Bleaching of Eucalyptus grandis *chemimechanical pulps*

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ABSTRACT

One-stage and two-stage bleaching trials were carried out to obtain high brightness levels in Eucalyptus grandis *chemimechanical pulps of 49.5% (Elrepho) initial brightness. Peroxide bleaching was performed in standard conditions at five levels of two variables: hydrogen peroxide concentration and sodium hydroxide concentration. The maximum brightness levels were 76.5% in the one-stage trials and 78% in the two-stage trials. Peroxide consumption in the one-stage process depended exclusively and linearly on the initial charge. Brightness reached a ceiling with higher charges of peroxide (approximately 78% with 4% of initial H_2O_2). In the range studied, brightness and mechanical resistance increased linearly with the initial NaOH charge. In the two-stage process, brightness varied quadratically with the initial peroxide charge, indicating a maximum around the central point. Optimum conditions were found when an equal proportion of reagent loads was distributed in each stage.*

Application:

A strategy for optimizing alkali and peroxide charges during bleaching of chemimechanical pulp.

BLEACHING TRIALS WERE PERformed to obtain high brightness in *Eucalyptus grandis* chemimechanical pulps. Eucalyptus is currently one of the principal hardwood raw materials used in the pulp and paper industry, with *E. grandis* being the most cultivated species in Misiones, Argentina. The low brightness levels of chemimechanical pulps make difficult their use for printing and writing paper [brightness requirement about 80% ISO *(1)*].

Hydrogen peroxide is the oxidizing chemical reagent most often used. If applied under moderate conditions, H_2O_2 acts as a bleaching agent, not as a delignifying agent, improving pulp brightness with little loss of yield *(2)*. The advantages of peroxide lie in its easy handling and use, its versatility, and the nontoxic and innocuous nature of its reaction products. Bleaching is normally carried out at a moderate temperature with a buffered and stabilized liquor. It can be performed in one or two stages. In two-stage bleaching, the residual liquors of the second stage are recycled to the first one, thus increasing the efficiency of the process *(1, 3-5)*.

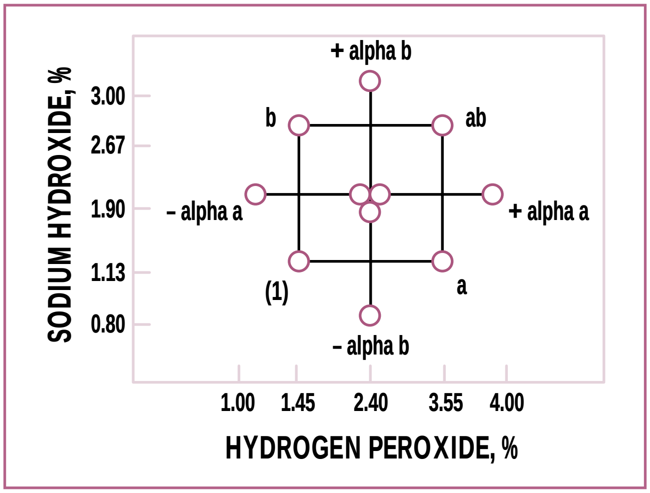
The brightness increase depends on the species used. It is generally related to the age of the trees and their extractives content. The quality of the wood is of the utmost importance *(5, 6)*. The metallic transition ions present in wood, and those originated in the pulping system, bring about decomposition and other undesirable reactions with the H_2O_2 *(7)*. The pulp therefore must be pretreated with a complexing agent prior to bleaching *(3)*. Diethylene triamine pentaacetic acid (DTPA) is an effective chelating agent in peroxide bleaching systems *(6)*.

Total liquor alkalinity must be high enough to ensure the desired concentration of the active bleaching species (perhydroxyl ion: OOH^-) during the bleaching process. High pH also reduces hydrogen peroxide decomposition and inhibits metasilicate acid precipitation (H_2SiO_3 or $SiO_2 \cdot H_2O$, generated at pH values under 9.5). Even then, it must not be so high as to produce chromophoric groups. Various authors *(6)* found that there is an optimum concentration of sodium hydroxide. Maximum brightness is reached at the pH level in which the bleaching reaction surpasses the generation of chromophoric groups. Total alkali and hydrogen peroxide levels therefore must be balanced to ensure that a small amount of residual hydrogen peroxide is present near the end of the bleaching reaction. If the alkali is completely consumed, perhydroxyl anions will not be generated, and bleaching will not occur. If the hydrogen peroxide is totally consumed under high pH conditions, brightness will be lost because of reversion *(8, 9)*. It therefore is necessary to optimize the NaOH and H_2O_2 charges in order to obtain the maximum increase in brightness.

