Comparison of various hardwood kraft pulp pre-bleaching techniques

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ABSTRACT: We examined five pre-bleaching methods with the same starting hardwood kraft brownstock pulp to determine their effects on reducing bleaching costs. Each pretreated pulp was subjected to a D(EP)D bleaching sequence. A D_1 brightness curve as a function of the percent applied chlorine dioxide (ClO_2) was obtained for each of these pre-bleaching methods and for a baseline pulp sample. For each of the pre-bleaching methods, we calculated the amount of ClO_2 required to obtain D_1 stage 79.1% ISO brightness and determined the net cost savings for each sequence. Pre-bleaching methods that produced a net savings in the D1 stage were also subjected to a four-stage bleaching sequence of D(EP)DD to 89%ISO brightness. We also determined net cost savings resulting from pretreatment of the fully bleached pulps. The methods examined were mild acid pretreatment, xylanase enzyme pre-bleaching, brownstock peroxide pretreatment, acidic brownstock peroxide treatment, and xylanase enzyme followed by acidic peroxide pretreatment. Enzyme pretreatment and small applications of acidic peroxide pretreatment resulted in net D_1 stage cost savings at 79.1% ISO brightness. Only enzyme pretreatment resulted in a net savings at 89% ISO.

Application: Pulp mills can use this information to better assess the relative impacts on cost structure of various pre-bleaching methods.

Various methods of lowering bleaching costs through the use of pre-bleaching additives have been reported. Several of these methods (e.g., oxygen delignification [1], hot acid treatment [2], and NOx pretreatment [3]) require the installation of significant capital equipment with marginal returns. Other pretreatment methods can be retrofitted into an existing bleach plant with little or no capital investment. Xylanase enzymes [4-6], brownstock peroxide [7], and acidic brownstock peroxide pretreatments [8] have been shown to exhibit significant cost reductions in specific pulp mills without the need for costly equipment installation or additional washing prior to entering the bleach plant.

Although peroxide and enzymatic pretreatments on pulp before the main bleaching sequence have been in commercial operation for many years, it is unclear which method is optimum for a mill seeking to select a pretreatment method to reduce operating costs. To determine which of the low-capital pretreatment methods provides the best cost advantage to a mill, we performed laboratory-scale bleaching to a constant brightness with various pre-bleaching techniques employed upon the same starting brownstock pulp. By performing various pre-bleaching techniques and then bleaching the pulps in a standard three- and four- stage bleaching sequence with varying applied kappa factors, it was possible to obtain D_1 and D_2 stage brightness vs. percent total applied ClO_2 curves for each of the pre-bleaching methods. Each data set was subjected to various regression techniques to obtain a best fit equation of brightness as a function of total applied ClO_2. We evaluated each equation at the target brightness to obtain the amount of applied ClO_2 required to reach the target brightness level. The cost of the pretreatment chemicals was subtracted from the ClO_2 savings to obtain the net savings for each of the pretreatment methods.

Enzyme pretreatment

For many years, Canadian mills have used enzymes. Bleach plants have used xylanase enzyme pretreatment to help reduce chlorinated compounds in the effluent [9]. The United States and other countries have shown an interest in using enzymes primarily to reduce chemical costs and increase brightness ceilings. Xylanase is widely used because of its versatility; it can be used for hardwood or softwood furnishes, in continuous or batch processes, with or without pulping additives, and with conventional or O_2-delignifed brownstock [10].

When xylanase is used as a pretreatment in bleaching, it removes xylan from the surface of the fiber. Xylan is a hemicellulose that is initially removed during pulping but re-deposits on the fibers at the end of pulping [11]. Re-deposited xylan tends to consume significant quantities of ClO_2 in the first bleaching stage. The xylan concentration on fiber surfaces and in the secondary wall is dramatically reduced during an enzyme pretreatment, particularly for hardwoods that contain more xylan; this reduction in xylan concentration appears to increase the permeability of fiber surfaces, thereby improving bleachability [12]. Because most of the xylan removal would have occurred during the initial ClO_2 bleaching stage, overall pulp yield does not appear to be impacted by an enzyme treatment.

