THE INFLUENCE OF THE BLEACHING MEDIUM ON CHLORINE DIOXIDE DELIGNIFICATION

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ABSTRACT

Chlorine dioxide delignification (D_0) stages performed in 90% ethanol resulted in post-D_0 kappa numbers that were 2 to 2.5 units lower than those performed in water. In spite of the reduction in kappa number, various gravimetric and UV spectroscopic techniques for measuring residual lignin indicated that the ethanol medium did not significantly enhance D_0 stage lignin removal. Differences in post-D_0 kappa numbers between the ethanol-based and aqueous systems were ascribed to how the bleaching medium affects ClO_2 oxidation of residual lignin. Ethanol-based D_0 stages resulted in an oxidized lignin that contains fewer muconic acid structures and more quinone structures than the aqueous-based systems. Indirect evidence from sodium hydrosulfite reduction implied that quinone moieties consume less $KMnO_4$ than aromatic structures in lignin during the kappa number test.

INTRODUCTION

Recent research has explored innovative pulping and bleaching methods to remove lignin and to decolorize the pulp without adversely affecting pulp strength. Of particular interest to us is the application of organic solvents to pulping[2,3] and bleaching processes.[4–6] Several researchers have observed that bleaching selectivity with acidic oxygen-based systems, especially with ozone, can be greatly improved by employing an organic solvent-water mixture instead of water as the bleaching medium.[4–5] It is generally believed that certain organic solvents, such as ethanol or acetic acid, help to scavenge nonselective radical species.

Our research has focused on ethanol-assisted bleaching with chlorine dioxide delignification (D_0) and subsequent caustic extraction (E).[7–9] We hoped to learn more about how an organic solvent-water medium would impact other chemical and physico-chemical mechanisms associated with bleaching other than radical scavenging. In previous reports, we have shown that caustic extraction is inhibited when an ethanol-rich medium ($> 50\%$ v/v) is employed. These studies provided evidence that E stage delignification was limited by the *alkali* solubility of the oxidized lignin in ethanol-rich media;[8] lignin transport limitations caused by fiber deswelling in ethanol-rich media were shown to be insignificant.[7] Subsequent studies on acid extraction stages indicated that oxidized lignin is more extractable in ethanol than in water under *acidic* conditions.[8–10]

During our initial investigations with the ethanol-assisted DE sequence, we observed that the kappa numbers of pulps treated by an ethanol-based D_0 stage were 2 to 3 units lower than its aqueous-based counterpart.[9] However, when these D_0 pulps were subjected to an aqueous E stage, the kappa numbers of these pulps converged. Does the lower post-D_0 kappa number of the ethanol-assisted system indicate an improvement in D_0 delignification through enhanced lignin dissolution? Or, does the lower post-D_0 kappa number represent an oxidized lignin that consumes less permanganate ($KMnO_4$)? In this paper, we will examine these issues.

RESULTS AND DISCUSSION

Determination of Residual Lignin of Post-D_0 Pulps

A series of D_0 stage bleaching runs were performed on an unbleached softwood kraft pulp (30.1 kappa) using 1.8% ClO_2 on pulp (0.16 kappa factor (KF)), and either an aqueous or 90% ethanol bleaching medium. Besides kappa number measurements, Klason and acid-soluble lignin

Table 1. Determination of Total Residual Lignin in Unbleached and D_0 Stage Pulps

Type of Pulp	Kappa Number	Lignin Percentage on Oven-Dried Pulp Mass (%)			
		Klason	Acid-Soluble	Klason + Acid-Soluble	UV Spectroscopy
Unbleached Pulp					
Trial #1	30.1	4.42	0.22	4.64	4.61
Trial #2	30.1	4.40	0.27	4.67	4.61
Average	30.1	4.41	0.25	4.66	4.61
Aqueous D_0 Stage					
Trial #1	18.5	2.68	0.46	3.14	3.12
Trial #2	18.0	2.62	0.50	3.12	3.18
Trial #3	18.0	2.70	0.51	3.21	3.20
Average	18.2	2.67	0.49	3.16	3.17
90% EtOH D_0 Stage					
Trial #1	16.2	2.60	0.58	3.18	3.14
Trial #2	15.6	2.64	0.55	3.19	3.16
Trial #3	16.3	2.66	0.48	3.14	3.24
Average	16.0	2.63	0.54	3.17	3.18

analyses were used to determine the residual lignin contents of the resulting pulps. The results of these analyses are reported in Table 1.

