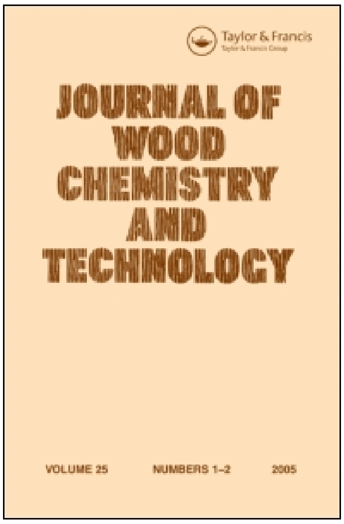

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New Insights into Lignin Modification during Chlorine Dioxide Bleaching Sequences (IV): The Impact of Modifications in the (EP) and (EOP) Stages on the D_1 Stage

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Abstract: Peroxide-reinforced extractions ((EP) or (EOP)) of D_0 pulps lower both post-extraction kappa numbers and Klason lignins more than either E or (EO). An oxygen-reinforced extraction (EO) results in lower kappa numbers, but affords comparable Klason lignins as an E stage ($\sim$1.2% lignin). Quinonoid structures in (EO) stocks are similar to those of the D_0 pulps (1.7 mmol/g lignin). Peroxide inclusion in EP and EOP appeared to eliminate *both* quinonoid *and* muconic acid moieties. These observations were confirmed with (EP) treatment of reference pulps (periodate or periodate-peracetic acid) that contain significant levels of either quinones or muconic entities. The D_1 bleachability order, from easiest to hardest, was $D_0(EOP) > D_0(EP) \approx D_0(EO) > D_0E$. An identical order was found for how quickly the yellow chromophores (b* value) are eliminated. All extracted pulps, regardless of the type of extraction employed, approach a common D_1 asymptotic brightness ($\sim$86 ISO) and b* value ($\sim$4.2) when excess ClO_2 is applied. The main difference among these pulps was how quickly the asymptotic limits are approached as a function of ClO_2

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

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consumed. The bleachability study indicates that various extracted pulps have similar residual D_1 chromophores limiting the brightness ceiling.

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

INTRODUCTION

Chlorine dioxide has become the most widely employed oxidant for bleaching kraft pulps in North American.[1–4] Likewise, the use of oxygen and/or hydrogen peroxide in the alkaline extraction stage (i.e., (EO), (EP), or (EOP)) has gained broad acceptance as an integral part of these elemental chlorine-free (ECF) bleach sequences because of their ability to reduce bleaching cost with low capital investments.[5] Chlorine dioxide (D_0) modifies and fragments the residual lignin and, subsequently, this modified lignin is further altered, solubilized, and removed during oxidative extraction. It is recognized that the future brightness development and limitations of a pulp (i.e., bleachability) with these ECF sequences can be greatly influenced by its previous pulping and bleaching delignification history.[3,4,6–9]

Unfortunately, we currently lack a comprehensive description of what occurs during bleaching and how stages in a given ECF sequence work in concert with one another to delignify and decolorize pulps. This is particularly true regarding the oxidative extraction stages. How do oxygen and/or hydrogen peroxide modify the D_0 residual lignin, and how do these oxidants in the alkaline extraction impact the fundamental chemistry of the subsequent D_1 brightening stage? Several investigators have attempted to define how certain oxidants modify and fragment model compounds that are representative of unbleached lignin.[10–19] However, very few inquiries have been made as to how oxygen and/or hydrogen peroxide might interact with D_0 oxidized lignin structures.[20–22]

The intent of our work is to provide a unified bleaching theory for chlorine dioxide bleaching sequences, 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. Our investigations have studied chlorine dioxide delignification (D_0)[23,24] and extraction (E and EO).[25,26] In this article, we propose how peroxide modifies residual D_0 lignin during (EP) and (EOP) stages and how it impacts the D_1 bleaching stage. We utilize facile *in-situ* methods we have developed to track salient functional groups in the oxidized pulp.[23,24] Through the results of this work, we hope to establish some of the fundamental chemistry that occurs during the (EP), (EOP), and D_1 stages.

BACKGROUND ON THE FUNDAMENTAL REACTIONS FOR (EP) AND (EOP) STAGES

Peroxide inclusion in the extraction stage (i.e., an (EP) stage) was first patented by Luth *et al.* in the mid-1930s.[27] In the late 1980s, Liebergott and van Lierop[28] performed an extensive study on oxidative-reinforced extraction for chlorinated pulps (e.g., C or (CD)) and noted that the post-extraction kappa numbers could be lowered by ~0.8 units by the addition of peroxide to the E stage. These investigators also showed that combinations of oxygen and peroxide in the extraction stage (i.e., (EOP)) decreased the post-extraction kappa number by ~3 units versus an E stage, and by ~1 unit versus an (EO) stage. Basta and co-workers[29] reported for D_0 treated softwood pulps that peroxide additions of 0.5 to 1% in the (EOP) stage lowered the extracted kappa numbers by 1 to 2.5 units versus the (EO) stage. In general, the inclusion of peroxide in E and (EO) stages boosted the post-extraction brightness 2 to 10 points based on the amount applied.[5,28,29] The earlier results with peroxide in extraction are somewhat analogous those observed in an (EO) stage applied to chlorinated pulps, which drops the kappa number 2 to 4 units compared to an E stage. Usually, these oxygen reactions occur within the first few minutes when sufficient oxygen pressure is applied [~0.21 MPa (~30 psig)].[5,28,30–32]

The earlier observations imply that there are labile groups within these oxidized lignins that are readily oxidized by peroxide or combinations of oxygen and peroxide during alkaline extraction. Investigations by Brogdon *et al.*[23–25] have provided evidence that the D_0 stage oxidizes phenolic groups in the unbleached lignin to *both* quinonoid and muconic acid-type structures in ~2-to-1 ratio, respectively. Based on this information, it is estimated that ~30% of the D_0 residual lignin is composed of quinonoid structures. Alkaline treatment of the D_0 pulp in an E stage, in addition to removing solubilized lignin, was shown to convert these quinones to polyphenols (via 1,4-reductive Michael addition of hydroxide to quinones, Figure 1), somewhat analogous to hydrosulfite reduction (Y) of D_0 pulps.[25] These new polyphenols can be easily oxidized to hydroxyquinones by either oxygen in an (EO) stage (Figure 1) or with chlorine dioxide (Figure 2) in a subsequent D_1 stage.[26]