In laboratory experiments, improved bleachability occurred on a D(EP)D sequence when an enzyme pretreatment was introduced. The pretreatment resulted in an 88% ISO-brightness,

a 30% decrease in active chlorine consumption, decreased bleach plant color, reduced zeta potential, and a slight change in spectral reflectance and brightness reversion [13].

Mill data are also available on the use of enzyme pretreatment. Xylanase pretreatment on the ClO_2 limited fiberline at NEXFOR Fraser Paper in Thurso, Quebec, resulted in a kappa factor reduction of 10.9% to maintain final product properties. It also allowed an increase of feed kappa number of 0.8 units, decreased steam consumption of 0.21 GJ/a.d.t., and increased bleach plant production by 10 a.d.t./day [14]. Xylanase application at the Lewiston, Idaho, mill, using a novel high temperature and high pH enzyme, increased the operating temperature of press washers that improved brownstock washing and the bleaching efficiency of the first bleaching stage [15]. Long-term data analysis has found that xylanase pretreatment does not affect overall hardwood pulp yield [16].

Acid pretreatment

Various pulp mills have discussed the issue of acidification prior to the bleach plant as the source of chemical reduction obtained in xylanase pre-bleaching methods. Hot acid [2] and hot ClO_2 [17] treatments have successfully removed hexenuronic acids from hardwood pulps, especially eucalyptus pulps. The presence of hexenuronic acid groups has been shown to be a dominant contributor to the pulp kappa number for some hardwoods. Hexenuronic acid groups consume bleaching chemical and require more chemical to reach a given target brightness. These groups can likely be removed from the pulp with acid [2]. To isolate the enzyme impact from the acid contribution, we evaluated the acid-only pretreatment under the same conditions as employed in the enzyme pre-bleaching stage. Our goal was to understand the effect on ClO_2 reduction independent of enzymes.

Alkaline peroxide pretreatment

The application of peroxide into the brownstock high density (HD) storage tank can substantially reduce bleaching costs under some mill operating conditions. There are two potential mechanisms for the success of alkaline peroxide pretreatment. First, peroxide is believed to react with the lignin in the pulp, thus reducing the kappa number of the pulp going to the bleach plant. Studies conducted at PAPRICAN have shown that a 1% peroxide application can lower the kappa number going to the bleach plant by 0.8 points. When chelation was performed for removal of metals before brownstock peroxide addition, even better results were obtained. Second, peroxide applied in the brownstock HD storage tank consumes excessive carryover that would otherwise consume bleaching chemicals.

Acidic peroxide pretreatment

The easiest form of alkaline peroxide pretreatment consists of applying peroxide into the pulp going to the brownstock HD storage tank. Such use of peroxide has been shown to provide variable results and may not be cost effective and, in the presence of certain transition metals, may also result in poor pulp quality [8]. Peroxide pretreatment under acidic conditions has recently been shown to improve bleaching performance by reacting with transition metals to form Fenton's Reagent. Peroxide reacting under Fenton chemistry conditions may more rapidly and fully consume carryover into the bleach plant than alkaline peroxide. Recent data published by Tembec's Skookumchuck mill [8] suggests the use of acidic peroxide has substantially reduced their pulp bleaching costs.

Enzymes with acidic peroxide pretreatment

As part of our study, we proposed a novel combination of the enzyme pretreatment with the acid peroxide pretreatment. The potential mechanisms differ greatly so we decided to examine whether performing the two pretreatments sequentially would produce any synergistic effects. Under mill conditions, standard enzyme pretreatment would be conducted in the brownstock HD storage tank. Additional acid and peroxide would be added to the dilution water at the bottom of the HD storage tank prior to ClO_2 addition. Fenton chemistry is relatively fast reacting, so only a short retention time would be required for this part of the pretreatment.