Again, as we observed earlier,[9] the ethanol-based D_0 stage afforded pulps with a lower kappa number than its aqueous counterparts. However, both the ethanol-based and aqueous D_0 pulps showed no significant differences in the individual amounts of Klason or acid-soluble lignin.

Another method used to determine total residual lignin in these pulps was the UV spectroscopy technique. This method involves dissolving a known quantity of the pulp in cadoxen, a colorless cellulose solvent; the amount of residual lignin is determined from the UV absorption of the solution at 295 nm. Sjöström and Enström,[11] and Mallet[12] have claimed that the UV method has sufficient sensitivity to detect differences in lignin concentrations as small as $\sim 0.1\%$ between different pulp samples.

The results from the UV spectroscopy analysis are compared with the previous lignin analysis in Table 1. The UV technique, like the Klason/acid-soluble lignin method, showed that the bleaching medium had a negligible effect on the amount of residual lignin removed during the D_0 stage. This assertion is based on the assumption that the absorptivity of the lignin at

295 nm is the same for both D_0 pulps. This assumption was at least partially validated by comparing the UV-spectra of the two solutions over the 240 to 400 nm range, and noting that the absorption spectra for the two samples were nearly identical.[9] Interestingly, both the UV and the Klason/acid-soluble lignin methods provided similar values for total residual lignin content in unbleached and D_0-treated pulps.

As a final check on the amount of lignin removal from the ethanol- and the aqueous-based D_0 stages, we examined the amount of lignin dissolved in the bleaching effluents. The amount of dissolved lignin in the D_0-effluents was estimated from the UV absorption at 280 nm.[13] This analysis showed that the aqueous D_0 stage removed ~1.3 to 1.5% of the residual lignin, whereas the ethanol D_0 stage removed ~1.4 to 1.8%. These estimates for the amount of lignin in the effluents are close to the calculated 1.4 to 1.5% differences in total residual lignin content between the unbleached and D_0 treated pulps. Again, these results corroborate our earlier findings presented in Table 1.

Various Chlorine Dioxide Charges in Ethanol-Based D_0 Stages

Several D_0 stage experiments were conducted on the 30.1 kappa brownstock using various ClO_2 charges and either an aqueous or a 90% ethanol medium. The purpose of these experiments was to see if the ethanol medium in the D_0 stage affected the kappa number and residual lignin of the ensuing pulp in a way analogous to that observed for the 0.16 KF ClO_2 charge. Again, the ethanol-based D_0 stage yielded pulps that were ~2 units lower in kappa number than the aqueous-based D_0 stage pulps with all ClO_2 charges examined (Table 2). The amount of total lignin remaining in these pulps was affected only when the applied ClO_2 charge was changed. There were no perceived differences in delignification when the bleaching medium was changed from water to 90% ethanol.

Various Alcohol-Based D_0 Stages

Several D_0 stage experiments, at a given 1.8% ClO_2 charge (0.16 KF), were performed using various 90% alcohol solutions as the bleaching medium. The objective of these tests was to see if other water-miscible alcohols would have the same effect on the post-D_0 kappa number and residual lignin content as a 90% ethanol medium (Table 3). Chlorine dioxide stages performed in primary alcohol media, such as methanol and *n*-propanol, produced pulps that had lower kappa numbers than the corresponding

Table 2. Kappa Number and UV Total Lignin for D_0 Delignified Pulps at Various Chlorine Dioxide Charges

Type of Pulp	Kappa Number	UV Spectroscopy Total Lignin (%)	Total Lignin-to-Kappa Ratio
Unbleached Pulp	30.1	4.61	0.154
Aqueous D_0 Stage			
0.10 KF	22.8	3.96	0.173
0.16 KF	18.2	3.17	0.174
0.22 KF	16.9	3.00	0.178
90% EtOH D_0 Stage			
0.10 KF	20.3	3.90	0.192
0.16 KF	16.0	3.18	0.199
0.22 KF	14.7	2.98	0.203

Table 3. Influence of Various Alcohol-Based D_0 Stage on Kappa Number and Residual Lignin. D_0 Stage Pulps Conducted with 0.16 KF ClO_2 Charge

