# *Oxygen delignification as a pretreatment for acetosolv pulps bleaching*

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**ABSTRACT:** Experiments on oxygen bleaching, planned in accordance with an incomplete factorial design $3^3$, has allowed the study of the influence of temperature, soda concentration, and time on lignin and xylan contents and on brightness of *Eucalyptus globulus* acetosolv pulps. It has been found in the interval of conditions assayed that the $O_2$ treatment increases the degree of delignification of pulps obtained without noticeable changes in their viscosity. Those conditions of operation have been selected which, preserving the polysaccharides, lead to an important reduction of residual lignin in the pulp.

***Application:*** The information from this study can help mills in optimizing the bleaching process based on oxygen pre-treatments.

Most bleached-kraft pulp production processes include one or various stages of delignification with oxygen to reduce lignin contents as a preparation for the bleaching sequence. Pre-treatment of raw pulp or the use of different additives can further improve the selectivity and efficiency of this process.

The use of oxygen allows a 40%-45% reduction of lignin contents, on up to 60% in some cases, depending on wood type and washings previous to the oxygen stage *(1)*. Nevertheless, as lignin is eliminated, the free radicals formed during the delignification process break cellulose chains, giving rise to a decrease in pulp viscosity and, therefore, a deterioration of its physical and mechanical characteristics *(2)*.

In an earlier work *(3) Eucalyptus globulus* acetosolv pulps obtained under differing conditions of delignification were bleached under varying conditions. That study confirmed that the characteristics of those pulps depend both on the bleaching sequence selected and on the conditions of the delignification stage from which they are obtained. The preliminary study suggested the convenience of carrying out delignification with oxygen ($O_2$) following the delignification with acetic acid. The aim of this treatment with $O_2$ carried out before hydrogen peroxide ($H_2O_2$) bleaching is to reduce the lignin contents and to achieve a higher efficiency in the bleaching process, making it cheaper by reducing the use of reactants.

This paper studies the influence of operating conditions [temperature, time, and sodium hydroxide (NaOH) concentration] in oxygen delignification of *E. globulus* acetosolv pulp. The aim is the selection of those conditions that permit the elimination of the greater part of residual lignin without significantly reducing pulp yield and without deteriorating pulp physical characteristics.

## EXPERIMENTAL

### *Delignification with acetic acid*

Experiments in delignification of *E. globulus* wood with acetic acid have been carried out using different conditions (**Table I**). The pulps obtained have been submitted to different bleaching sequences with hydrogen peroxide (P), after being washed with water (L) (until a neutral filtrate has been obtained) and/or soda extraction (E). Some of the pulps underwent a bleaching pre-treatment with oxygen (O) at a manometric pressure of 6 bar and at 100ºC (373 K) in an alkaline environment.

The acetic acid delignification in this experiment was carried out in a 17 L stainless steel reactor (Hallestoy C276) with temperature and agitation speed control systems. We introduced the wood, the acetic acid, and the water into the reactor at room temperature, and added the catalyst when the temperature of reaction blend reached 100ºC (373 K). As the set time lapsed, measured from the moment of reaction temperature (which is different in each case), the suspension was cooled and filtered. The pulp obtained is washed with acetic acid and plenty of water.

The experiments with alkaline extraction and those of bleaching with peroxide were carried out in polyethylene bags with consistencies of 4% and 10% respectively. The alkaline extraction was performed at room temperature, for 0.5 hours, using a 0.3% (% based on liquor) NaOH concentration. In the peroxide bleaching experiments, temperature was maintained at 80ºC (353 K) for an hour, using 10% $H_2O_2$, 2% NaOH, 0.2% EDTA, and 0.5% Epsom salt (magnesium sulfate heptahydrate, $MgSO_4 \cdot 7H_2O$) (% based on o.d. pulp). In Run 25 and 26, however, the conditions were T = 90ºC (363 K), 2% $H_2O_2$, 3% NaOH, 0.2% EDTA, and 0.5% Epsom salt. The lignin content was determined in the bleached pulps obtained, expressed as kappa number (SCAN-C1:77), brightness (ISO 3688), viscosity (SCAN-C, 15:62), fiber length [using Kajaani FS-200 (T233 sm 53)], and the indexes for resistance to traction, bursting, and tearing.