EXPERIMENTAL

We obtained conventional hardwood kraft pulp, kappa no. 15.5, from the third stage of the "C Line" brownstock washing system at a Covington, Virginia, mill. A target D_1 brightness of 79.1% ISO, a target D_2 brightness of 89% ISO, and the condi-

	Consistency (%)	Temperature (°F)	Time (min.)	% chemical on o.d. pulp	Terminal pH
D_0	3.5	135	45	1.4, 1.27, 1.14 and 1.01%	2.4-2.8
EP	10.0	160	60	1.2% NaOH 0.2% H_2O_2	10.5-11.0
D_1	10.0	180	120	1.2% ClO_2 0.15% NaOH	3.1-3.4
D_2	10.0	180	150	0.57% ClO_2 0.25% NaOH	3.4-3.8

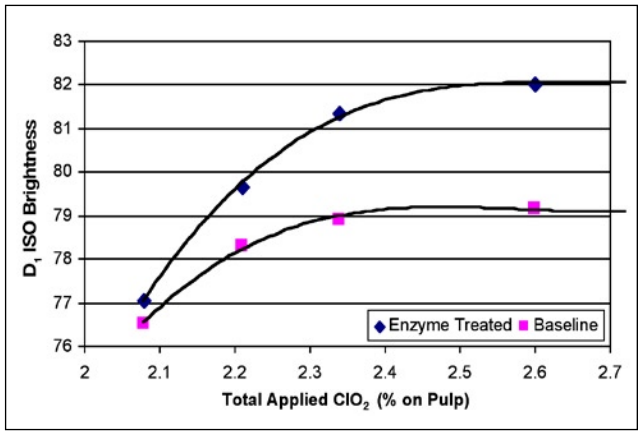
I. Baseline bleaching conditions. D_0 chemical addition was varied to obtain D_1 stage and D_2 stage brightness curves.

tions in **Table I** were employed for the study using a D(EP)D and a D(EP)DD bleaching sequence. Pulp was pre-heated at 135°F for 30 minutes prior to the pretreatment to represent typical brownstock HD storage conditions. Excluding the peroxide pretreatments and the base case, pulp pH was adjusted to 6.5 with sulfuric acid. The acidic peroxide pretreatment pH was adjusted to 3.5 prior to peroxide addition.

Pretreatment dosages were 0.24 lb/ton BioBrite® UHB enzyme supplied by IOGEN Corp. (Ottawa, Ontario, Canada) for the enzyme and enzyme followed by acidic peroxide pretreatments. Peroxide dosages were 3, 5, and 10 lb/ton and acidic peroxide dosages were 1, 3, and 5 lb/ton for the respective pretreatments. The combination pretreatment of enzyme followed by acidic peroxide tested a constant dosage of enzyme (0.24 lb/ton) and varied acidic peroxide dosages of 3, 5, and 10 lb/ton. The pretreatment stage was held at 135°F for 45 min., except for the acidic peroxide, which was held for 15 min.. Filtrate samples were taken after the enzyme and peroxide pretreatments to determine the amount of xylose released into and the amount of residual peroxide remaining in solution. If xylose was found to be present in the filtrate, it was assumed that the enzyme treatment had been performed correctly.

Following the pretreatment, the pulp was separated into four separate batches. Bleaching chemicals were added to each of these batches to start the first bleaching stage. Washing was not performed between pretreatment and the first bleaching stage. Table I shows the conditions for each stage in the $D_0(EP)D_1$ bleaching sequence. The $\%ClO_2$ charge on o.d. pulp was varied in the first bleaching stage at 1.4%, 1.27%, 1.14%, and 1.01% to generate brightness curves.