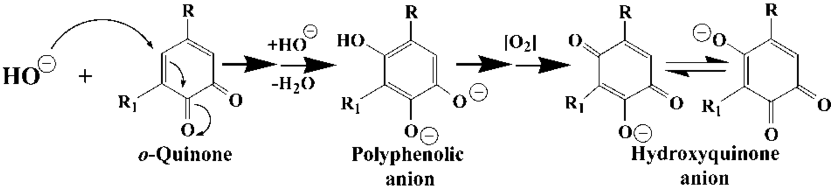

Figure 1. Postulated reactions of *o*-quinones during an (EO) stage treatment of D_0 and oxidized pulps.[26] **R** = lignin side chain and $\mathbf{R_1}$ = H or OCH_3.

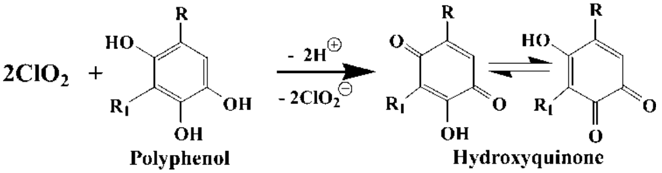

Figure 2. Postulated reactions ClO_2 with polyphenolic structures during the D_1 stage treatment of D_0E pulps.[17,26] **R** = lignin side chain and $\mathbf{R_1}$ = H or OCH_3.

The reactions of peroxide with D_0 oxidized lignin during (EP) or (EOP) stages is expected to be more varied and complex than those with oxygen in an (EO) stage.[10,12,18–22] As we noted earlier, most of the labile phenolic groups that are reactive toward oxygen and/or peroxide in the unbleached lignin have been oxidized by ClO_2 in the D_0 stage.[10,11,24] Initially, peroxide in an (EP) stage likely oxidizes polyphenolic structures to hydroxyquinones (like Figure 1) through its decomposition intermediates, such as oxygen and/or superoxide anion/perhydroxyl radicals.[21] Numerous model lignin and quinone model studies[10,12,18–22] have shown that perhydroxyl anion (HOO^-) is reactive toward quinonoid structures, generally decomposing these moieties to low molecular weight organic acids (Figure 3), such as oxalic and acetic acid, and to carbon dioxide/carbonate. [It should be noted that several researchers[33] have indicated that hydroxyquninones react slowly with peroxide. Gellerstedt *et al.*[22] however, have demonstrated such structures are reactive toward peroxide at pH 11.] These HOO^- reactions further rupture and fragment the lignin ring structure, generally leaving behind the aliphatic side chain and an oxidized lignin that contains fewer carbon-carbon double bonds.[10,12,18–22]

A second HOO^- reaction that likely occurs with the D_0 oxidized lignin involves the muconic acid-type structures. Several investigations[34–36] including our recent study[24] propose that D_0 oxidized lignins contain signi-

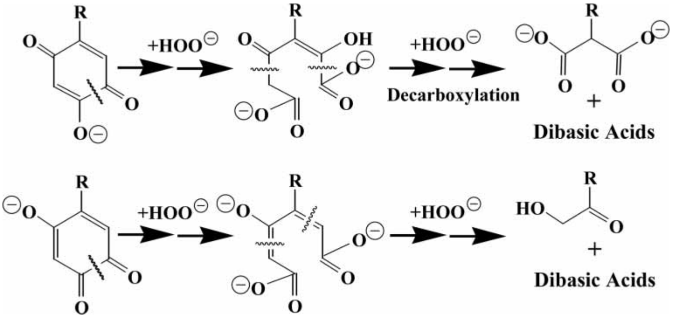

Figure 3. Postulated reactions of hydroxyquinones in (EP) and (EOP) stage treatment of D_0 and periodate oxidized pulps. **R** = lignin side chain.

ficant levels of muconic acid-type components, roughly $\sim$1 mmol/g lignin ($\sim$15% of the D_0 lignin structure). Such structures, as show in Figure 3 as an intermediate peroxide decomposition product of quinonoids,[10,12,18–22] are susceptible to HOO^- attack. Muconic oxidation by peroxide affords dibasic acids fragments and the remains of the aliphatic lignin side chain. Such reactions have been proposed but have not been specifically studied with model muconic acid structures, like those with quinones or unbleached lignin.

Combinations of oxygen and peroxide during extraction (i.e., (EOP)) are anticipated to be more effective than either oxidant alone. Oxygen would rapidly oxidize polyphenolic to quinonoid compounds (Figure 1),[37–41] thus allowing the peroxide to further degrade these quinones, as well as the muconic acid-type structures, to further reduce the overall amount of residual lignin carbon-carbon double bonds (Figure 3).

How would the degradation of the D_0 lignin by peroxide in (EP) and (EOP) stages impact Klason lignin, post-extraction kappa number, and the ratio of these values? Several investigations have established that acidic $KMnO_4$ stoichiometrically reacts with the carbon-carbon double bonds contained in the rings of aromatic[42,43] and quinonoid units[23] of model lignin. In the case of the (EO) stage, Brogdon and Lucia[26] have showed that (EO) pulps have identical lignin/kappa ratio values as D_0 pulps (i.e., 0.18), and have similar Klason lignin contents as D_0E treated pulps. The difference in the lignin/kappa ratio between D_0E and $D_0(EO)$ (0.15 vs. 0.18, respectively) was related to the autoxidation of the newly formed polyphenolics in the E stage (Figure 1).[26] Thus, the lignin/kappa ratio generally increases above 0.15 when the number of carbon-carbon double bonds decreases in the oxidized lignin versus the unbleached lignin.[23–25]

It is expected that small levels of peroxide will likely indirectly oxidize polyphenolic structures to hydroxyquinones, similar to that observed for (EO) stages;[26] this should result in lower kappa numbers and an increase in lignin/kappa ratio to $\sim$0.18 versus an E stage. However, as the peroxide level is increased in an (EP) stage, or as peroxide is added to an (EO) stage (i.e., (EOP)), one would expect the lignin/kappa ratio to increase beyond 0.18 as the unsaturated bonds in the $D_0(EP)$ and $D_0(EOP)$ residual lignin are further eliminated by the action of HOO^-.