In the pre-delignification experiments with acetic acid carried out on *E. globulus* wood (Table I), as well as those on *Pinus pinaster* wood (forthcoming), we ascertained that potassium iodide (KI) as a catalyst improves the selectivity of the process. In addition, for a given degree of delignification, higher pulp yield is obtained as compared to other acid catalysts such as hydrogen chloride (HCl), and that the mechanical characteristics of the pulp are preserved. For those reasons, we chose to precede oxygen delignification of *E. globulus* wood by using KI as a catalyst under the following conditions: 80% acetic acid concentration (based on liquor), 0.227% KI concentration (based on liquor), 1:10 (w/w) solid-

| RUN | T, °C | [NaOH], % | t, h | YIELD, % | KAPPA NUMBER | ARA, % | XYL, % | GAL, % | MAN, % | GLUC, % | BRIGHTN. ISO | VISCOS., mL/g (Pa.S) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 0 | - | - | - | 50.30 | 9.69 | 2.63 | 5.27 | 0.35 | 1.49 | 87.07 | 26.2 | 1082(0.110) |
| 1 | 80 | 1.5 | 0.5 | 95.85 | 4.74 | 0.78 | 4.82 | 0.28 | 1.29 | 74.41 | 38.1 | 1114 (0.124) |
| 2 | 80 | 2.5 | 0.5 | 95.83 | 4.64 | 0.96 | 4.71 | 0.31 | 1.14 | 75.95 | 39.1 | 1120 (0.127) |
| 3 | 80 | 2.5 | 1.5 | 95.59 | 3.93 | 0.98 | 4.33 | 0.32 | 1.41 | 70.25 | 44.4 | 1114 (0.124) |
| 4 | 80 | 1.5 | 1.5 | 96.20 | 3.66 | 0.94 | 4.52 | 0.34 | 1.31 | 79.30 | 45.9 | 1138 (0.138) |
| 5 | 120 | 2.5 | 0.5 | 93.26 | 4.15 | 0.71 | 4.03 | 0.26 | 1.07 | 80.27 | 48.4 | 1095 (0.115) |
| 6 | 120 | 2.5 | 1.5 | 92.48 | 3.14 | 0.97 | 3.54 | 0.43 | 1.40 | 88.16 | 53.9 | 1082 (0.110) |
| 7 | 120 | 1.5 | 1.5 | 95.30 | 5.53 | 1.41 | 4.37 | 0.65 | 1.09 | 86.57 | 45.4 | 1076 (0.107) |
| 8 | 120 | 1.5 | 0.5 | 100.00 | 5.85 | 0.82 | 4.78 | 0.42 | 1.47 | 84.23 | 43.2 | 1120 (0.127) |
| 9 | 100 | 2.5 | 1.0 | 93.89 | 3.96 | 0.31 | 3.61 | 0.21 | 1.20 | 71.64 | 49.3 | 1126 (0.131) |
| 10 | 100 | 2.0 | 1.5 | 88.08 | 5.18 | 1.19 | 5.35 | 0.43 | 1.97 | - | 47.4 | 1107 (0.121) |
| 11 | 100 | 1.5 | 1.0 | 89.34 | 5.12 | 0.43 | 4.41 | 0.12 | 1.62 | 82.68 | 46.3 | 1095 (0.115) |
| 12 | 100 | 2.0 | 0.5 | 94.44 | 4.85 | 0.45 | 3.90 | 0.42 | 1.38 | 82.58 | 46.7 | 1250 (0.189) |
| 13 | 80 | 2.0 | 1.0 | 94.93 | 4.35 | 0.64 | 4.32 | 0.20 | 1.48 | 84.38 | 49.1 | 1126 (0.131) |
| 14 | 120 | 2.0 | 1.0 | 90.87 | 5.37 | 0.96 | 4.06 | 0.19 | 1.16 | 80.84 | 46.1 | 1101 (0.118) |
| 15 | 100 | 2.0 | 1.0 | 94.99 | 4.36 | 0.25 | 4.09 | 0.26 | 1.60 | 83.37 | 47.7 | 1132 (0.134) |
| 16 | 100 | 2.0 | 1.0 | 94.02 | 4.68 | 0.31 | 4.02 | 0.15 | 1.02 | 84.24 | 47.0 | 1126 (0.131) |
| 17 | 100 | 2.0 | 1.0 | 94.94 | 4.60 | 0.48 | 4.11 | 0.40 | 1.83 | 78.47 | 48.2 | 1126 (0.131) |

