

LACCASE N-HYDROXYBENZOTRIAZOLE FULL SEQUENCE BLEACHING WITH HYDROGEN PEROXIDE AND CHLORINE DIOXIDE

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ABSTRACT

The bleachability of laccase/N-hydroxybenzotriazole (L stage) delignified kraft pulps was studied using an oxidatively reinforced extraction stage and chlorine dioxide. Research studies demonstrated that post-oxygen delignified softwood kraft pulp treated by an L stage and subsequently alkaline extracted provided 50% delignification. Oxidative reinforcement of the extraction stage provided an additional 20% delignification. Interestingly, the L(EOP) pulp was found to respond favorably to a second LE treatment. This pulp was then bleached with chlorine dioxide to yield fully bleached pulps with +87 ISO brightness values.

INTRODUCTION

Enzymatic-mediator delignification systems for kraft pulps have been extensively studied over the past decade. One of the earliest enzymatic systems investigated was lignin peroxidase (1, 2). This bio-delignification system uses hydrogen peroxide to oxidize the active site of lignin peroxidase which then oxidizes veratryl alcohol to a radical cation. The radical cation then diffuses into the pulp and oxidizes lignin. Delignification of kraft pulps with manganese peroxidase operates in a similar manner. The Mn peroxidase system oxidizes Mn(II) to Mn(III) in the presence of a chelant and H₂O₂. The chelated Mn(III) then diffuses into the pulp and oxidizes the lignin (3, 4).

The use of laccase and 2,2'-azino-bis(3-ethylbenzthiazoline-6-sulfonic acid) (ABTS) to delignify kraft pulps was shown to operate in a similar enzyme-mediator manner (5, 6, 7). Recently, Call proposed that N-hydroxybenzotriazole is a more efficient mediator for laccase (8). Comparative laccase bleaching studies using ABTS and N-hydroxybenzotriazole (9) suggested that the latter mediator is more effective at catalyzing the delignification of kraft pulps.

While several obstacles remain for commercial bleaching with laccase-mediator systems, the recent advances in mediator chemistry have certainly increased the likelihood that this type of bio-delignification system will have practical applications in the future. So as to advance this

field of biotechnology, several researchers have begun to investigate the delignification chemistry of a laccase/N-hydroxybenzotriazole bleaching stage. Residual lignin studies by Poppius-Levlin (10) and Sealey (11) suggest that the residual lignin remaining after LE is depleted of phenoxy groups, demethylated, and enriched in acid groups. The changes in residual lignin structure are all the more notable since the mediator itself is not stable under the biobleaching conditions and eventually is converted to an inactive form (12).

Future applications of a laccase-mediator delignification stage will require that the biobleached pulps be amenable to subsequent chemical bleaching technologies. Several researchers have begun to examine this issue. Using a laccase/N-hydroxybenzotriazole stage Poppius-Levlin et al. (13) performed LEQP, LEQPP, LEQPPP, and OOLEQP bleaching sequences on kraft pine pulp to obtain brightness values greater than 80. Call and Mucke (14,15) had similar results performing an LELEQP sequence on oxygen-delignified softwood kraft pulp. Flink and Ek (16) examined the bleachability of a softwood kraft pulp (starting kappa number of 15.7) employing OQP and LEQP. ISO brightness values indicated that the LEQP treated pulp was 2.8 points higher in brightness with slightly improved viscosity values than pulp bleached with an OQP sequence. In summary, laccase-mediator bleached pulps have been shown to exhibit favorable bleaching responses to many TCF bleaching agents when used with kraft and sulfite pulps. In contrast, the bleachability of LE-delignified kraft pulps with chlorine dioxide has not been as extensively studied and this paper addresses that issue.

EXPERIMENTAL

Materials

All bleaching studies employed a commercial post-oxygen delignified softwood kraft pulp. The pulp was washed with nanopure water, filtered to approximately 30% solids, fluffed, and stored at 4°C. The well-washed pulp was characterized as having a 13.6 kappa number and a 17.8 CED viscosity. All chemicals employed for these studies, with the exception of chlorine dioxide, were commercially purchased and used as received. An *Aspergillus* laccase, kindly provided by Novo Nordisk, was used in the L stage with an activity of 584,000 U/mL.

