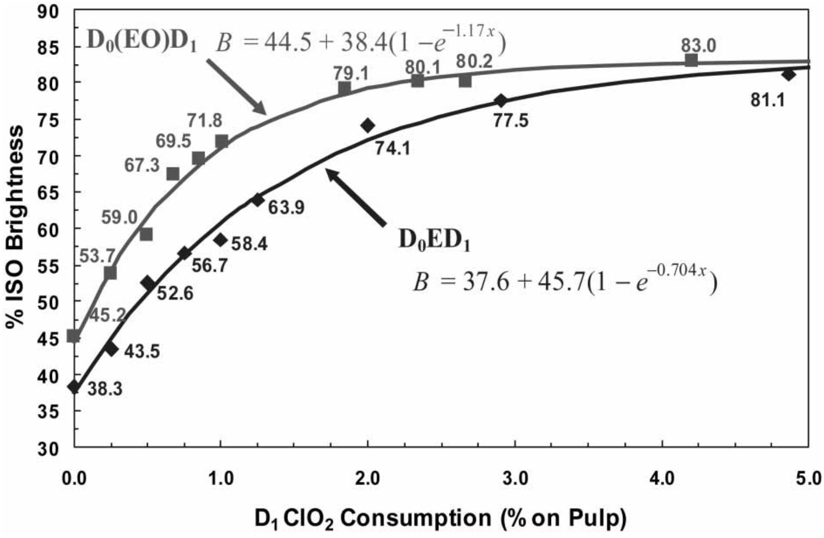

***Figure 3.*** $D_1$ stage brightness response curves for $D_0E$ and $D_0(EO)$ pulps. Data points are fitted to the curve based on Eq. 1.

Equation 1 reasonably modeled the data in Figure 3 for both pulps ($R^2 > 0.99$). The $D_0E$ and $D_0(EO)$ pulps are predicted to reach a common $D_1$ brightness ceiling of ~83% ISO. The $D_1$ initial response factor, $b_1 \cdot b_2$, represents the initial slope of the brightness response curve (Eq. 1). A high $b_1 \cdot b_2$ value indicates a quick brightening response to a low level of consumed $ClO_2$. The lower $b_1 \cdot b_2$ value for the $D_0E$ pulp (i.e., 32.2) versus $D_0(EO)$ pulp (i.e., 44.9) clearly indicates the slower brightening response of the $D_0E$.

The $D_0E$ stocks consumed significantly more $ClO_2$ in the $D_1$ stage than the $D_0(EO)$ pulps, generally twice the amount for a given brightness level, albeit, both pulps contained ~1.7% residual lignin. It was observed that there was no $ClO_2$ residual after $D_1$ for the $D_0E$ pulps until 3% $ClO_2$ was applied, whereas the $D_0(EO)$ pulps showed significant residuals at $\geq 1.25\%$ applied $ClO_2$. These results seem to support our hypothesis that the oxygen in the (EO) stage helps to oxidize polyphenolic structures formed during extraction that would otherwise consume additional $ClO_2$ in a subsequent $D_1$ stage (Figure 2).

We also examined the impact of $D_1$ stage on the yellowness of the $D_0E$ and $D_0(EO)$ pulps (Figure 4). The data in Figure 4 was modeled with the following equation, which we adapted from Eq. 1:

$$b^* = c_0 - c_1(1 - e^{-c_2 x}) \tag{2}$$

where $b^*$ is the predicted b* value, $x$ is the consumed amount of $ClO_2$, $c_0$ is the entering b* value, and $c_1$ is the b* value reduction across the $D_1$ stage.