To test these hypotheses, we examined the effect of E, (EO), (EP), and (EOP) stages on D_0 pulps, and how these treatments affected ClO_2 oxidation in a subsequent D_1 stage. As a reference, comparisons of E, (EO), (EP), and (EOP) treatments were conducted on periodate oxidized pulps, which are known to contain significant levels of *o*-quinones.[23–26] A second reference pulp, a periodate-peracetic acid (Paa) oxidized pulp, was treated with an (EP) stage to examine how peroxide impacts muconic acid structures. Periodate-Paa oxidized pulps are known to contain significant levels of muconic acid-type structures.[23] 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.[23–26] In addition, we investigated how (EP) and (EOP) stages affected ClO_2 oxidation in a subsequent D_1 stage in terms bleachability in comparison to (EO) and E stages.

RESULTS AND DISCUSSION

Initial Analysis of D_0(EP) and D_0(EOP) Residual Lignins

A black spruce kraft pulp free of hexeneuronic acids (HexA) was oxidized with either ClO_2 in a D_0 stage (0.20 KF) (Table 1), or with excess sodium *meta*-periodate (Table 2). The 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,[23–26] ClO_2 and periodate oxidation caused the lignin/kappa ratio to shift from 0.15 to 0.18. This shift in the ratio for these pulps has been correlated to quinone levels contained in residual lignin. The amount 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 ~1.7 and 2.0 mmol quinones/g residual lignin, respectively. These values closely correspond to ~30% reduction in the methoxyl group content (~1.6 mmol methoxyl

Table 1. Analysis of residual lignin in kraft pulps after the D_0 stage and various alkaline extractions reinforced with peroxide and/or oxygen

Pulp[a]	Kappa number	Klason lignin (%)	Lignin/ Kappa ratio	mL 0.1*N* $KMnO_4$/g lignin	mmol quinones/g lignin
Unbleached	25.0	3.7	0.15	670	Non-detectable
D_0 (0.20 KF)	14.0	2.5	0.18	560	1.7
D_0E	7.8	1.2	0.15	650	Non-detectable
D_0(EO)	6.2	1.1	0.18	570	1.6
D_0(EP) 0.5% H_2O_2	5.8	0.7	0.12	770	Non-detectable
D_0(EP) 1.0% H_2O_2	5.4	0.6	0.11	830	Non-detectable
D_0(EOP) 0.5% H_2O_2	5.7	0.6	0.10	860	Non-detectable
D_0(EOP) 1.0% H_2O_2	5.4	0.5	0.09	870	Non-detectable

[a] KF denotes Kappa Factor charge of ClO_2 in D_0 stage.

Table 2. Analysis of residual lignin in kraft pulps after periodate oxidation and various alkaline oxidative extractions

Pulp[a]	Kappa number	Klason lignin (%)	Lignin/ Kappa ratio	mL 0.1*N* $KMnO_4$/g lignin	mmol quinones/g lignin
Unbleached	25.0	3.7	0.15	670	Non-detectable
Periodate	19.1	3.5	0.18	550	2.0
Periodate-E	16.8	2.5	0.15	670	Non-detectable
Periodate-(EO)	13.0	2.4	0.18	540	2.1
Periodate-(EO)-Y	13.4	2.1	0.16	640	Non-detectable
Periodate-(EP) 1% H_2O_2	13.9	2.5	0.18	540	1.8
Periodate-(EP) 2% H_2O_2	12.3	2.1	0.17	590	1.0
Periodate-(EP) 3% H_2O_2	11.4	1.7	0.15	670	Non-detectable
Periodate-(EP) 4% H_2O_2	9.1	1.1	0.12	770	Non-detectable
Periodate-(EOP) 1% H_2O_2	10.5	1.8	0.17	590	1.1
Periodate-(EOP) 2% H_2O_2	10.1	1.5	0.15	670	Non-detectable
Periodate-(EOP) 3% H_2O_2	9.4	1.4	0.15	670	Non-detectable
Periodate-(EOP) 4% H_2O_2	9.0	1.0	0.12	770	Non-detectable

[a] Y denotes hydrosulfite reduction.

groups/g lignin) we measured in spruce kraft lignin after ClO_2 or periodate oxidation. Demethoxylation is an indirect indicator of *o*-quinone formation.[24]

The D_0 and periodate pulps in Tables 1 and 2 were subjected to either caustic extraction (E) or oxidative-reinforced alkaline extraction with oxygen (EO), peroxide (EP), and combinations of the two (EOP). The E stage caused the lignin/kappa ratio of D_0 and periodate pulps to return back to 0.15, comparable to that of the unbleached lignin and is consistent with our earlier investigations.[25,26] 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 and consume additional $KMnO_4$ during the kappa number test. The (EO) stage treatment, however, 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. The (EO) stage did not result in additional lignin removal, as is noted by the Klason lignin, when compared to the E stage. Estimates of the quinone levels in the (EO) pulps are similar to those found in the previous D_0 or periodate oxidative stage. To confirm the presence of the quinones, we treated the periodate-(EO) pulp with hydrosulfite, which reduces the quinones to their respective hydroquinones. This action should cause the modified lignin to consume similar amounts of $KMnO_4$ as the unbleached residual lignin;[23–26] this was the observed result (Table 2). These results are consistent with our earlier (EO) study.[26]

The (EP) and (EOP) stage treatments of the D_0 pulp (Table 1), unlike the above E or (EO) stages, did not cause the lignin/kappa ratio of the D_0 and periodate oxidized pulps to remain at 0.18, or return to 0.15. Instead, this proportion decreased to values between 0.09 and 0.12. We observed similar results when D_0E and D_0(EO) pulps were treated with high ClO_2 charges (>1%) in a D_1 stage.[26] It is interesting to note that peroxide addition in (EP) and (EOP) stages, unlike oxygen addition, resulted in reductions of *both* the kappa number (~2.3 unit drop) and the Klason lignin (0.6% unit drop) when compared to an E stage.