Laccase/N-Hydroxybenzotriazole (L Stage)

The L stage was performed in a pressurized reactor at 10% pulp consistency. The pulp slurry was initially warmed to 45°C; N-hydroxybenzotriazole (2% charge) was added with stirring and after 3 minutes the pH of the solution was adjusted to 4.5 using glacial acetic acid. Laccase (3 mL/10g OD pulp) was then added to the pulp mixture with vigorous stirring. After mixing for 1 minute the reactor was sealed, pressurized with oxygen (145 psi) and mixed at 45°C for 4hr. Upon completion of the L stage, the pulp was thoroughly washed and then alkaline extracted.

Alkaline Extraction Stage

A routine E stage was performed in a sealed bag at 70°C and 10% consistency with a 2% alkali charge on a pulp oven-dry weight basis for 1 hr. The (EO) and (EOP) extraction stages were performed in a Parr reactor with a 2% alkali charge at 70°C and 10% consistency for 1hr. The oxygen reinforcement was accomplished by pressurizing with 60 psig O₂ for the first 15

minutes. The pressure was then decreased by 20 psig every 5 minutes until atmospheric pressure was reached. A hydrogen peroxide charge of 0.5% was used for the (EOP) stage. Alkaline extracted pulp samples were washed with 2000 mL per 60g o.d. pulp allowed to air dry and then characterized.

Chlorine Dioxide and Hydrogen Peroxide Bleaching Stages

The chlorine dioxide bleaching stages were performed at 10 % consistency for 3 hours in a sealed bag at 70°C after the initial pH was adjusted to 10 with NaOH. The hydrogen peroxide stages were performed at 10% consistency at 90°C in a sealed bag for 4 hr. An equal charge of NaOH was added at the same time as the H₂O₂ for pH control. After treatment, the pulp samples were washed with distilled water (2000 mL/g o.d. pulp), air dried and tested.

Pulp Characterization

The pulp properties determined were kappa number, pulp viscosity, and ISO brightness measurements. The kappa number was performed in accordance with TAPPI Method UM-246 (17) and typical experimental standard deviations for this procedure were determined to be ± 0.3 . Pulp viscosity values were determined in accordance with TAPPI Standard T-230 om-89 (18) (standard deviations ± 0.6).

Pulp brightness measurements were reported as ISO brightness and were performed in accordance with TAPPI Standard T-525 om-92 (18). The handsheets were made using TAPPI Standard T-231 cm-85 (18). Reverted brightness measurements were taken on handsheets, which were thermally reverted for 10 hours at 90°C at 50% relative humidity.

RESULTS AND DISCUSSION

Since the initial reports by Call, several groups have examined the delignification of kraft pulps with laccase/N-hydroxybenzotriazole. In general, post-oxygen delignified pulps responded more favorably to this bio-bleaching system than pre-oxygen delignified pulps. The bulk of the lignin removed from a laccase-mediator stage occurs during the subsequent alkaline extraction stage.

Our initial goal in this study was to examine the effects of reinforcing the alkaline extraction stage with an oxidant. To accomplish this, we treated a post-oxygen delignified softwood kraft pulp with laccase/N-hydroxybenzotriazole. Although our procedure followed the general method of Call, we have found that the optimal bio-delignification conditions are very dependent on the source of the laccase and the biobleaching stage must be optimized for the enzyme used. After treating the pulp with laccase/N-hydroxybenzotriazole for 4 hours with 145 psig of O₂ pressure, the pulp was washed and extracted using E, EO, and EOP. A control study was also performed using identical conditions of time, temperature, and pressure, with no laccase or mediator added. The results of the control clearly indicate the delignification obtained is from the oxidation reactions of the laccase/N-hydroxybenzotriazole and not the pressurized O₂.