Type of Pulp	Kappa Number	UV Spectroscopy Total Lignin (%)	Total Lignin-to-Kappa Ratio
Unbleached Pulp	30.1	4.61	0.153
Aqueous D_0 Stage	18.2	3.17	0.174
90% EtOH D_0 Stage	16.0	3.18	0.199
90% MeOH D_0 Stage	16.5	3.12	0.189
90% n-PrOH D_0 Stage	16.6	3.13	0.189
90% i-PrOH D_0 Stage	17.6	3.15	0.179
90% t-BuOH D_0 Stage	18.1	3.18	0.177

aqueous D_0 stage; however, D_0 stages performed in secondary and tertiary alcohols yielded pulps with kappa numbers similar to those of the aqueous D_0 pulps. The overall delignification, as denoted by the total UV residual lignin, remained unaffected by the bleaching medium.

Residual Lignin-to-Kappa Number Ratio for D_0 Treated Pulps

Clearly, the differences in the post-D_0 kappa numbers between the aqueous- and ethanol-based systems do not reflect the amount of total residual lignin contained in these pulps. If one assumes the lignin-to-kappa ratio

is unaffected by bleaching (i.e., ratio $= 0.15$),[14] then the predicted lignin content of the aqueous- and the ethanol-based D_0 pulps with a 0.16 KF ClO_2 charge would be 2.7% and 2.4%, respectively. These estimates are $\sim 20\%$ lower than the total residual lignin values determined from the various other methods employed in this study (Table 1).

van Lierop et al.[15] showed that the estimated lignin content of C and (D/C) bleached pulps from the kappa number analysis were 15 to 40% lower than that measured by gravimetric and UV analysis. In addition, these authors demonstrated that the lignin/kappa ratio varies with the oxidant or combination of oxidants employed during delignification. Closer examination of the kappa numbers and total residual lignin values of D_0-pulps in Tables 2 and 3 shows that the lignin/kappa ratio is affected by ClO_2 oxidation and the bleaching medium used.

It was expected that the lignin/kappa ratio would not be constant for semibleached pulps. Li and Gellerstedt[16,17] examined the $KMnO_4$ oxidation of lignin models and isolated residual lignins under the typical conditions employed during the kappa number test. The authors observed that $KMnO_4$ stoichiometrically reacts with phenylpropane units in a $\sim$ 3-to-1 molar ratio, indicating that $KMnO_4$ primarily reacts with the carbon-carbon double bonds of the aromatic ring. The lignin in semi-bleached pulps has been partially oxidized, and thus, has fewer carbon-carbon double bonds compared to unbleached lignin; thus it may consume less $KMnO_4$.

Lignin Structural Differences in Post-D_0 Kappa Numbers

Does an ethanol or an alcohol medium affect how ClO_2 oxidizes kraft residual lignin as compared to an aqueous medium, and if so, could this influence the post-D_0 kappa numbers? Recent ClO_2 studies with lignin models indicate that the bleaching medium can affect the distribution of reaction products. In general, ClO_2 primarily reacts with phenolic end units of residual lignin during the D_0 stage and forms chlorous ester quinols **1** (Fig. 1).[18–22] These unstable chlorite esters react with available nucleophiles in the system, such as water or alcohols, to afford either muconic acid monoesters/diesters **2** or *o*-quinones **3**. The participation of the bleaching medium during the oxidation of lignin is not unusual, as has been noted with the ozonation of lignin model compounds.[23]

Studies with phenolic lignin models[19,21,22] and isolated residual lignins[24] suggest that an aqueous reaction medium yields roughly equal amounts of muconic acid monomethyl esters (and/or lactones, resulting from muconic acid cyclization), and *o*-quinones. On the other hand, as has been pointed out by McKague et al.,[21,22] ClO_2 reactions with phenolic
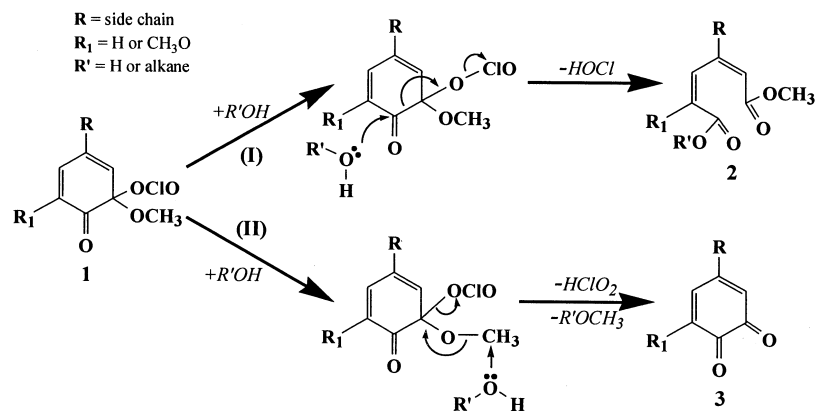
Figure 1. Nucleophilic attack of a protic solvent on the unstable chlorite ester intermediate (**1**) formed during ClO_2 oxidation of phenolic lignin.