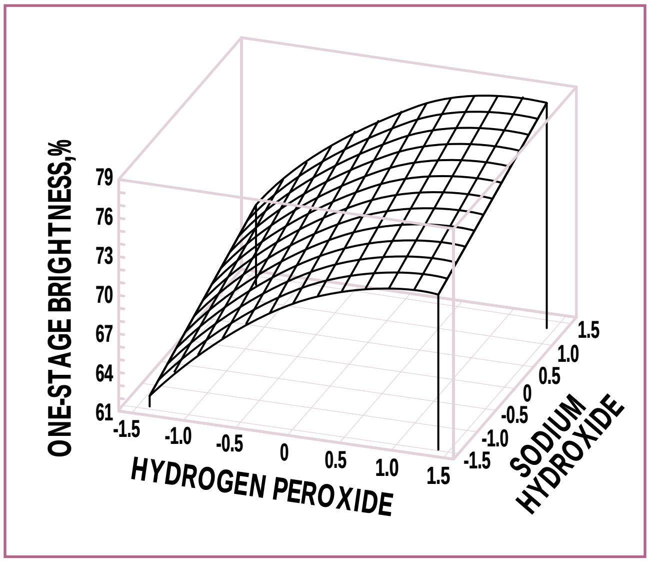
EXPERIMENTAL

The chemimechanical pulps' raw material consisted of *E. grandis* chips obtained at a Celulosa Argentina mill in Puerto Piray, Misiones, Argentina *(10)*. Final freeness was 45°SR, and unbleached pulp brightness was 49.5% Elrepho. The physical properties were: tensile index, 12 N·m/g; burst index, 0.24 kPa·m^2/g; tear index, 6.3 mN·m^2/g; bulk, 3.2 cm^3/g; water retention value, 130%.

A central-composite experimental design was applied to the system, shown in **Fig. 1,** consisting of two variables at five levels (factorial 2^2 + star + 3 central-point repetitions *(11)*). For the hydrogen peroxide, the lower concentration limit was set at 1% on o.d. (oven-dry) pulp and the upper limit at 4%. The other levels were automatically set. The limits



1. Central composite design levels of NaOH and H_2O_2 for one-stage bleaching



2. Effects of hydrogen peroxide and sodium hydroxide on brightness in one-stage bleaching

for NaOH charge were set at 0.8% and 3% on o.d. pulp. The design was applied to the one- and two-stage bleaching systems. The trials were carried out in random order to reduce systematic errors.

The pulp was initially pretreated with DTPA under the following conditions: consistency, 3%; time, 15 min; temperature, 60°C; DTPA concentration, 0.5% on o.d. pulp. Subsequently it was thickened to 15% consistency and put into polyethylene bags. Demineralized water was used at all times. The bleaching liquor, which consisted of a mixture of H_2O_2 and NaOH (in the proportions set by the design), Na_2SiO_3 (3% on o.d. pulp), DTPA (0.05% on o.d. pulp) and $MgSO_4 \cdot 10H_2O$ (0.05% on o.d. pulp), was added to the pretreated pulp. Immediately after mixing the liquor and the pulp, initial pH was measured. The bags containing the pulp were then sealed and placed in a temperature-controlled bath. Reaction time (120 min), pulp consistency (15%), temperature (70°C), and pulp quantity (50 g o.d.). were kept constant. The pulps were remixed manually at 30-min intervals to achieve a proper liquor–pulp homogenization.

At the end of the bleaching time, liquor samples were taken to determine final pH and residuals (CPPA standard J.16P). The pulps were diluted to 1% consistency and then neutralized with sodium metabisulfite in order to decompose the residual H_2O_2 and stabilize the brightness. Handsheets for physical and optical tests (Elrepho brightness) and physical properties of the pulps were performed according to TAPPI test methods.