Figure 1, which contains the data from these studies, indicates the LE stage is capable of reducing the kappa number by 48% relative to the starting post-O₂ pulp. Employing an O₂ reinforced alkaline extraction stage (EO) increased this delignification to 59%, and using a O₂

and H_2O_2 reinforced alkaline extraction stage (EOP) further increased the delignification to a 73% reduction relative to the starting post- O_2 pulp. Figure 1 also contains a control treatment

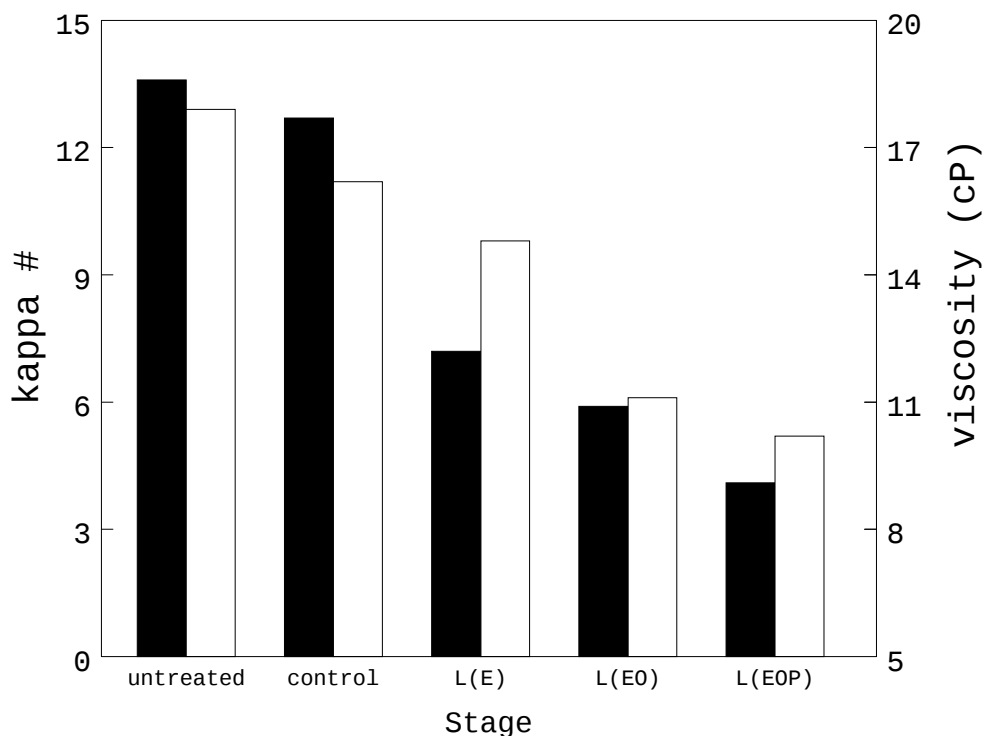


Figure 1. The effect of E, (EO), and (EOP) extraction on a post-oxygen delignified softwood kraft pulp treated to an L stage. Solid bar is kappa number and open bar is viscosity.

The L(EOP) pulp was further treated with a second L and E stage, which induced a further kappa decrease of 80% delignification relative to the starting post- O_2 pulp. Inspection of the CED viscosity data indicate the selectivity of this biobleaching system also appears to be equal to, if not significantly better than, many TCF stages (19). The L(EOP)LE treated pulps was then divided and subjected to various H_2O_2 and ClO_2 brightening stages. This was done to provide a measure of how easily the laccase/N-hydroxybenzotriazole treated pulp could be brightened (**Figures 2 and 3**). The H_2O_2 treated pulp approached 80 ISO brightness with the highest H_2O_2 charge.

Comparing Figures 2 and 3, it can be clearly seen the L(EOP)LE pulp responded better to ClO_2 than H_2O_2 , reaching an 85 ISO brightness pulp with a 1.0% charge of ClO_2 . Even low dosages of ClO_2 were able to reach 78 ISO brightness values. A comparison of the thermally reverted brightness values indicated that ClO_2 brightened pulps exhibited less brightness reversion than pulp bleached with H_2O_2 .