compounds conducted in alcohol-rich media (50% v/v) typically yield *o*-quinones as the dominant reaction products.

In order to determine if the bleaching medium affected the distribution of oxidation products in the residual lignin, we examined the amount of carboxylic acid groups in the D_0 stage (0.16 KF) pulps. Conductometric titrations on these saponified pulps indicated that the aqueous D_0-treated pulp contained 102 mmol/Kg pulp of carboxylic groups, whereas the ethanol D_0-treated pulp only contained 76.5 mmol/Kg pulp. These results corroborate the findings from the model studies on ClO_2 oxidation that an alcoholic bleaching medium affords fewer muconic acid structures than an aqueous medium.[21,22]

In the second part of this study, the D_0 stage (0.16 KF) pulps were reduced with sodium hydrosulfite, and the kappa numbers and the UV residual lignin were measured. Sodium hydrosulfite has been shown primarily to react with quinones to form their corresponding dihydroxybenzene structures.[18,25] This reduction results in the formation of a carbon-carbon double bond, and in the aromatization of the oxidized lignin moiety. Converting *o*-quinones to catechols should cause this modified lignin to consume similar amounts of $KMnO_4$ as unbleached residual lignin, and thus, cause the lignin to kappa number ratio of D_0 pulps to approach that for unbleached pulps (i.e., ~0.15).

Treatment of the D_0 stage pulps with hydrosulfite resulted in ~0.4 to 0.5% residual lignin removal as measured by UV spectroscopy (Table 4). The kappa number of the ethanol D_0 pulp increased by ~1 unit, whereas the aqueous D_0 pulp remained almost the same. Interestingly, the total

Table 4. Kappa Number and Residual Lignin Measurements of D_0 Stage Pulps Before and After Sodium Hydrosulfite Reduction. D_0 Stages Conducted with 0.16 KF Charge on a 24.8 Kappa Brownstock

Type of Pulp	Kappa Number	UV Spectroscopy Total Lignin (%)	Total Lignin-to-Kappa Ratio
Unbleached Pulp	24.8	3.81	0.154
Aqueous D_0 Stage	14.3	2.45	0.171
Reduced Aqueous D_0 Stage	14.2	1.99	0.140
90% EtOH D_0 Stage	12.9	2.53	0.192
Reduced 90% EtOH D_0 Stage	14.2	2.00	0.141

lignin-to-kappa ratio for both hydrosulfite-reduced pulps approached the value for unbleached residual lignin. This finding, as well as a recent $KMnO_4$ study with quinones,[26] indicates that quinone structures consume less $KMnO_4$ than their analogous phenolic structures. Hydrosulfite reduction had a much stronger effect on decreasing the lignin-to-kappa ratio of the ethanol D_0 pulp than its aqueous counterpart, thus suggesting that the ethanol D_0 pulp contained more quinone-type structures. In addition, the information from these experiments indirectly implies that muconic structures consume similar amounts of $KMnO_4$ as unbleached residual lignin even though the muconic structures have one less carbon-carbon double bond. Evidence from the literature[26] suggests that α,β-unsaturated carboxyl groups consume more $KMnO_4$ than other unsaturated bonds due to intermediate decarboxylation reactions.