Run 0, % yield based on o.d. wood. Run 1-17, % yield based on o.d. pulp

***I. Delignification and bleaching sequence conditions. Kappa number and brightness in the pulps obtained.***

| RUN | PULP | [AcOH], % (w/w) | [HCL], [KI], % (w/w) or $O_2$ PRESSURE, BAR | T (°C) | t (h) | BLEACHING PROCESS | KAPPA NUMBER | BRIGHTNESS, ISO |
|---|---|---|---|---|---|---|---|---|
| 18 | $P_{140,\ 4h}$ | 80 | 0.025 (HCl) | 140 | 4 | LEPP | 0.9 | 75.4 |
| 19 | $P^{160,4h}$ | 80 | 0.025 (HCl) | 160 | 4 | LEPP | 0.6 | 77.1 |
| 20 | $P^{180,2h}$ | 80 | - | 180 | 2 | LPPPP | 1.1 | 77.4 |
| 21 | $P^{180,2h}$ | 80 | - | 180 | 2 | EPPP | 0.9 | 83.3 |
| 22 | $P^{160,O2}$ | 80 | 1 ($O_2$) | 160 | 2 | EPPP | 3.0 | 64.7 |
| 23 | $P^{140,\ O2}$ | 80 | 1 ($O_2$) | 140 | 4 | LEPP | 4.4 | 65.0 |
| 24 | $P^{160,\ KI}$ | 80 | 0.14 (KI) | 160 | 2 | LEPP | 1.7 | 73.1 |
| 25 | $P^{140,KI}$ | 80 | 0.227 (KI) | 140 | 6 | O/PP | 1.5 | 65.6 |
| 26 | $P_{140,KI}$ | 80 | 0.455 (KI) | 140 | 6 | O/PP | 1.3 | 69.3 |

***II. Yields and characteristics for the raw pulp (Run 0) and for the pulps obtained in the oxygen delignification experiments.***

| | Y1 | Y2 | Y3 |
|---|---|---|---|
| $a_{0j}$ | 4.77 | 4.00 | 47.67 |
| $a_{1j}$ | 0.27 | -0.19 | 2.04 |
| $a_{2j}$ | -0.51 | -0.27 | 1.62 |
| $a_{3j}$ | -0.28 | -0.16 | 2.15 |
| $a_{12j}$ | -0.53 | -0.16 | 1.78 |
| $a_{13j}$ | NS | NS | NS |
| $a_{23j}$ | NS | NS | NS |
| $a_{11j}$ | NS | 0.35 | NS |
| $a_{22j}$ | -0.30 | NS | NS |
| $a_{33j}$ | NS | NS | -2.42 |
| $r^2$ | 0.8509 | 0.8958 | 0.7439 |
| F-Ratio | 12.55 | 17.19 | 6.39 |
| Prob $F_{exp}>F_{tab}$ | 0.0003 | 0.0001 | 0.0051 |

***III. Model coefficient (equation 1) for $Y_1$ (kappa number), $Y_2$ (xylose %) and $Y_3$ (ISO brightness) for statistical parameters. NS = not significant for 95% reliability level.***

liquid ratio, temperature 140ºC, and time 6 h (Run 0, **Table II**).

The cellulose pulp yield and its lignin and polysaccharide contents were determined. We expressed the lignin contents as kappa number. The polysaccharides were determined as monosaccharides by means of gas chromatography following its conversion into alditol acetates *(4)*. We also determined brightness and viscosity as previously explained.

### *Delignification with oxygen*

The experiments were planned following an incomplete factorial design $3^3$. The variables selected and their corresponding variation intervals were as follows: temperature (T) 80º-120ºC (353-393 K), soda concentration ([NaOH]), 1.5%-2.5% (based on oven-dried pulp), and time (t), 0.5-1.5 h (see Table 1).