To obtain some clues as to how particular structures in the D_0 lignin are being modified by peroxide in (EP) and (EOP) stages, we treated the periodate pulp with (EP) and (EOP) stages (Table 2). Low levels of peroxide in the (EP) stage (i.e., <1%) caused the lignin/kappa ratio of the periodate-(EP) pulp to increase to 0.18. This implies that peroxide is oxidizing the polyphenolics to quinonoid structures, at a level of ~1.8 mmol/g lignin, similar to that occurring with oxygen in the (EO) stage. Increasing the peroxide to 3% in the (EP) stage decreased the lignin/kappa ratio of the periodate-(EP) pulps to 0.15; this ratio decreased further to 0.12 when 4% peroxide was applied. The Klason lignin of the periodate-(EP) and -(EOP) pulps decreased as the amount of peroxide was increased from 1 to 4%. Treatment of the periodate pulps with (EP) or (EOP) stages afforded pulps that had lower kappa and Klason lignin values than either E or EO treated pulps, and caused the lignin/kappa value to decrease to 0.12. These observations signify that peroxide has modified and degraded the structures contained in periodate oxidized lignin.

Impact of Peroxide in Alkaline Extraction on the Lignin/Kappa Ratio

The shift in the lignin/kappa proportion for (EP) and (EOP) treated pulps to values <0.15 was not initially anticipated. Decreasing lignin/kappa values to <0.15 would imply that the amount of carbon-carbon double bonds had increased in the post-(EP) or (EOP) residual lignin versus the E stage or unbleached lignin. Van Lierop *et al.*[44] reported lignin/kappa values as low as 0.12 for extracted pulps previously treated with C, CD, and DC stages. It is known that these chlorinated and extracted pulps have had their residual lignin extensively oxidized and modified;[10,12] although these results would also suggest an increase in the amount of carbon-carbon double bonds in the post-extraction lignin.

One explanation for the shift to values <0.15 for post-(EP) and -(EOP) pulps, as well as for extracted chlorinated pulps, is the acid hydrolysis and solubilization of degraded aliphatic lignin side chains during the Klason analysis. [This would be somewhat similar to the carbohydrate hydrolysis and solubilization that occurs to afford the insoluble Klason lignin for unbleached lignin isolation.] Solubilization and removal of the degraded aliphatic lignin side chains would lower the measured gravimetric yield of the insoluble lignin recovered from the Klason analysis, thus causing the lignin/kappa ratio to decrease.

To examine this hypothesis, we re-analyzed the kappa numbers of the various periodate pulps in Table 2 without washing the pulp. In these tests, the pulps after their extraction treatments were measured without removing the extraction effluent (Table 3). The kappa numbers of these pulps with their included extraction effluents were much higher than the corresponding well-washed pulps. If the ratios of these new kappa numbers to the known amount of lignin coming into the extraction stage (i.e., the periodate pulp lignin (3.5%)) are calculated, the results show a different trend in the lignin/kappa ratio, as shown in Table 3.

In this second analysis, both (EP) and (EOP) treatment of the periodate pulp shows that the lignin/kappa value increases above 0.18 as the peroxide level is increased above 1%. It should be noted, however, that the periodate-(EOP) pulp treated with 4% peroxide had some trace residuals of peroxide in the (EOP) effluent, which contributed to $KMnO_4$ consumption during the kappa test and resulted in a higher measured kappa number of the pulp plus extraction effluent.

The results of pulp plus extraction effluents presented in Table 3 seem to confirm our premise that (EP) and (EOP) lignins contain fewer carbon-carbon double bonds than E or (EO) lignins because the lignin/kappa ratio increased above 0.18. It also appears that the drop in the Klason lignin in the washed (EP) and (EOP) pulps is partially related to the acid dissolution of degraded aliphatic lignin side chains of the highly oxidized lignin during the Klason analysis.

Closer examination of the data in Table 3 shows a subtle difference between (EP) and (EOP) stages. The E stage treatment initially decreased the 0.18 ratio for the periodate pulp to 0.14; but as the amount of peroxide is increased from 0 to 1% in the (EP) stage, this ratio then increased from 0.14 to 0.18. The periodate-(EOP) pulps, unlike the (EP) treatment, showed a steady increase in the ratio from 0.18 in the periodate and periodate-(EO) pulps to 0.23 as peroxide was applied. These results are congruent with our earlier assessments that oxygen in the extraction stage helps oxidizes polyphenolic structures arising during the alkaline treatment of D_0 and periodate oxidized lignins.[26] The shift in the ratio for the (EP) pulps also indicates that initially that peroxide is causing the oxidation of polyphenolics to hydroxyquinones; excess peroxide in theses stage can further modify hydroxyquinone structures.

Table 3. Analyses of residual lignin in kraft pulps after periodate oxidation and various oxidative extraction treatments without and with extraction effluents

Pulp	Kappa number[a]	Klason lignin (%)[a]	Lignin/ Kappa ratio[a]	Kappa number pulp w/E stage effluent	Re-calculated lignin/kappa ratio of pulp w/E stage effluent[b]
Periodate	19.1	3.5	0.18	—	—
Periodate-E	16.8	2.5	0.15	24.9	0.14
Periodate-(EP) 0.5% H_2O_2	ND	ND	ND	23.1	0.15
Periodate-(EP) 1% H_2O_2	13.9	2.5	0.18	19.4	0.18
Periodate-(EP) 2% H_2O_2	12.3	2.1	0.17	18.9	0.19
Periodate-(EP) 3% H_2O_2	11.4	1.7	0.15	17.4	0.20
Periodate-(EP) 4% H_2O_2	9.1	1.1	0.12	16.1	0.22
Periodate-(EO)	13.0	2.4	0.18	19.9	0.18
Periodate-(EOP) 0.5% H_2O_2	ND	ND	ND	18.4	0.19
Periodate-(EOP) 1% H_2O_2	10.5	1.8	0.17	17.2	0.20
Periodate-(EOP) 2% H_2O_2	10.1	1.5	0.15	15.5	0.23
Periodate-(EOP) 3% H_2O_2	9.4	1.4	0.15	15.9	0.22
Periodate-(EOP) 4% H_2O_2	9.0	1.0	0.12	18.6[c]	0.19[c]

[a] ND = not determined.