Interpretation of the Differences in the D_0 Residual Lignins

The above evidence strongly suggests that the change in the D_0 stage bleaching medium from water to 90% ethanol impacts the resulting ClO_2 oxidation product distribution in the residual lignin, which also affects the measured kappa number. Re-examining the data from Table 3 provides further evidence on the potential mechanism causing this product shift. Water is a relatively poor nucleophile.[27] Alcohols are better nucleophiles than water because (1) alkyl groups in alcohols are electron-feeding, and (2) alcohols will be less solvated than water.[27] If steric hindrance of the substrate under attack is a factor, primary alcohols (methanol, ethanol,

and propanol) will be better nucleophiles than secondary (*i*-propyl) and even bulkier tertiary (*t*-butyl) alcohols. The data in Table 3 indicate that *o*-quinone production, based on the lignin/kappa ratio, follows the order: methanol ≈ ethanol ≈ propanol > *i*-propanol > *t*-butanol ≈ water. This order parallels an expected nucleophilicity order and suggests that the strength and steric hindrance of the nucleophile is important to attack the methyl group of the chlorite ester (Fig. 1, path II), and only primary alcohols effectively follow this path.

Attack by a nucleophile at the carbonyl carbon, leading eventually to a muconic acid structure (Fig. 1, path I), should be relatively easy; the carbon is planar and carries a large partial positive charge. Given a choice, a weak nucleophile is more likely to attack the carbonyl than participate in a simple aliphatic substitution reaction. For a 90% alcohol system, in which the alcohol is a poor nucleophile because of steric hindrance, water could be the only reacting nucleophile.

CONCLUSIONS

Kraft pulps in an ethanol-based D_0 stage consistently yielded lower kappa numbers than pulps delignified in an aqueous D_0 stage. Results from gravimetric and UV spectroscopic techniques for measuring residual lignin demonstrated that there was no significant improvement of lignin removal when a 90% ethanol bleaching medium was used instead of water. These findings implied that the enhanced solubility of oxidized lignin in acidic ethanol solutions, as noted in our earlier studies,[8–10] was not augmenting D_0 stage delignification.

The differences in the above post-D_0 kappa numbers were ascribed to how the bleaching medium affects ClO_2 oxidation reactions with lignin. Apparently, an ethanol bleaching medium shifts the oxidation of phenolic groups to quinone structures instead of muconic acid structures. Conductometric titrations showed that pulps delignified in an ethanol D_0 stage contained fewer carboxylic acid groups than pulps delignified in the corresponding aqueous system. Hydrosulfite reduction provided indirect evidence that ethanol D_0 pulps contained more quinone structures than aqueous D_0 pulps, and that quinones consume less $KMnO_4$ than aromatic structures in lignin; thus, the differences in kappa numbers of D_0 pulps are probably related to differences in quinone concentration. The change in the lignin/kappa number ratio for D_0-treated kraft pulps, irrespective of the bleaching medium, is likely due to the formation of quinones during ClO_2 oxidation. Future studies will examine how the bleaching medium will impact pulp bleachability.[28]

EXPERIMENTAL

Chlorine Dioxide Delignification

A conventional kraft pulp (southern pine) was obtained from a mill and used throughout this study. Additional details about the pulping conditions are provided in previous reports.[7,9] Unbleached pulps employed in this study had kappa numbers of 30.1 or 24.8. The D_0 stage was performed under the following conditions: 0.10 to 0.22 kappa factor, 3% consistency, initial pH 4.2–4.6 prior to ClO_2 addition, 45°C, and a 30-min. reaction time. All D_0 effluents had an exit pH of ~ 2.4 and no measurable ClO_2 residual.

Unbleached softwood kraft pulps that were subjected to the 90% (v/v) alcohol D_0 stage were solvent exchanged from water to ethanol or other alcohols by the following method.[9] The pulp was dewatered to ~ 40 to 55% by pressing at $600\,kPa$ ($\sim 90\,psi$) for five minutes. The pressed pulp was briefly soaked in the corresponding alcohol at $\sim 1.5\%$ consistency for 1 hour at room temperature ($\sim 20°C$). Afterwards, the pulp was drained of excess alcohol and pressed to $\sim 40\%$ consistency. The solvent-exchanged pulp was then ready for D_0 stage treatment. The above solvent-exchange treatment of the pulp did not significantly decrease the residual lignin content. All D_0 stages performed in this study used an aqueous solution of ClO_2 as the oxidant source.