Temperature (70°C), time (60 min), and pulp consistency (15%) remained identical in each stage of the two-stage process. After the first stage, the pulps were washed and thickened for the next one. The bleaching liquor was added in the concentrations predetermined for each trial. Initial pH values were measured, and the bags were set in the bath, according to the procedures described previously. In all cases, totals of H_2O_2 and NaOH were 4% and 3%, respectively.

RESULTS

The results for the one-stage bleaching experiments appear in **Table I**.

The relation between brightness and the independent variables in the one-stage bleaching is represented by the following equation (r^2 = 0.85; the regression only applies for alkali and peroxide levels within the domain of the experimental set):

$$\text{Brightness} = 67.8 - (0.15 \times \%H_2O_2) + (1.88 \times \%NaOH) + [0.72 \times (\%H_2O_2)^2]$$

The contour curves for brightness are shown in **Fig. 2**.

The first-stage results of the two-stage bleaching experiments are shown in **Table II**, and the second-stage results of the two-stage bleaching experiments appear in **Table III**.

The theoretical regression for two-stage bleaching experiments (within the domain of the experimental set) is:

$$\text{Brightness} = 77.5 - [1.45 \times (\%H_2O_2)^2]$$

DISCUSSION

One-stage bleaching

Maximum brightness achieved for one-stage bleaching was 76.5% (an increase of 27 points), as shown in Table I. These values are similar to those found by other authors *(12)* using similar treatments but working with other eucalyptus species.

Even though medium consistency (15%) was used in this study, higher brightness levels might be

TRIALS	1	2	3	4	5	6	7	8	9	10	11
H_2O_2, % on o.d. pulp	1.45	3.55	1.45	3.55	1.00	4.00	2.50	2.50	2.50	2.50	2.50
NaOH, % on o.d. pulp	1.13	1.13	2.67	2.67	1.9	1.9	0.8	3.0	1.9	1.9	1.9
Initial pH	10.4	10.6	11.7	11.4	11.4	10.7	10.2	11.3	10.5	11.1	11.4
Consumed H_2O_2, % on o.d. pulp	1.17	1.85	1.38	2.54	0.93	2.82	1.67	2.11	1.83	1.81	1.79
Residual H_2O_2, % on o.d. pulp	0.28	1.70	0.11	1.01	0.07	1.18	0.83	0.39	0.67	0.69	0.71
Residual alkali, % on o.d. pulp	0.05	0.02	0.23	0.11	0.10	0.05	0.02	0.20	0.08	0.06	0.06
Final pH	8.8	8.5	9.8	9.3	9.4	8.8	8.5	9.6	9.0	9.0	8.9
Brightness, % Elrepho	66.9	74.0	70.0	76.5	62.9	76.4	68.1	74.8	73.5	74.1	75.0
Brightness increment, points	17.4	24.5	20.4	27.0	13.4	26.9	18.6	25.3	24.0	24.6	25.5
Tensile index, N·m/g	13.9	13.5	17.1	15.1	15.4	14.3	12.5	18.4	15.5	14.8	13.8
Tear index, mN·m²/g	4.56	4.78	5.20	4.61	4.74	4.35	4.22	5.62	4.84	5.09	5.56
Burst index, kPa·m²/g	0.44	0.42	0.52	0.49	0.50	0.49	0.41	0.57	0.54	0.51	0.47
Bulk, cm³/g	2.93	3.02	2.78	2.85	2.84	2.91	2.97	2.72	2.89	2.87	2.97
Water retention value, %	122	132	132	143	123	130	146	94	143	127	134