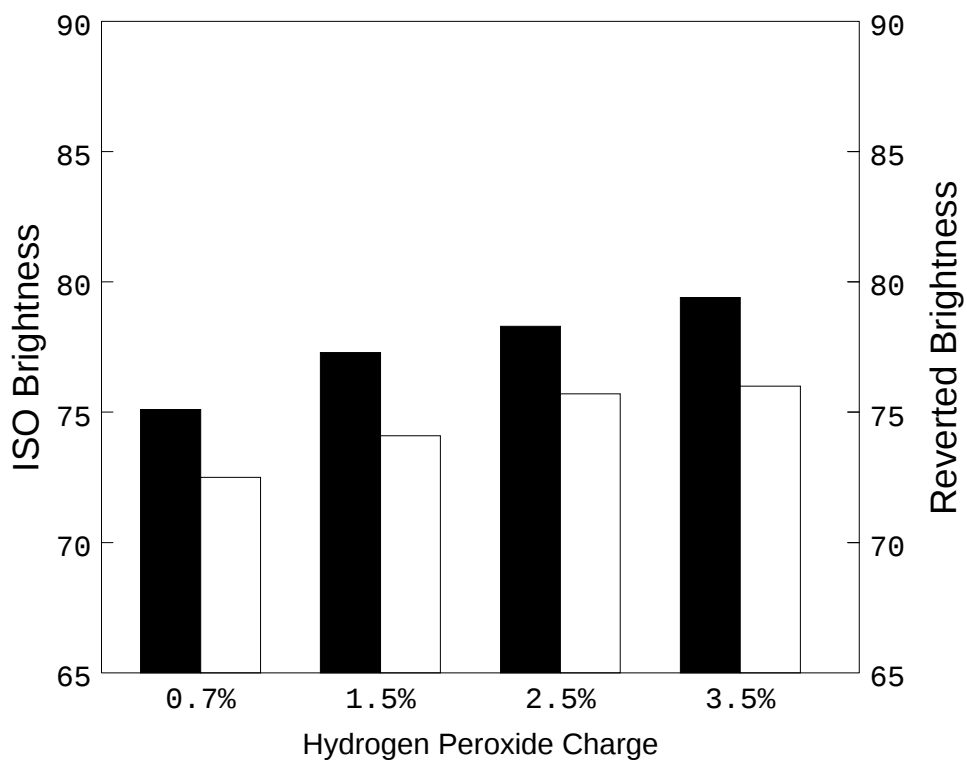


Figure 2. Hydrogen peroxide brightening of L(EOP)LE pulp with different H₂O₂ charges. Solid bar is ISO brightness and open bar is the reverted ISO brightness.

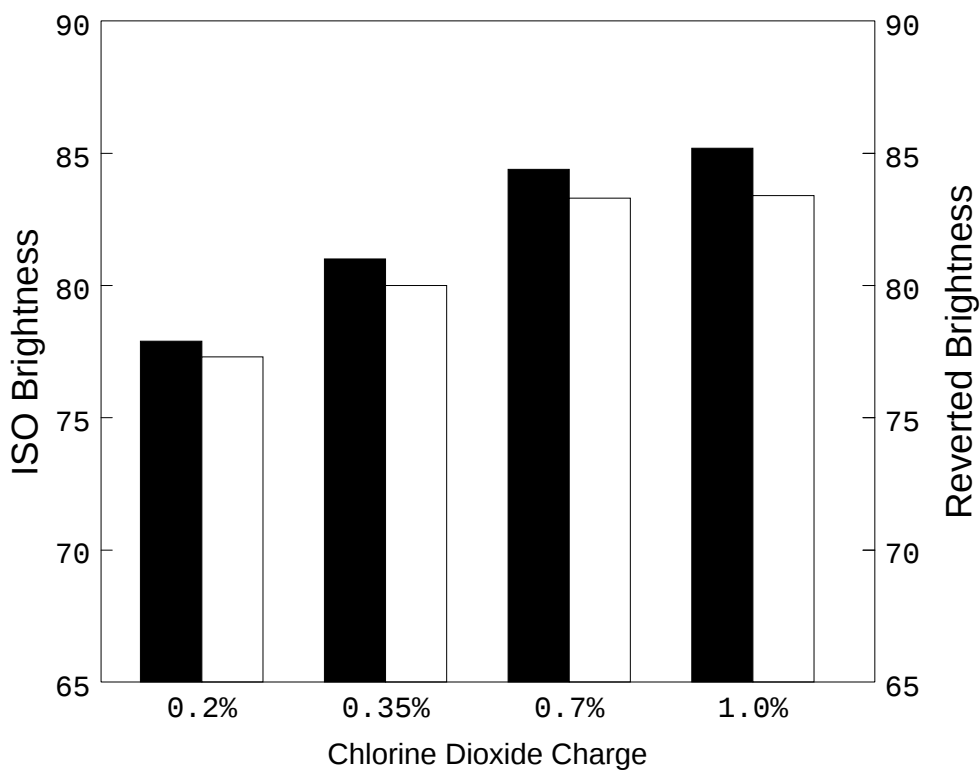


Figure 3. Chlorine dioxide brightening of L(EOP)LE pulp with different ClO₂ charges. Solid bar is ISO brightness and open bar is the reverted ISO brightness.