[b] Lignin/kappa ratio of pulp with extraction effluent are calculated based on the Klason Lignin of Periodate pulp (3.5%) entering into the extraction stage.

[c] Effluents contained residual peroxide that contributed to higher $KMnO_4$ consumption.

Impact of Peroxide in Alkaline Extraction on the Muconic Acid Structures in Residual Lignin

In addition to the earlier experiments, we examined how peroxide in the E stage affects the muconic acid structures by examining the (EP) treatment of periodate-Paa pulps. Brogdon[23] demonstrated with muconic models and lignins enriched with muconic structures (i.e., sequentially oxidized by periodate and then Paa) that these moieties consumed comparable amounts of $KMnO_4$ as aromatic units in unbleached lignin, even though such structures contain fewer carbon-carbon double bonds than unbleached lignin. Comparable results were observed when we treated the periodate pulp with Paa (Table 4). Alkaline treatment of periodate-Paa oxidized pulp did not affect the lignin/kappa ratio. However, the inclusion of 0.5% peroxide during extraction resulted in a significant decrease in the Klason lignin (0.7) and lignin/kappa ratio (0.12). This result implies that peroxide is also reactive toward muconic acid structures in D_0 and periodate-Paa residual lignin, possibly degrading such moieties to residual aliphatic lignin side chains. The downward shift in the ratio is analogous to (EP) and (EOP) treatments of quinonoid-enriched pulps (Table 3). The reactivity of HOO^- with muconic structures was anticipated because such structures are formed as intermediates from the initial attack of quinonoid structures by HOO^-.

Impact of (EP) and (EOP) on D_1 Bleachability and Brightness Ceiling

The extracted pulps described in Table 1 were bleached with various levels of ClO_2 in a D_1 stage to examine how the extraction stage conditions impact D_1 stage bleachability. The brightness and CIE color coordinates values (i.e., L, a*, and b*) of these pulps, as well as the initial brownstock and the D_0 pulps are provided in Table 5. The D_0 stage caused an increase in the b* value, which indicates the pulp contains more yellow chromophores. The addition of 0.5% peroxide in the (EP) stage boosted the brightness by ~9 points versus the E stage. Likewise, the inclusion of 0.5% peroxide in the (EOP) stage increased the brightness by ~6 points over the (EO) stage. The various extraction processes generally caused the a* value to approach 0. The b* values for all pulps examined tended to be more dominant versus the a* values. Extractions reinforced with peroxide (i.e., (EP) and (EOP)) generally had lower b* values than either the E or (EO) counterparts.

Table 4. Analysis of residual lignin in kraft pulps after periodate oxidation and various oxidative extraction treatments

Pulp[a]	Kappa number	Klason lignin (%)	Lignin/ Kappa ratio	mL 0.1*N* $KMnO_4$/g lignin	mmol quinones/g lignin
Unbleached	25.0	3.7	0.15	670	Non-detectable
Periodate	19.1	3.5	0.18	550	2.0
Periodate-E	16.8	2.5	0.15	670	Non-detectable
Periodate Paa	11.5	1.8	0.16	640	Non-detectable
Periodate Paa-E	7.1	1.1	0.15	670	Non-detectable
Periodate Paa-(EP) 0.5% H_2O_2	6.3	0.7	0.12	770	Non-detectable

[a] Paa denotes peracetic acid oxidation.

Table 5. Influence of D_0E, $D_0(EP)$, $D_0(EO)$, and $D_0(EOP)$ 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	25.0	3.7	33.2	75.7	3.4	20.4
D_0 (0.20 KF)	14.0	2.5	35.0	79.1	3.5	23.7
D_0E	7.8	1.2	46.2	84.5	1.4	19.4
$D_0(EP)$ 0.5% H_2O_2	5.8	0.7	54.9	88.6	0.3	17.3
$D_0(EO)$	6.2	1.1	50.2	86.5	0.8	18.5
$D_0(EOP)$ 0.5% H_2O_2	5.7	0.6	59.6	90.6	−0.3	16.0

Figure 4 shows the brightening responses of the pulps in Table 3 in the D_1 stage. The data in this figure were fitted to a brightening model to numerically quantify D_1 bleachability:[3,4,9,26]

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

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. The sum $(b_0 + b_1)$ represents the brightness ceiling of the D_1 stage, and the last parameter, b_2, denotes the relative rate at which this ceiling is approached. The parameters values for Equation 1 for the D_1 pulps in Figure 4 are shown in Table 6.

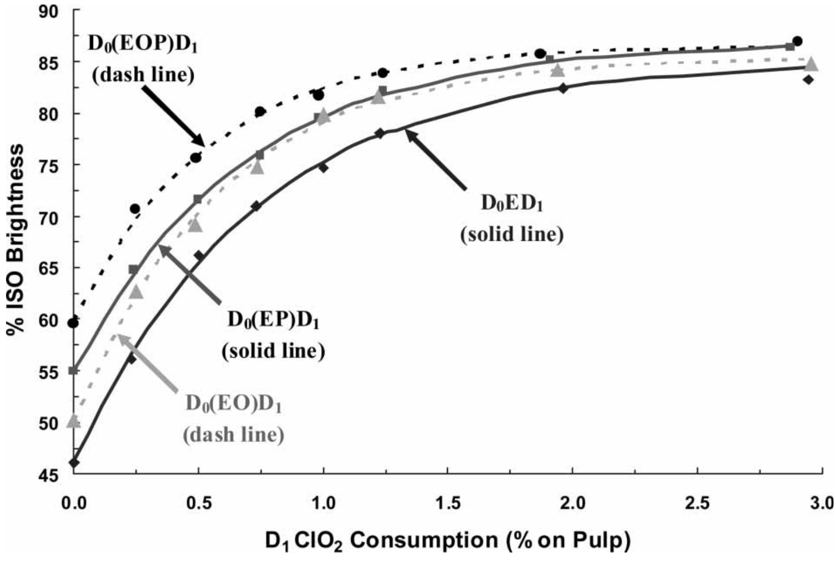

Figure 4. D_1 stage brightness response curves for D_0E, $D_0(EO)$, $D_0(EP)$, and $D_0(EOP)$ pulps. Data points are fitted to the curve based on Eq. 1.