The delignification was carried out in a 700 mL stainless steel reactor, lined inside with teflon and equipped with a thermostat. In each experiment, 20 g of dry pulp was mixed with the water-solved soda necessary to achieve a consistency of 10%, and 0.5% (based on oven-dried pulp) $MgSO_4 \cdot 7H_2O$ was added. We brought the mixture to reaction temperature and maintained it there until the set time lapsed. All the experiments were carried out at a manometric $O_2$ pressure of 5.5 bar.

After filtering the suspension and washing the pulps with water, yield, kappa number, polysaccharide content, brightness and viscosity are determined.

## RESULTS AND DISCUSSION

The bleached pulp obtained (Table I) showed acceptable kappa numbers

even if, in most cases, this led to low global yield. Furthermore, we observed that both brightness degree and kappa number are closely related to the structural characteristics of residual lignin in the pulp and are dependent on the delignification conditions as well as on pre-treatments. In none of the cases did we obtain satisfactory results for traction, bursting, and tearing indexes due to low viscosity values [~500 mL/g ($14.9\times10^{-3}$ Pa×s)] and fiber length (< 0.5mm). This suggested the convenience of applying oxygen pre-treatment in an alkaline environment to reduce lignin contents without significant modification of pulp viscosity.

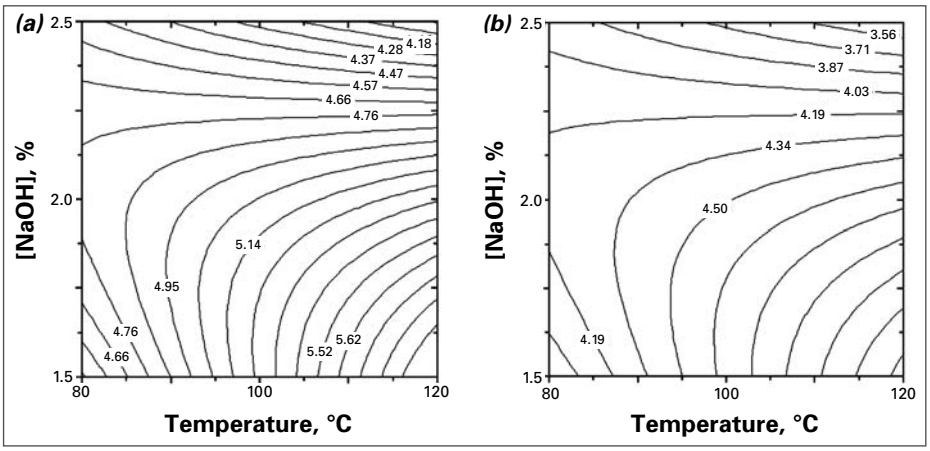
We also considered the influence of $O_2$ delignification temperature, NaOH concentration, and time on the yield and on some of the properties of the pulp obtained, such as kappa number, brightness, monosaccharide contents, and viscosity. The experimental results are presented in Table II (Run 1-7), with those corresponding to raw pulp (Run 0).

A multiple regression analysis has allowed us to correlate, in some of the cases, the experimental results through the following type of equations:

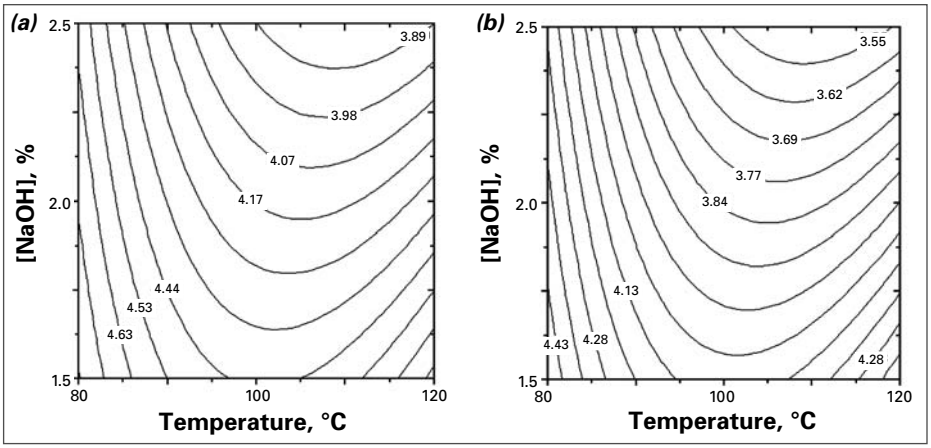
$$Y_j = a_{0j} + a_{1j} \cdot X_1 + a_{2j} \cdot X_2 + a_{3j} \cdot X_3 + a_{11j} \cdot X_1^2 + a_{12j} \cdot X_1X_2 + a_{13j} \cdot X_1X_3 + a_{22j} \cdot X_2^2 + a_{23j} \cdot X_2X_3 + a_{33j} \cdot X_3^2$$