Residual Lignin Measurement and Quantification

Kappa numbers were determined by micro-kappa number measurements (TAPPI Useful Method UM-246). Klason and acid-soluble lignin analyses were done in accordance with TAPPI Standard T-222 om-85 and TAPPI Useful Method UM-250, respectively. The insoluble lignin was separated from the acid supernatant using Millipore® filter funnel instead of the medium-porosity filtering crucible as denoted in T-222 om-85. The filter funnel contained a pre-weighed Whatman® glass microfiber filter ($\geq 1.5\,\mu m$ particle retention capacity).[9]

The UV spectroscopic method[9] used to measure the amount of residual was adapted from Mallett[12] and from Sjöström and Enström.[11] A known amount of a D_0-treated or an unbleached pulp was placed in a 25-mL flask with a ground stopper. To the flask was added 10 mL of prepared cadoxen (*infra vide*) and some 6 mm glass beads. The flask was secured on a gyratory shaker and shaken for 1 to 4 hours until the pulp was completely dissolved. Afterwards, the solution was diluted

with 10 mL of ultrapure DI water and shaken again for 1 hour. The UV spectrum of the clear solution was recorded over a 240 to 400 nm range in a 1-cm cell path. Corrections for the cadoxen and carbohydrates absorptions were made by measuring the absorption of an appropriate cotton linter solution and subtracting this absorption from the measured absorption for the unbleached and D_0-treated pulps. The lignin content in the pulp was determined from the corrected absorption at 295 nm where the absorptivity for residual lignin in cadoxen was reported to be 19.6 L/(g·cm).[12] The amount of pulp to be used during this test, ~20 oven-dried (o.d.) mg for D_0-treated and ~13 o.d. mg for unbleached pulps, was fixed so that the 295 nm corrected absorption of the solution was between 0.5 to 1.0.[11]

Tris(ethylenediamine) cadmium dihydroxide (cadoxen) was prepared according to Sjöström and Enström.[11] Ethylenediamine (Aldrich reagent grade) was distilled to remove impurities. The purified ethylenediamine was carefully diluted to 30% (w/w) with ultrapure DI water, and the resulting solution was cooled to −5°C. Approximately 130 g of cadmium oxide (Aldrich reagent grade) was slowly added to 2000 g of the cooled solution of aqueous ethylenediamine under vigorous agitation. The resulting solution was centrifuged the to remove any undissolved or precipitated materials. Afterwards, the centrifuged solution was stored at room temperature in amber reagent bottles under a nitrogen atmosphere until needed.

Quantification of Dissolved D_0 Stage Lignin

The UV absorptions of selected D_0 stage effluents were measured by the following method.[9] A 1-mL sample of the effluent was added to a 5 mL volumetric flask and ultrapure DI water was added to the mark. The dilution caused no noticeable precipitation. The UV spectra of the resulting clear solutions were recorded over the 220 to 400 nm range in a 1-cm cell path. The concentration of dissolved lignin was estimated by the reported absorptivity values for acid chlorite oxidized lignin[13] of 7.6 to 9.6 L/(g·cm) at 280 nm.

In Situ Determination of Oxidized Groups in D_0 Stage Residual Lignin

The number of carboxylic acid groups in D_0 stage treated pulps was measured by employing the conductometric titration method described by Katz et al.[29] An unbleached kraft pulp (24.8 kappa) was treated with

either an aqueous or 90% ethanol D_0 stage using a 0.16 KF ClO_2 charge (1.5% ClO_2 on pulp). These D_0 pulps, prior to performing the titration, were saponified in order to convert any muconic monoester/diester structures to dicarboxylic acid structures. Saponification reactions were carried out in Kapak®/Scotchpack heat-sealable pouches under the following conditions: 2.2% NaOH on pulp, 20% consistency (in a 100% ethanol medium), 60°C, and 4 hours reaction time. An ethanol medium was used to minimize the *alkali* solubility of the lignin[8] and thus minimize oxidized lignin removal from the pulp. The pulps, after the saponification reaction, were pressed to $\sim$50% consistency and placed into cold storage until the conductrometric titrations could be performed. Titrations on these saponified pulps were repeated in triplicate, and the reported carboxylate values had coefficient of variation of $<$3%.

The number of quinone structures was measured indirectly by reducing the above D_0 pulps with sodium hydrosulfite, and measuring the residual lignin and kappa number of the pulps before and after reduction. Hydrosulfite reductions were carried out in heat-sealable pouches under the following conditions: 5% $Na_2S_2O_4$ on pulp, 20% consistency, 70°C, and 2 hours reaction time.