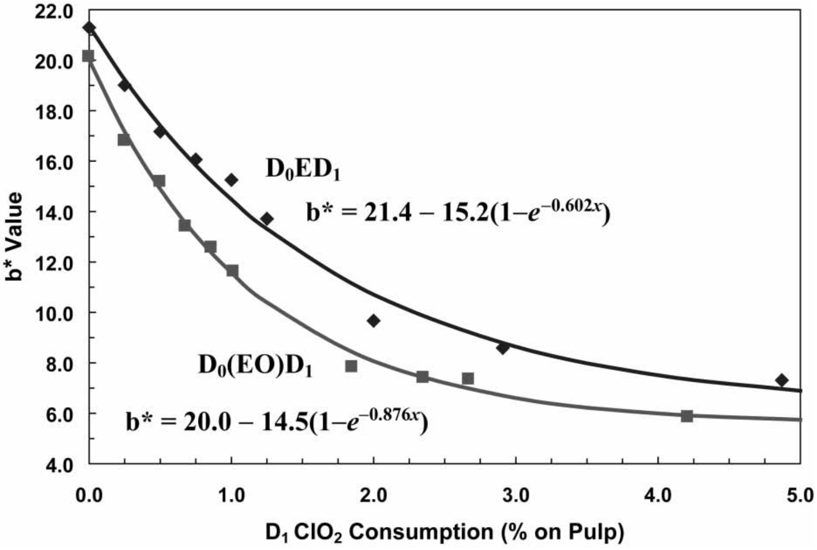

*Figure 4.* $D_1$ stage b* response curves for $D_0E$ and $D_0$(EO) pulps. Data points are fitted to the curve based on Eq. 2.

The difference $(c_0 - c_1)$ represents the asymptotic b* value limit of the $D_1$ stage, and the last parameter, $c_2$, denotes the relative rate at which this asymptotic limit is approached.

Equation 2 modeled the b* data in Figure 4 with precision for both pulps ($R^2 > 0.99$). Both the $D_0E$ and $D_0$(EO) pulps are predicted to reach a common b* value ~6. The results from this model imply that the brightness of both $D_0E$ and $D_0$(EO) pulps are limited by similar yellow chromophoric structures.

We also examined the impact of the $D_1$ stage on a* and L values. Overall, the a* for both pulps decreased to $\sim -0.8$. This change in the a* value indicates a shift in the overall red chromophoric (positive a* values) groups to slightly more green chromophoric groups (negative a* values). However, it should be noted that the b* values dominated the a* values (based on the absolute values), signifying that the yellow chromophoric groups are likely the chromophores influencing the $D_1$-brightness ceilings of the $D_0E$ and $D_0$(EO) pulps. Examination of the L values of $D_0E$ and $D_0$(EO) pulps mirrors the brightness curves shown in Figure 3, with both $D_0E$ and $D_0$(EO) pulp reaching a common L value ceiling of ~96 at excessive $ClO_2$ levels in $D_1$ stage.

## General Discussion

The findings from this investigation indicate that the polyphenolic structures arising from the alkaline treatment of $D_0$ lignin are readily oxidized to hydroxyquinones by $ClO_2$ in the $D_1$ stage,[25] or by the oxygen in the (EO) stage. The addition of oxygen to alkaline extraction does not result in additional lignin removal as indicated by the Klason lignin value. The lower kappa number of (EO) versus E pulps reflects a more oxidized lignin, which is likely related to fewer carbon-carbon double bonds.

Oxygen addition to alkaline extraction has a profound effect on the chemistry, as well as early brightness development, of the subsequent $D_1$ stage. As shown in Figures 1 and 2, the oxidation of the polyphenolic moieties by oxygen in the (EO) stage results in less $ClO_2$ being consumed in the $D_1$ stage, which allows the $ClO_2$ to react with other structures in the (EO) residual lignin. Although the $D_0$E pulps showed lower $D_1$ bleachability than $D_0$(EO) pulps, both pulps seem to reach a common brightness ceiling and floor-level b* value when excess $ClO_2$ is applied. This indicates that both $D_0$E and $D_0$(EO) pulps have similar chromophoric structures that limit the $D_1$ brightness ceiling; but it is unknown what these limiting chromophores are.

Hydroxyquinones in the $D_0$(EO) pulp appear to be removed during the $D_1$ stage, as well with the DE pulps at excessive $ClO_2$ levels, because the lignin/kappa ratio decreases downward to 0.15. It is known that $ClO_2$ reacts very slowly with *o*- and *p*-quinones,[18,19] much like the reaction rate of $ClO_2$ with non-phenolic structures.[13–15] It is unknown if the hydroxyl group on the hydroxyquinones might make the structure more reactive toward $ClO_2$. Hydroxyquinone structures have pKa values of 4 to 5,[43] which would be partially ionized under typical $D_1$ stage conditions, and possibly, increase their $ClO_2$ reactivity. It is also known that hydroxyquinones can undergo one-electron radical oxidation reactions with certain agents, such as cerium(IV) compounds.[44] Analogous reactions could be occurring with $ClO_2$. Future model compound work is needed to study how polyphenolic structures and hydroxyquinones are modified and fragmented by $ClO_2$ and $O_2$; the knowledge gained from such investigations could further our understanding of how ECF bleach sequences work in concert with one another.