Table 6. Influence of D_0E, $D_0(EP)$, $D_0(EO)$ and $D_0(EOP)$ stages on the brightness parameters of Eq. 1 for describing D_1 bleachability

Pulp	b_0	b_1	b_2	ISO brightness ceiling (b_0+ b_1)	R^2
D_0E	46.0	38.7	1.41	84.7	0.998
$D_0(EP)$ 0.5% H_2O_2	55.0	32.0	1.47	87.0	0.999
$D_0(EO)$	50.1	35.3	1.70	85.4	0.998
$D_0(EOP)$ 0.5% H_2O_2	59.9	32.0	1.85	86.5	0.998

Equation 1 reasonably modeled the data in Figure 4 for all four pulps ($R^2 > 0.99$), and the b_0 values closely correspond to the actual initial brightness levels in Table 5. The D_0E and $D_0(EO)$ pulps are predicted to reach a common D_1 brightness ceiling of ~85% ISO, whereas the $D_0(EP)$ and $D_0(EOP)$ pulps are predicted to reach a slightly higher brightness ceiling of ~86.8% ISO.

The D_0E pulp consumed 50% more ClO_2 than $D_0(EO)$ or $D_0(EP)$ to reach a target D_1 brightness. Both $D_0(EO)$ and $D_0(EP)$ pulps exhibited similar brightening responses for similar amount of ClO_2 consumed. The inclusion of oxygen in the (EOP) stage reduces the ClO_2 requirements by ~30 to 40% compared to the $D_0(EP)$ pulp. These results suggest that combinations of oxygen and peroxide in the (EOP) stage affords a residual $D_0(EOP)$ lignin that requires less ClO_2 to decolorize than either oxidant alone in the extraction stage. The high ClO_2 charges needed to brighten the D_0E pulp seem to support our hypothesis that the oxygen or peroxide in the (EO) or (EP) stage helps to oxidize polyphenolic structures formed during extraction that would otherwise consume additional ClO_2 in a D_1 stage (Figure 2).

We examined the impact of the D_1 stage on the yellowness of the D_0E, $D_0(EO)$, $D_0(EP)$, and $D_0(EOP)$ pulps (Figure 5). The data in Figure 5 was modeled with the following equation, which we adapted from Eq. 1:[26]

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

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. 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 5 with precision ($R^2 > 0.99$, Table 7). All four extracted pulps were predicted to reach a common b* value ~4 to 4.5. The model suggests that all four pulps have similar "floor-level" yellow chromophoric groups, which are contributing to the D_1 brightness ceiling. The main differences among the four pulps is how quickly the "floor-level" b* values and the brightness ceiling are approached as the amount of ClO_2 is increased.

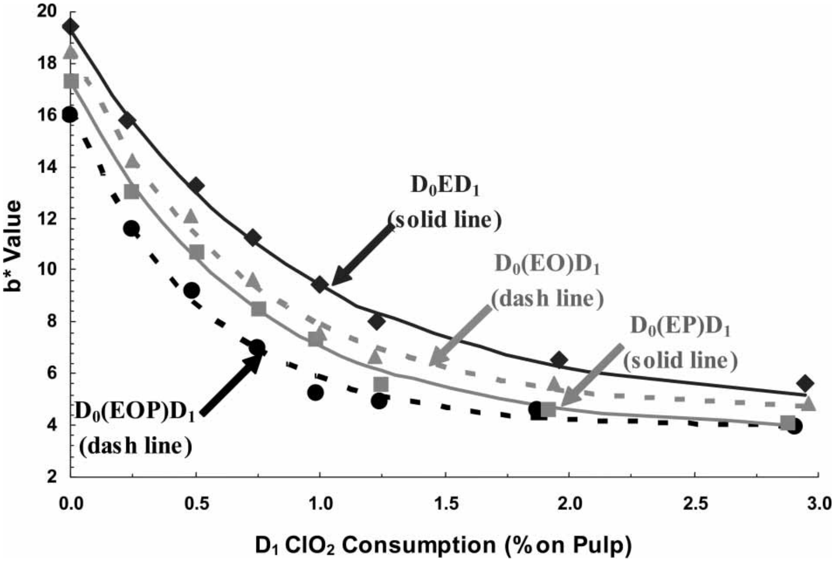

Figure 5. D_1 stage b* response curves for D_0E, $D_0(EO)$, $D_0(EP)$, and $D_0(EOP)$ pulps. Data points are fitted to the curve based on Eq. 2.

We also studied the impact of the D_1 stage on a* and L values. Overall, the a* values for all extracted pulps decreased to values ~ -0.9; 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, the b* values dominate over the a* values (based on the absolute values), signifying that the yellow chromophoric groups are likely the chromophores influencing the D_1-brightness. Examination of the L values for the various extracted pulps mirrors the brightness curves in Figure 4, where all the extracted pulps approach a common L value ceiling of ~96.5 at excessive ClO_2 levels.

Table 7. Influence of D_0E, $D_0(EP)$, $D_0(EO)$ and $D_0(EOP)$ stages on the model parameters of Eq. 2 for predicting b* values

Pulp	c_0	c_1	c_2	Floor-level b* value ($c_0 - c_1$)	R^2
D_0E	19.3	14.7	1.11	4.6	0.997
$D_0(EP)$ 0.5% H_2O_2	17.3	13.5	1.41	3.8	0.997
$D_0(EO)$	18.5	14.0	1.42	4.5	0.996
$D_0(EOP)$ 0.5% H_2O_2	16.1	12.2	1.85	3.9	0.994

General Discussion

The findings from this study, along with our earlier investigations,[23–26] have afforded some insights as to how stages in chlorine dioxide bleach sequences work in concert with one another to delignify the residual lignin in kraft pulps. We envision that the general global reactions depicted in Figure 6 illustrate how the reactive phenolic groups in unbleached kraft residual lignin are modified in each bleaching stage of an ECF sequence, and how reinforcing the extraction stage with oxygen and/or peroxide impacts the ECF sequence. Chlorine dioxide in the D_0 stage oxidizes phenolic groups to *both* quinones and muconic acid structures, generally in a 2-to-1 ratio, respectively. The alkali of the extraction stage further modifies these two structures by caponizing the methyl esters of muconic groups and aromatizes quinone groups to reactive polyphenolic structures (Figure 6, [I]).