Between the D_0 stage and the EP stage, the pulp was well washed with 1 L of de-ionized water. The pulp was also washed between the EP, the D_1, and the D_2 stages. Samples for brightness pads were taken after each stage and tested for ISO brightness. We calculated net cost savings for each prebleaching condition at a constant D_1 stage brightness of 79.1% ISO. Each method that produced a net cost savings was expanded and subjected to a four-stage bleaching sequence at a target brightness of 89% ISO. For these tests, acidic peroxide at 1 and 3 lb/ton and enzymes at 0.12, 0.24, and 0.48 lb/ton were investigated.



1. Comparison of enzyme pretreatment brightness curve and a baseline curve.

Chemical	Cost (USD)	Unit
Chlorine dioxide	0.46	USD/lb ClO_2
Caustic	0.25	USD/o.d. lb NaOH
Sulfuric acid	0.039	USD/lb 93% H_2SO_4
Hydrogen peroxide	0.3255	USD/lb H_2O_2
Enzymes	4.40	USD/lb

II. Typical chemical costs for various bleaching chemicals.

RESULTS AND DISCUSSION

We compared the brightness results from five different pretreatment methods followed by a three-stage bleaching sequence D(EP)D to the brightness results of the D_1 stage of a bleaching sequence without a pretreatment at 79.1% ISO brightness. **Figure 1** is a brightness curve showing the results of an enzyme pretreatment sequence with the baseline for reference. A trendline was fit to each of the bleaching data sets to generate an equation relating ClO_2 required and brightness. The amount of ClO_2 required to obtain the target D_1 stage brightness of 79.1% ISO was determined using the best fit equation. This process was repeated for each of the different pretreatment methods we studied.

We calculated the change in ClO_2 between the baseline pulp and the pretreated pulp required to obtain a constant brightness and converted it into a gross bleach plant savings using a typical mill cost for ClO_2. **Table II** lists the costs used for each of the bleaching and pretreatment chemicals.

To determine the most effective pretreatment system, we calculated the chemical cost and subtracted it from the gross savings of each method. **Table III** lists the net cost savings for each pretreatment method.

The data from Table III clearly indicate that only the use of enzymes and acidic peroxide at 1 lb/ton resulted in a D_1 stage cost savings. Although several of the methods reduced the amount of ClO_2 required, the reduction was not enough to result in a substantial cost saving once the pretreatment costs were added into the bleaching sequence. When each method was examined using the same starting hardwood kraft brownstock, only enzymes provided a substantial costs savings.

Each of the alkaline peroxide-based pretreatments increased the overall bleaching costs. As peroxide was added, more ClO_2 was required to obtain the target brightness. Filtrate samples indicated that peroxide was not carrying over into the D_0 stage but was consuming additional chemical. Peroxide residual tests indicated that only trace amounts of peroxide carried over into the D_0 stage. It is possible that the peroxide pretreatment fractures carryover lignin fragments into smaller pieces with oxidizable endgroups that consume

Pretreatment	% ClO_2 for 79.1% ISO	% ClO_2 reduction	Pretreatment cost USD/ton	Gross ClO_2 cost savings USD/ton	Net ClO_2 cost savings USD/ton
Baseline	2.42	---	0.00	---	---
Enzyme 0.24 lb/ton	2.20	9.09	1.10	2.02	0.93
Enzyme + acidic peroxide 3 lb/ton	2.30	4.96	2.08	1.10	-.97
Enzyme + acidic peroxide 5 lb/ton	2.38	1.65	2.73	0.37	-2.36
Enzyme + acidic peroxide 10 lb/ton	2.48	-2.48	4.35	-0.55	-4.91
Peroxide 3 lb/ton	2.35	2.89	0.98	0.64	-0.33
Peroxide 5 lb/ton	2.51	-3.72	1.63	-0.83	-2.46
Peroxide 10 lb/ton	2.58	-6.61	3.26	-1.47	-4.73
Acidic peroxide 1 lb/ton	2.35	2.89	0.42	0.64	0.22
Acidic peroxide 3 lb/ton	2.34	3.31	1.07	0.74	-0.33
Acidic peroxide 5 lb/ton	2.27	6.20	1.73	1.38	-0.35
Acid alone	2.40	0.83	0.04	0.04	0.14

III. Chlorine dioxide (ClO_2) reduction and net savings for various pretreatment methods, D_1 stage at 79.1% ISO brightness.