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REFERENCES

1. Current address: Vinings Industries, Inc.; 1525 Church St. Extension; Marietta, GA, 30060-1023; USA.
2. H.L. Hergert and E.K. Pye, *TAPPI Solvent Pulping Symp. Proc.*, Boston, MA, 9 (1992).
3. B.N. Brogdon and D.R. Dimmel, *J. Wood Chem. Technol.* 16(3), 297 (1996).

4. Y. Ni, A.H.P van Heiningen, J.H. Lora, L. Magdzinski and E.K. Pye, *J. Wood Chem. Techol. 16*(4), 367 (1996).

5. M. Solinas and T. Murphy, *Pulp & Paper 70*(3), 133 (1996).

6. A. Brolin, J. Gierer and Y. Zhang, *6th Int'l. Symp. on Wood and Pulping Chem.*, Melbourne, Australia, 205 (1991).

7. B.N. Brogdon, D.R. Dimmel and T.J. McDonough, *J. Pulp Paper Sci. 23*(10), J499 (1997).

8. B.N. Brogdon, D.R. Dimmel and T.J. McDonough, *J. Wood Chem. Technol. 19*(4), 307 (1999).

9. B.N. Brogdon, *Effects of Ethanol Media on Chlorine Dioxide and Extraction Stages for Kraft Pulp Bleaching, Ph.D. Dissertation*, IPST, Atlanta (1997).

10. B.N. Brogdon, D.R. Dimmel and T.J. McDonough, "A Fundamental Study of a Novel Extraction Stage for an Organosolv-Based Bleaching Sequence", *In: Further Advances in the Forest Products Industries*, P.W. Hart (ed.), New York, AIChE, 42 (1996).

11. E. Sjöström and B. Enström, *Svensk Papperstidn. 69*:469 (1966).

12. S.E. Mallett, *Pulp Paper Mag. Can. 72*(2):65 (1971).

13. P.A. Ahlgren, W.Q. Yean and D.A.I. Goring, *Tappi J. 54*(5):737 (1971).

14. J.E. Tasman, *Pulp Paper Can. 60*:231 (1959).

15. B. van Lierop, N. Liebergott, G. Teodorescu and G.J. Kubes, *Bleach Plant Operations Seminar Proc.*, Atlanta, Tappi Press, 45 (1991).

16. J. Li and G. Gellerstedt, *Nord. Pulp Paper Res. J. 13*(2):147 (1998).

17. J. Li and G. Gellerstedt, *Nord. Pulp Paper Res. J. 13*(2):153 (1998).

18. J. Gierer, *Holzforschung 44*(5):387 and *44*(6):395 (1990).

19. Y. Ni, X. Shen and A.R.P. van Heiningen, *J. Wood Chem. Technol. 14*(2):243 (1994).

20. C. Brage, T. Eriksson and J. Gierer, *Holzforschung 45*(1):23 and *45*(2):147 (1991).

21. A. McKague, G. Kang and D. Reeve, *Nord. Pulp Paper Res. J. 9*(2):84 (1994).

22. A. McKague, D. Reeve and F. Xi, *Nord. Pulp Paper Res. J 10*(2):114 (1995).

23. T. Eriksson and J. Gierer, *J. Wood Chem. Technol. 5*(1):53 (1985).

24. Y. Sun and D. Argyropoulos, *Holzforschung 50*(2):175 (1996).

25. C.W. Dence, "Chemistry of Mechanical Pulp Bleaching", *In: Pulp Bleaching: Principles and Practice*, C.W. Dence and D.W. Reeve (eds.), Atlanta, Tappi Press (1996).

26. B.N. Brogdon, "Influence of Quinones on the Estimation of Residual Lignin of Chlorine Dioxide Delignified Pulps by the Kappa Number Test", *TAPPI Pulping Conf. Proc.*, Boston, MA (2000).

27. F.A. Carey and R.J. Sundberg, *Advanced Organic Chemistry*, 2nd Ed., Part A, New York, Plenum Press, 263–271 (1977).

28. B.N. Brogdon, D.R. Dimmel and T.J. McDonough, *9th Int'l. Symp. on Wood and Pulping Chem.*, Montréal, Québec, A2-1 (1997).

29. S. Katz, R.P. Beatson and A.M. Scallan, *Svensk Papperstidn.* *87*(6):R48 (1984).

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