To further examine the reactivity of laccase/N-hydroxybenzotriazole treated pulps with ClO_2 , we performed a series of experiments using an OL(EOP)DED sequence. The ClO_2 charges were 0.75% and 1.25% in the D_1 stage, and 0.50% and 0.75% in the D_2 stages. The ISO brightness and reverted brightness values are shown in **Figure 4**. The brightness data indicate that the OL(EOP) delignified pulp responded well to the D_1 and D_2 stages, achieving a final brightness of greater than 87. Our experience indicates the bleachability of these pulps are similar to DEDED or D(EO)DED sequences, as similar chlorine multiple applied in the D_1 and D_2 stages were capable of reaching similar brightness levels (20).

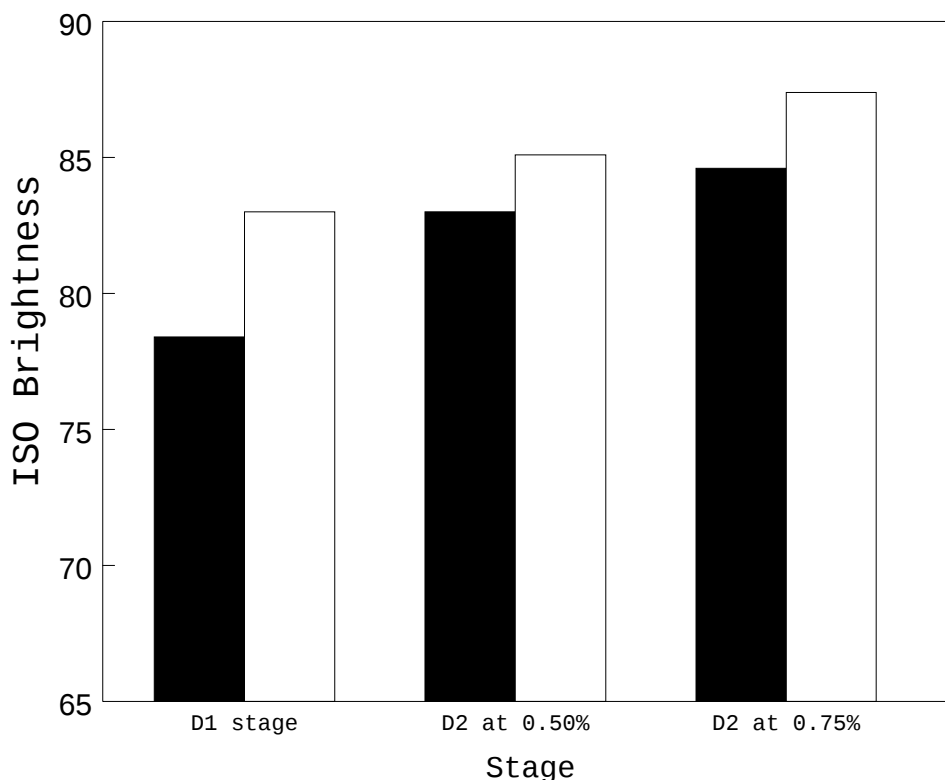


Figure 4. Chlorine dioxide brightening of L(EOP)DE pulp with different ClO_2 charges. Solid bar represents a D_1 charge of 0.75%, the open bar represents a D_1 charge of 1.25%.

CONCLUSIONS

Pulp bleached with the laccase/N-hydroxybenzotriazole system exhibited favorable bleachability properties. The extraction of the pulp after a laccase/N-hydroxybenzotriazole stage benefited from the presence of an extra oxidant. The ability to extend the delignification effect with a second LE treatment is very interesting since the L stage appears to destroy unsubstituted phenolic structures. The mechanism for this delignification effect clearly needs additional studies.

The bleaching sequence L(EOP)LED produced a 85 ISO brightness while L(EOP)LEP bleached pulp appears to be limited to 79-80 ISO brightness. Further investigation into the

bleachability of laccase/N-hydroxybenzotriazole bleached pulp revealed a 85 ISO brightness was capable with an OL(EOP)DED sequence.

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