Table I. One-stage bleaching experimental results

TRIALS	1	2	3	4	5	6	7	8	9	10	11
H_2O_2, % on o.d. pulp	0.95	3.05	0.95	3.05	0.50	3.50	2.00	2.00	2.00	2.00	2.00
NaOH, % on o.d. pulp	0.80	0.80	2.20	2.20	1.50	1.50	0.50	2.50	1.50	1.50	1.50
Initial pH	11.3	9.5	11.7	11.2	11.2	10.8	10.4	11.5	11.4	10.9	11.1
Consumed H_2O_2, % on o.d. pulp	0.73	1.61	0.89	2.02	0.48	1.98	1.15	1.68	1.40	1.43	1.46
Residual H_2O_2, % on o.d. pulp	0.22	1.44	0.06	1.03	0.02	1.52	0.85	0.32	0.60	0.57	0.54
Residual alkali, % on o.d. pulp	0.08	0.02	0.04	0.15	0.24	0.06	0.05	0.24	0.09	0.07	0.07
Final pH	9.2	8.8	10.4	9.5	10.1	9.0	8.2	9.9	9.2	9.2	9.4

Table II. First-stage results of two-stage bleaching experiments

TRIALS	1	2	3	4	5	6	7	8	9	10	11
H_2O_2, % on o.d. pulp	3.05	0.95	3.05	0.95	3.50	0.50	2.00	2.00	2.00	2.00	2.00
NaOH, % on o.d. pulp	2.20	2.20	0.80	0.80	1.50	1.50	2.50	0.50	1.50	1.50	1.50
Initial pH	11.6	11.5	10.7	10.8	10.9	11.4	10.5	10.8	11.5	11.0	11.1
Consumed H_2O_2, % on o.d. pulp[a]	1.41	0.56	1.21	0.35	1.70	0.30	1.31	0.62	0.89	0.55	1.00
Total consumed H_2O_2, % on o.d. pulp[b]	2.14	2.17	2.10	2.37	2.18	2.28	3.46	2.30	2.29	1.98	2.46
Residual H_2O_2, % on o.d. pulp	1.64	0.39	1.84	0.60	1.80	0.20	0.69	1.38	1.11	1.45	1.00
Residual alkali, % on o.d. pulp	0.75	0.85	0.50	0.71	0.61	0.84	0.77	0.53	0.67	0.69	0.61
Residual pH	10.3	10.7	10.4	10.6	10.4	10.7	9.5	10.5	10.4	10.4	10.7
Brightness, % Elrepho	77.6	76.6	75.3	76.7	73.3	74.9	77.4	77.4	77.9	76.7	76.4
Brightness increment, points	28.1	27.1	25.8	27.2	23.8	25.4	27.9	27.9	28.4	27.2	26.9
Tensile index, N·m/g	20.3	24.4	19.9	23.6	22.3	23.1	17.4	20.8	18.1	20.1	14.4
Burst index, kPa·m²/g	0.70	0.76	0.59	0.68	0.62	0.77	0.50	0.79	0.64	0.59	0.64
Tear index, mN·m²/g	5.76	6.68	5.84	6.14	6.29	7.05	6.32	4.92	7.48	5.25	4.33
Bulk, cm³/g	2.58	2.52	2.65	2.60	2.63	2.57	2.97	2.59	2.65	2.66	2.80
Water retention value, %	114	162	142	152	154	152	65	151	103	146	136

[a]First stage
[b]First and second stages

Table III. Second-stage results of two-stage bleaching experiments

	r^2	a	b (x %H_2O_2)	c (x %NaOH)
Consumed H_2O_2	0.84	1.81	0.56	…
Residual alkali	0.86	0.09	−0.03	0.07
Final pH	0.97	9.05	−0.20	0.42
Tensile index	0.77	14.9	…	1.64
Burst index	0.72	0.49	…	0.05
Bulk	0.74	2.89	…	−0.08

Table IV. Statistical parameters of the regression equations for one-stage bleaching and for the second stage of two-stage bleaching

obtained in similar conditions but using consistencies up to 30%. High consistency produces a greater concentration of H_2O_2 in the bleaching liquor, thus increasing the reagent load within the fiber structure. This accelerates the reaction rate and reduces hydrogen peroxide consumption by undesirable secondary reactions *(1, 6)*.

At initial charges of hydrogen peroxide of approximately 3.6%, brightness reached a plateau near 78% (Fig. 2). Higher charges of this reagent apparently do not have a positive effect on brightness. Within the range studied, brightness increased linearly with the initial NaOH charge.