## CONCLUSIONS

Chlorine dioxide delignification ($D_0$) introduces *both* quinones and muconic structures into the oxidized lignin. Caustic extraction (E) removes solubilized lignin and converts quinone moieties to polyphenols. The oxygen in an EO stage does not cause more lignin to be removed versus an E stage, as measured by the Klason lignin, but appears to oxidize polyphenols to hydroxyquinones, as reflected by the lower kappa number. Polyphenols in DE pulps consume additional $ClO_2$ in a $D_1$ stage to form hydroxyquinones ($\sim$1.8 mmol/g lignin). Pulps treated by $D_0$E have a lower $D_1$ bleachability versus $D_0$(EO) pulps, as was quantified by a simple bleaching model. Both $D_0$E and $D_0$(EO) pulps approach a common brightness ceiling ($\sim$83 ISO) and asymptotic b* value ($\sim$6) when excess $ClO_2$ is applied. This indicates that both pulps have similar residual chromophores. Hydroxyquinone structures appear to be eliminated in the $D_1$ stage for $D_0$(EO) pulps, and at high $ClO_2$ levels for $D_0$E pulps, as is shown by the decrease in the lignin/kappa ratio from 0.18 to 0.15.

## EXPERIMENTAL

### Pulp Bleaching

A conventional softwood kraft pulp (black spruce [*Picea marianna*]) was used throughout this study and was produced from the mature wood fraction of a single tree. The pulp was produced using a laboratory pilot digester using the following conditions: 18.5% active alkali (on o.d. wood as $Na_2O$), 30% sulfidity, liquor : wood of 4 : 1 L/kg, 90 min. to 172°C, and an H-factor ~1700. The resulting pulp had a kappa number of 24.0, a viscosity of 23.0 mP · s, and a screened yield of 51.1%. The pulp was well washed prior to use, pressed to ~30% consistency and stored in a cold room (at ~4°C) until needed. Samples of the unbleached pulp were subjected to acid hydrolysis at pH 3.5 and 100°C for 2 hours to check for hexeneuronic acids (HexA);[45] no significant changes in the kappa number were observed, indicating that the pulp contained negligible HexA structures.

Chlorine dioxide delignification ($D_0$) was performed on the mature wood pulp under the following conditions: 0.15 kappa factor (KF), 10% consistency, initial pH 4.2–4.6 prior to $ClO_2$ addition, 70°C, and a 30-min. reaction time. Periodate oxidations were performed at the following conditions on the unbleached kraft pulp: 5% $NaIO_4$ on pulp, 10% consistency, initial pH 2 to 2.2 prior to $NaIO_4$ addition, 70°C, and a 120-min. reaction time. Hydrosulfite reductions on selected pulps were carried out in vacuum-sealed pouches at the following conditions: 5% $Na_2S_2O_4$ on pulp, 20% consistency, 70°C, and 120-min. reaction time. Caustic extractions (E) were conducted on selected pulps at the following conditions: 2% NaOH on pulp, 10% consistency, 70°C, and 60-min. reaction time.

All bleaching and oxidation treatments, except for the (EO) stage, were conducted in heat-sealable plastic bags. The (EO) stage was performed in a 2-L Parr Bomb reactor at similar conditions as the E stage with 0.42 MPa (~60 psig) of oxygen; the oxygen pressure was decreased by ~0.07 MPa (~10 psig) every 5 minutes. Chlorine dioxide bleaching stages ($D_1$) were performed at the following conditions: 0.25 to 5% $ClO_2$ on pulp, 10% consistency, 70°C, and 90-min. reaction time. Caustic was added to $D_1$ stage runs such that the end pH was within 3.2 to 4.5.

### *In-Situ* Residual Lignin Analysis

Kappa numbers were determined by micro-kappa number measurements (TAPPI Useful Method UM-246). Klason lignin analyses were done in accordance with TAPPI Standard T-222 om-85 with one minor modification.[46] The insoluble lignin was separated from the acid supernatant using a Millipore® filter funnel instead of a medium-porosity filtering crucible as denoted in T-222 om-85. The filter funnel contained a pre-weighed Whatman® glass microfiber filter ($\geq$1.5 μm particle retention capacity). The amount of quinones in selected pulps was estimated from the kappa number and Klason lignin data by the method described by Brogdon.[23,24] Experiments were performed on periodate oxidized cotton linters to confirm that cellulose oxidation did not influence $KMnO_4$ uptake during the kappa test; results indicated the oxidized linters ($\sim$0.5 g) did not consume $KMnO_4$.[24]

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