These polyphenolic structures can be oxidized to hydroxyquinones either by oxygen or peroxide intermediates during an oxidative-reinforced extraction (Figure 6, [II] & [III]), or by ClO_2 in a subsequent D_1 stage. Oxidative-reinforced extraction aids with modification of these groups so that the ClO_2 in the D_1 stage is allowed to oxidize other lignin structures, such as quinonoid, muconic, and non-phenolic entities. These polyphenolic structures can be oxidized to hydroxyquinones either by oxygen or peroxide intermediates during an oxidative-reinforced extraction (Figure 6, [II] & [III]), or by ClO_2 in a subsequent D_1 stage. Oxidative-reinforced extraction aids with modification of these groups so that the ClO_2 in the D_1 stage is allowed to oxidize other lignin structures, such as quinonoid, muconic, and non-phenolic entities.

Peroxide inclusion in (EP) and (EOP) stages, depending on the amount that is used, can further promote the delignification of hydroxyquinone and muconic structures into low-molecular weight organic acid fragments (Figure 6, [III]); this results in a net decrease in carbon-carbon double bonds in the oxidized lignin entering into the D_1 stage. The reactivity of peroxide with muconic structures, as we demonstrated earlier with a lignin enriched with theses groups, was a major finding of this work. The lignin degradation observed in (EP) and (EOP) stages resembles the extensive oxidation and alteration of unbleached residual lignin reported for CE or (CD)E treated pulps, in which selected aromatic ring moieties are destroyed, leaving behind the aliphatic side chain.[10,12] The similarities of these stages for eliminating aromatic nuclei, although through completely different mechanisms, are illustrated by their comparable Klason lignin/kappa values (~0.10 to 0.12).[44] [As we have shown in Table 3, the steady decrease in lignin content with increasing peroxide charge in (EP) and (EOP) stages is likely due to the dissolution of the aliphatic side chain during Klason lignin analysis.] Peroxide reactions with hydroxyquinone and muconic structures in (EP) or (EOP) stages allows for the ClO_2 in the D_1 stage to react with other entities in the residual lignin, probably most notably with the non-phenolic moieties.[10–15]

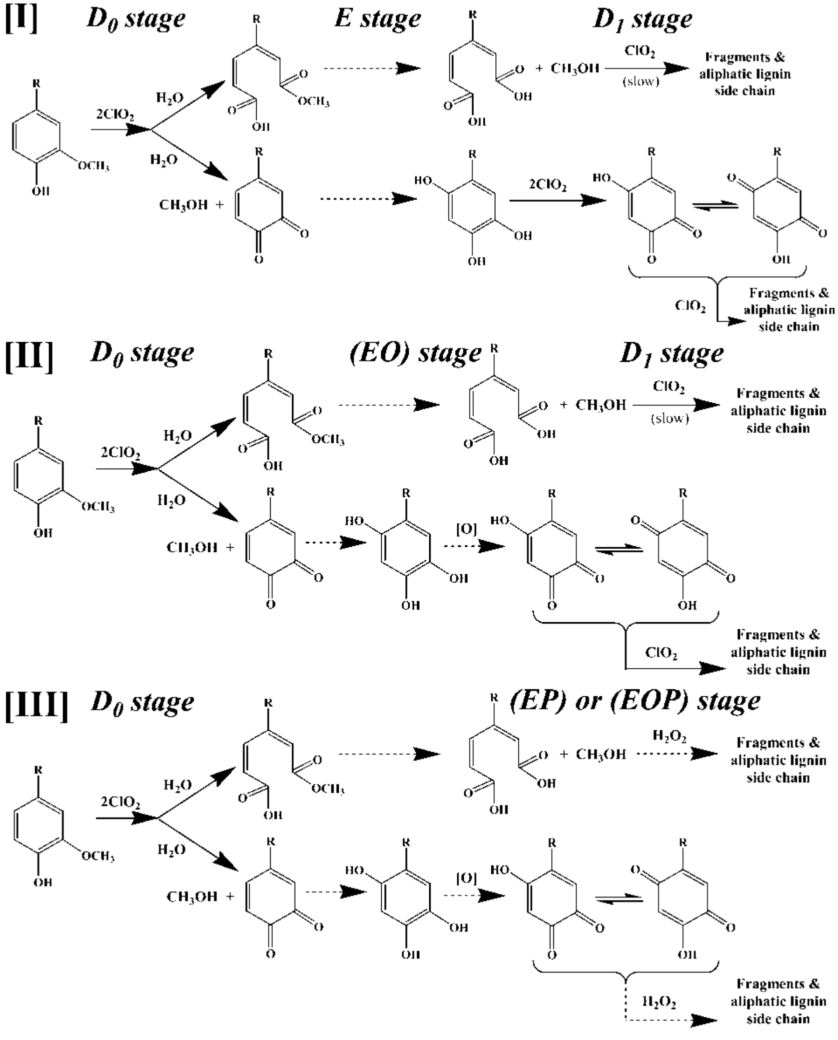

Figure 6. Postulated global reactions occurring with phenolic units in unbleached lignin and its oxidation products as it progresses through D_0ED_1 [I], $D_0(EO)D_1$ [II], $D_0(EP)D_1$ [III] and $D_0(EOP)D_1$ [III] bleaching sequences. Reactions occurring in D_0 and D_1 denoted with solid lines, and reactions in extraction or oxidative-reinforced extraction denoted with dotted lines. Reinforcing the extraction stage with O_2 and/or H_2O_2 helps to eliminate structures that consume ClO_2 in the D_1, allowing ClO_2 to react with non-phenolic entities. **R** = lignin side chain.

The outline of predominant reactions in Figure 6 helps to explain the observed D_1 bleachability order, from easiest to hardest, as we observed in Figure 4: $D_0(EOP) > D_0(EP) \approx D_0(EO) > D_0E$. The bleachability (i.e., how rapidly the D_1 brightness ceiling is approached as denoted by b_2 value of Eq. 1) is greatly influenced by the type of extraction stage used. However, it is quite notable that all four extracted pulps seem to approach common D_1 brightness ceilings (~86% ISO) and b* floor level values (~4.2), regardless of the extraction stage used. This suggests that there are other factors limiting the brightness ceiling. It is possible that other functional groups besides the oxidation products from phenolic entities of residual lignin contribute to the limiting D_1 brightness ceiling. Runge and Ragauskas[34] came to similar conclusions from their NMR analysis of D_1 lignins.