where $X_1$, $X_2$ and $X_3$ are the normalized variables (with values between -1 and 1) corresponding to T, [NaOH] and t, respectively. **Table III** presents the coefficients for $Y_1$ models (kappa number), $Y_2$ (xylan contents), and $Y_3$ (ISO brightness), along with the statistical parameters that confirm their validity. Coefficients marked with NS are not significant for a 95% confidence level.

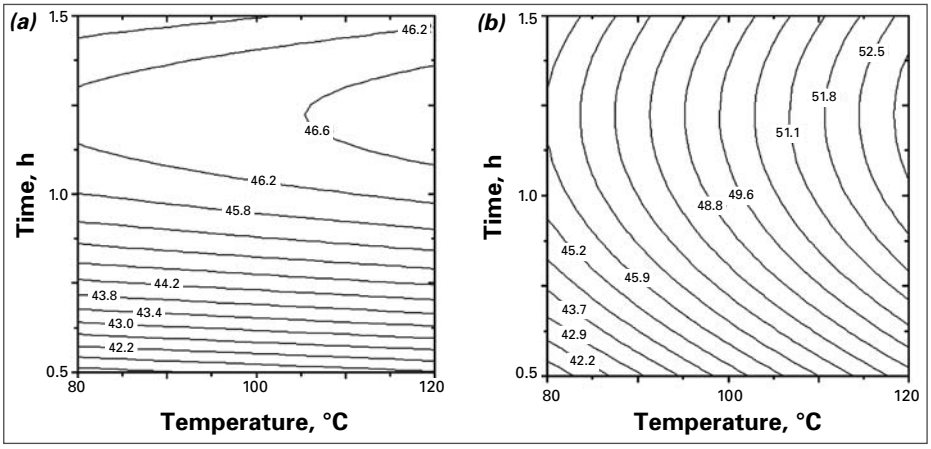
The three variables studied and the interactions T·[NaOH] and [NaOH]·[NaOH] were found to influence the kappa number of the pulp obtained. **Figures 1a and 1b** present the response surfaces for $Y_1$, as a function of the temperature and NaOH concentration, for two time values t=0.5 h and t=1.5 h, respectively. Independent of time, at temperatures above 100ºC (373 K) an increase in soda concentration gives rise to a decrease in kappa number, this variation being more acute the higher the temperature. For temperature values below 100ºC (373 K), the kappa number is hardly affected by changes in [NaOH]. For low [NaOH] values, a temperature