Both variables studied had a strong effect on brightness, but the effect of hydrogen peroxide was notably greater than that of NaOH (Fig. 2). In all cases, initial pH of the bleaching solution was higher than 10. Final pH was generally in the 9 to 10 range. Low pH levels were not conducive to the formation of perhydroxyl ions, thus reducing the bleaching efficiency. The contour curves found for brightness as a function of peroxide and alkali charge are similar to those found by other authors for one-stage bleaching *(4)*. Hydrogen peroxide consumption depended exclusively and linearly on the initial charge (**Table IV**), which was for maximum brightness 2.5% on o.d. pulp (residual, 1.5% on o.d. pulp).

Alkali residuals and final pH were positively influenced by the initial NaOH charge (p = 0.004) and negatively by the initial hydrogen peroxide charge (p = 0.02). NaOH levels below 1.5% were not sufficient to prevent solution acidification during the reaction. Mechanical properties increased linearly, while bulk decreased with soda charges, as Table IV indicates.

Two-stage bleaching

For two-stage bleaching, a maximum of 77.9% brightness was obtained, with an increase of 28.4 points, as shown in Table III. Significant differences in brightness were found with the alternate application of different H_2O_2 charges in each stage (Tables II and III). Brightness varied quadratically with initial peroxide, showing a maximum near the central point (2% H_2O_2) in both stages. The lowest brightness level (73.3%) was obtained with the highest hydrogen peroxide percentage in the second stage (3.5%) and the lowest in the first stage (0.5%). Other authors *(4)* found that the best brightness values were obtained by using the higher chemical charge in the second stage, but the results for this pulp did not confirm this. With equal charge of hydrogen peroxide in each stage, better results were obtained in the two-stage system than in the one-stage process.

At the point of maximum brightness, hydrogen peroxide consumption was 1.35% in the first stage (residuals, 0.65%), and approximately 1% (residuals, 1%) in the second stage. The residual levels obtained in one-stage bleaching and in the first stage of the two-stage process suggest that hydrogen peroxide charges below 1.5% should not be used.

The spent bleaching liquors in the one-stage process and those of the first stage in the two-stage process showed a large decrease in pH, usually produced by the acids generated during the reaction. Conversely, spent liquors of the second stage maintained high pH values at all times. This liquor can be considered to be more clean, free of extractives, metallic ion compounds, or other pulp-reaction products that are eliminated by washing in the interstage treatment.

The best utilization of bleaching reagents to reach the highest brightness levels might be obtained using high-consistency pulps in a two-stage process and recirculating the spent liquor from the second stage to the first *(13)*. Consequently, it is industrially possible to obtain high brightness levels (near 80%) using a two-stage bleaching process, with a liquor composed of 1.5% soda and 2% hydrogen peroxide in each stage. Taking residuals into account, recirculation of the spent liquor from the second stage to the first stage can be carried out using the required makeup of hydrogen peroxide and soda. This could be accomplished using a system such as a twin-roll press, where 50% of the spent liquor of the second stage would be recirculated. Another possibility would be to use a one-stage bleaching process, with 4% hydrogen peroxide and 3% soda, with the recirculation of part of the spent liquor *(14)* as a prebleaching treatment.

Even though the beneficial effects of sodium silicate on brightness and on hydrogen peroxide stability are well known, the makeup of

KEYWORDS
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this additive is not recommended, since silicate produces deposits in pipes and equipment *(15)*. Considering there is no loss of silica (it is found in a different chemical form in residual liquors), the NaOH added must be greater than 1.5% to satisfy the requirements of the alkali charge and to bring about the regeneration of sodium silicate. The addition of DTPA does not have that disadvantage, since quantities are negligible and its impact on total costs is minimal.

The combinations studied in the two-stage process did not significantly affect the mechanical properties, since they depend exclusively on the total value of the sodium hydroxide charge. Peroxide–alkali interaction was not significant in any of the experiments (Table IV).

CONCLUSIONS

The two-stage process showed a better bleaching performance than the one-stage process. The best combination consisted of distributing the load in both stages [2% hydrogen peroxide and 1.5% sodium hydroxide (o.d. pulp basis) in each stage]. The bleaching process improved the physical properties of the pulp in proportion to the alkali charge. **TJ**

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