Non-phenolic groups may represent a candidate that limits the D_1 asymptotic brightness (Figure 7). Such structures are known to slowly react with ClO_2 and peroxide, and are virtually inert toward O_2 oxidation. The composition of these non-phenolic entities (e.g., condensed structures) can be greatly influenced by the pulping conditions. McDonough and co-workers[3,4] have shown that changes in effective alkali during pulping can affect ECF pulp brightness ceilings. The ClO_2 oxidation of non-phenolic models is known to afford *p*-quinones, as well as some muconic acid derivatives.[10–15] *p*-Quinone generation could contribute to the yellow chromophoric groups in D_1 residual lignin and the associated brightness ceiling. Unfortunately, our Klason lignin and kappa number analyses are not sensitive enough to detect these quinones in the very low D_1 lignin levels (<0.5%) present in these pulps.

The results and interpretations that we have presented are based on the limited information on how various oxidized structures, such as quinones and muconic acids, respond to further oxidative treatments with alkali, peroxide, or chlorine dioxide. Future research work is needed to validate or modify the conclusions we have put forth in this work. Such model studies should examine the oxidation of D_0 oxidized compounds (e.g., polyphenols, hydroxyquinones, muconic-type structures) with ClO_2 and/or H_2O_2, along

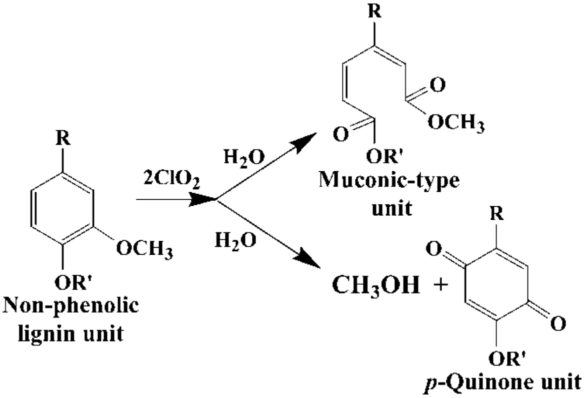

Figure 7. Reactions of ClO_2 with non-phenolic groups of residual lignin during a D_1 stage.[10–15] **R** = lignin side chain and **R′** = CH_3 or lignin.

with non-phenolic structures and their oxidation products, using newer analytical techniques currently available, such as HPLC and HPLC/MS, to provide clues as to how residual lignin is removed and modified in ECF bleaching sequences.

CONCLUSIONS

Peroxide-reinforced extractions (EP) or (EOP) of D_0 delignified pulps results in a 2 to 2.5 unit drop in the post-extraction kappa number, a 0.6% unit drop in Klason lignin and a 20 to 25 point increase in post-extraction brightness versus an E stage. Oxygen-reinforced extractions (EO) yield pulps that have a ~2 unit drop in kappa number, but contain comparable levels of Klason lignin as E pulps (~1.2% lignin). The level of quinonoid structures in the (EO) pulp, as determined from Klason lignin and kappa number analyses, are similar to those of D_0 pulp, ~1.7 mmol/g lignin. Peroxide addition to the alkaline extraction appeared to eliminate *both* quinonoid *and* muconic acid moieties, which was a significant finding of this work. These results were confirmed with the (EP) treatment of reference pulps (periodate or periodate-Paa) that contain significant levels of either quinones or muconic acid structures.

The following D_1 bleachability order was observed, based on the results of a simple bleaching model: $D_0(EOP) > D_0(EP) \approx D_0(EO) > D_0E$. An identical order was also found for how quickly the yellow chromophoric groups (b* value) are eliminated in the D_1 stage. All extracted pulps, regardless of the type of extraction employed, approach a common D_1 brightness ceiling (~86 ISO) and asymptotic b* value (~4.2) when excess ClO_2 is applied. This implies that these pulps have similar residual D_1 chromophores, which likely limits the upper brightness obtained. It is unknown at this time what comprises these chromophoric groups. However, our experimental evidence suggest that the degradation products of phenolic groups in unbleached kraft lignin, as it progresses through D_0 and extraction stages, are not the major contributing factors to the asymptotic D_1 brightness limit. Nonetheless, the oxidation products arising from such structures after D_0 and various extraction processes greatly influence how much ClO_2 is consumed in the D_1 stage and how quickly this asymptotic brightness limited is approached.

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 25.0, 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 h to check for hexeneuronic acids (HexA);[45] no significant changes in the kappa number were observed, indicating that the pulp contained negligible HexA structures. Metals analysis on the unbleached pulp yielded the following results (on o.d. pulp): 1000 ppm Ca, 190 ppm Mg, 96 ppm Mn, and 43 ppm Fe.

Chlorine dioxide delignification (D_0) was performed on the mature wood pulp under the following conditions: 0.20 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 vacuumed-sealed pouches at the following conditions: 5% $Na_2S_2O_4$ on pulp, 20% consistency, 70°C, and 120-min. reaction time. Peracetic acid (Paa) oxidation of periodate pulps was performed under the following conditions: 5% CH_3COOOH on pulp, 10% consistency, 70°C, initial pH 5.5 after CH_3COOOH addition, and 30-min. reaction time.

All extraction stages were conducted on selected pulps at the following conditions: 2.5% NaOH on pulp, 10% consistency, 70°C, and 60-min. total reaction time. All bleaching and oxidation treatments, except for the (EO) and (EOP) stages, were conducted in heat-sealable plastic bags. The (EO) and (EOP) stages were performed in a 2-L Parr Bomb reactor with 0.42 MPa (~60 psig) of oxygen for a 10-min. reaction time; afterward, the reactor was depressurized and allowed to run for 50-min. reaction time. Tests conducted on (EP) and (EOP) stage filtrates indicated that all the applied peroxide was consumed, unless otherwise indicated. Chlorine dioxide bleaching stages (D_1) were performed at the following conditions: 0.25 to 4% 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 3.2–4.5.

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 (≥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 (~0.5 g) did not consume $KMnO_4$.[24]

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