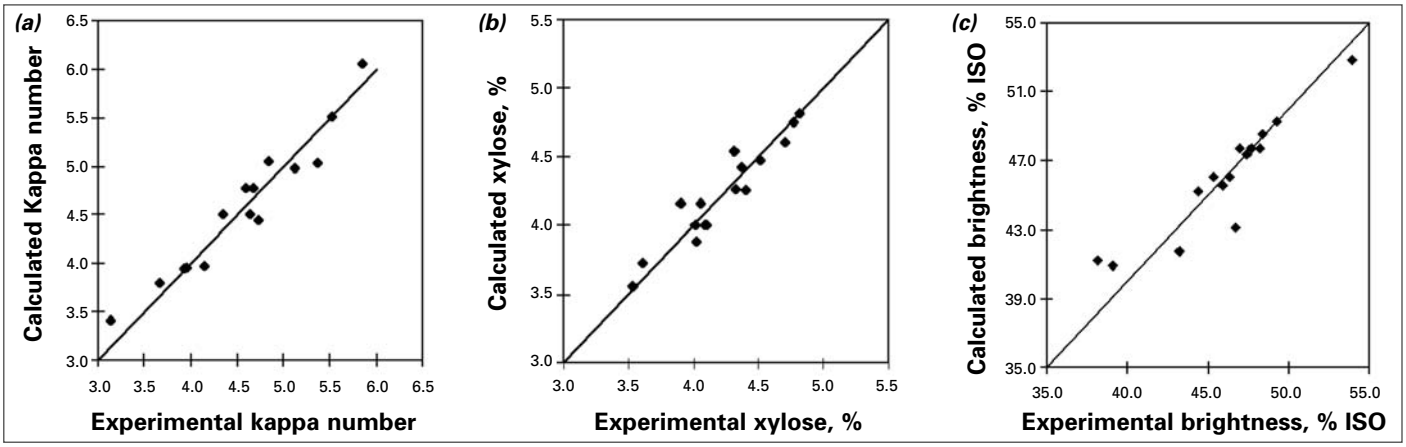

*1. Influence of temperature and [NaOH] on kappa number. Time t = 0.5 h (a) and t = 1.5 h (b).*



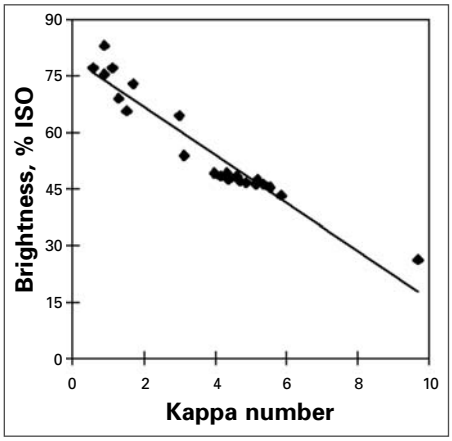

*2. Influence of temperature and [NaOH] on xylose content. Time t = 0.5 h (a) and t = 1.5 h (b).*




*3. Influence of temperature and time on brigthness. [NaOH] = 1.5% (a) and [NaOH] = 2.5% (b).*




*4. Measured kappa number a), xylose content b), and brightness c) vs. the calculated values obtained by means of the models $Y_1$, $Y_2$, and $Y_3$, respectively.*




*5. Measured kappa number vs. measured brightness.*

increase affects the process negatively, because the kappa number of the pulp increases. In contrast, kappa number is practically independent of temperature for high [NaOH]. On the other hand, a time increase to reach a given kappa number permits working with lower NaOH concentrations and lower temperatures.

The results obtained suggest that alkali concentration is the most influential variable in $O_2$ delignification. From a certain alkali level, an increase in concentration, independent of temperature, facilitates lignin hydrolysis, a fact that agrees with Vincent et al's observations *(5)*.

In delignification and bleaching processes it might be adequate to reduce hemicelluloses hydrolysis because in the pulp refining process for paper production, the fibers are hydrated, which gives rise to bloating and expansion of the hemicelluloses layer. This avoids cross-fiber and causes fibrillation and appearance of bonds between them, allowing refining speed and improving opacity and mechanical properties of the pulps *(6)*.

The xylose contents in the pulps, an important component of the hemicelluloses in *E. globulus* wood, is presented in Table II. In any of the operating conditions subject to essay, the xylane contents decreases after delignification with $O_2$ with respect to the one present in raw pulp. We noted a significant influence of temperature, [NaOH], and of time, as well as the interactions between T·T and T·[NaOH]. **Figures 2a and 2b** present the response surface for $Y_2$ as a function of temperature and [NaOH] for two time values, 0.5 and 1.5, respectively. An increase in [NaOH] always causes a decrease in xylose content. At temperatures close to the lowest end of the essayed interval, the changes in the NaOH concentration hardly affect the xylose %, its influence being more acute as temperature increases.