Pretreatment	% ClO_2 for 89% ISO	% ClO_2 reduction	Pretreatment cost USD/ton	Gross ClO_2 cost savings USD/ton	Net ClO_2 cost savings USD/ton
Baseline	2.97	---	0.00	---	---
Enzyme 0.12 lb/ton	2.72	8.59	0.56	2.35	1.82
Enzyme 0.24 lb/ton	2.60	12.56	1.10	3.38	2.32
Enzyme 0.48 lb/ton	2.45	17.68	2.16	4.83	2.72
Acidic peroxide 1 lb/ton	2.97	0.00	0.42	0.00	-0.42
Acidic peroxide 3 lb/ton	3.00	1.28	1.07	-0.72	-1.79

IV. Chlorine dioxide (ClO_2) reduction and net savings for various pretreatment methods, D_2 stage at 89% ISO brightness.

ClO_2 but do not contribute to pulp bleaching. Acidic peroxide appears to be more effective than alkaline peroxide treatment, but acidic peroxide treatment increased bleaching costs when applied at 3 and 5 lb/ton.

As both enzyme pretreatment and acidic peroxide pretreatment at 1 lb/ton resulted in a net cost savings for the D_1 stage, the treatment levels were expanded to 0.12, 0.24, and 0.48 lb/ton for enzymes and 1 and 3 lb/ton for acidic peroxide. We bleached these pretreated samples and a baseline sample in a four-stage D(EP)DD sequence to 89% ISO brightness. **Table IV** shows the net cost savings for the fully bleached 89% ISO pulp, which were determined in the same manner as for the three-stage sequence.

After four stages of bleaching to 89% ISO brightness, only enzymes resulted in a net cost savings. Acidic peroxide did not change the final chlorine dioxide demand when applied in small dosage and slightly increased ClO_2 requirements at higher dosages. Excellent cost savings resulted from the enzyme pre-bleached pulp.

CONCLUSIONS

Enzyme pretreatment successfully reduced the overall costs of bleaching to 89% ISO brightness by about USD 2.32/o.d. ton of pulp. The vast majority of the saving can be attributed directly to the enzyme treatment, as acidification alone only resulted in a net cost savings of USD 0.14/ton. All of the peroxide treatments resulted in an overall net increase in bleaching costs to obtain the final target brightness. Acidic peroxide appears to be a more effective pretreatment method than alkaline peroxide but it still results in a net increase in overall bleaching costs. **TJ**

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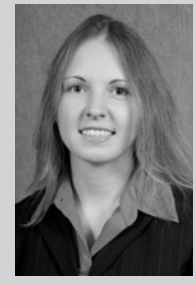
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INSIGHTS FROM THE AUTHORS

Several pre-bleaching methods have been developed, each claiming to provide an excellent solution to reducing bleaching costs. We performed each method under controlled conditions with the same starting material in an attempt to determine the best method for reducing bleach plant costs.

As far as we know, our study was the first to run side-by-side comparisons of bleaching methods using the same starting material and constant pulp brightness targets. The hardest aspect was determining the best pretreatment condition for each of the methods. When five different methods were compared, the sheer number of bleaching trials became prohibitive.

Interestingly, of all the pre-bleaching techniques we examined, enzyme pre-bleaching was the only consistently cost-effective method. While the other methods paid for themselves, at best, enzymes produced reasonable cost savings. Mills can use this information to better evaluate various methods of reducing bleaching cost through pre-bleaching techniques. The next step would be to conduct mill trials of one or more pre-bleaching methods.



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