It is generally accepted that an increase in temperature facilitates hemicelluloses degradation, and particularly that of xylans. However, we observed that at values close to the average temperature in the essayed interval [100ºC (373 K)], for a given alkali concentration, the xylose content in the pulps reaches a minimum, and that this value is lower the higher the [NaOH]. This can be explained if the NaOH, apart from facilitating the extraction of soluble polymers and the elimination of degradation products from the lignocellulosic matrix, also causes peeling reactions. Those reactions become more important as temperature and alkali hydrolysis of xylans and cellulose increase, degrading both *(6)*. An increase in treatment time leads—together with the already indicated effects of the other two variables, [NaOH] and T—to a decrease in xylose %.

As for the brightness of the pulps ($Y_3$), significant variables are temperature, soda concentration, time, and the interactions T·[NaOH] and t·t. The response surfaces for $Y_3$ as a function of temperature and time—the most significant variables in this case—are presented in **Figs. 3a and 3b** for two values of [NaOH] (1.5% and 2.5%, respectively).

For low alkalinity, temperature hardly influences the brightness of the pulps. At less than 1 h, for any temperature value, the degree of brightness increases with operation time. Any change in time beyond 1 h was of little significance. For pulps obtained with higher soda concentration (2.5%), an increase in temperature leads to a greater degree of brightness. We observed this same influence for time at values below ~1.25 h, a value where the degree of brightness goes through a maximum at a certain temperature.

**Figures 4 a, b, and c** present a quality assessment of the adjustment representing the experimental data, compared with the values calculated with previously obtained models for kappa number, xylose %, and brightness, respectively, where a satisfactory concordance was observed.

**Figure 5** represents brightness against kappa number in raw pulp (Run 0) of pulps obtained in delignification experiments with oxygen and the acetosolv pulps bleached in different bleaching sequences (Table 1). A lineal relationship is seen between brightness and kappa number. At low kappa numbers, however, this relationship does not hold and the brightness increases have to be explained by kappa number changes of little significance. During delignification and bleaching processes, lignin structure modification takes place, with elimination and formation of chromophore groups that contribute differently to lignin absorption spectrum *(7)*. As a result, methods based on absorbing (or reflecting) of electromagnetic radiation by functional groups in the lignin, such as the ISO brightness determining method, do not indicate that delignification necessarily implies elimination of lignin, and thus, kappa number reduction *(8)*.

From the analysis results obtained, we can conclude that oxygen delignification leads to an important reduction in lignin contents in acetosolv pulps, together with an increase in brightness, without significantly affecting their viscosity. With the aim to preserving hemicelluloses with acceptable kappa number and brightness degree, $O_2$ delignification at lower temperature and shorter time, and higher NaOH concentration than those of the essayed values should be carried out before hydrogen peroxide bleaching. **TJ**


## ACKNOWLEDGEMENTS

The authors are grateful to the Xunta de Galicia for financial support (Project XUGA 20901A96) and to CIE/ENCE for technical assistance.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*Received: March 2, 1999*
*Revised: September 17, 2001*
*Accepted: September 20, 2001*

This paper is also published on TAPPI's web site (www.tapppi.org) and summarized in the February *Solutions! for People, Processes and Paper* magazine (Vol. 85 No. 2)


## INSIGHTS FROM THE AUTHORS

This research focused on new bleaching technologies, which sometimes include an oxygen delignification stage as a treatment of the pulp before the bleaching process.

*Eucalyptus globulus* acetosolv bleached pulps obtained in previous experiments had low lignin contents, but their physical and mechanical properties were poor. This suggested the convenience of carrying out delignification with oxygen following the acetic acid delignification. The goal was to eliminate the greater part of the residual lignin without an important damage of the pulp characteristics and without reducing pulp yield significantly.

Due to the high number of variables involved, the most difficult aspect of this research was the selection of the variables to analyze and to apply the statistical analysis to the results to check that the models were significant.

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***González***

***Antorrena***

Of particular note to us was the finding that, for a given value of the kappa number (a measure of the lignin content), bleached acetosolv pulps exhibit lower brightness than bleached kraft pulps. This means that brightness depends not only on lignin content but also on the characteristics of the residual lignin.

The results we obtained from this study are promising. However, it is important to verify if the characteristics of the pulps after the hydrogen peroxide bleaching stages are acceptable and comparable to those of commercial kraft pulps.

— Gervasio Antorrena


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