STUDY OF 3 TCF BLEACHING PROCESSES APPLIED TO SODA-AQ *HESPERALOE FUNIFERA* PULP

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Three experimental designs with hydrogen peroxide (with temperature, time and hydrogen peroxide concentration as operating conditions), peracetic acid (temperature, time and concentration of peracetic acid) and sodium perborate (perborate concentration, time and concentration of peroxide) have been carried out. Each experimental design followed the influence of the operational variables on the properties of the bleached pulps obtained. The polynomial model used allows obtaining of equations that relate the dependent variables with the independent ones, and reproduce the experimental results with errors below 9, 4 and 8% for bleaching with hydrogen peroxide, peracetic acid and sodium perborate, respectively.

Keywords: *Hesperaloe funifera*, polynomial, bleaching, peroxide, peracetic, perborate

INTRODUCTION

In recent years, paper industry has been affected by environmental pressures on the development of new technologies that should protect the environment. Therefore, in view of the current legislation,[1] a pulp bleaching process using non-chlorine chemical agents, such as oxygen, hydrogen peroxide, ozone or enzymes, has been introduced in the bleaching sequences. TCF processes are characterized by: 1) complete removal of chlorine use, no effluents generated by the organochlorine components; 2) use of sequences with different stages and agents, for combining their effects on pulps and make better use of the agents; 3) removal of organochlorine compounds emissions into the atmosphere (such as dioxins and benzofurans, dangerous to both environment and humans); 4) higher recovery of black liquors.[2-4] Thus, the TCF bleaching stages are being studied on pulps of raw wood materials, such as *Eucalyptus globulus* and *Pinus radiate*, and also on non-wood ones, such as wheat straw, *Arundo donax*, EFB (Empty Fruit Bunches) and *Miscanthus x giganteus*.[5-10]

Currently, an increased use of hydrogen peroxide – as a total or partial substitute for chloride bleaching agents – for cellulosic pulp bleaching has been recorded. Its use as a bleaching agent can solve pollution problems related to industrial discharges. The reaction products are versatile and non-toxic, easy to manipulate and to apply; other properties include low volatility, portability and easy storage. The combination of temperature, pressure, pH or reaction time in different stages of the bleaching sequence is necessary for obtaining satisfactory brightness.[11,12]

Because of its high oxidation power and selectivity towards lignin, the peracetic acid is another bleaching agent often used in bleaching cellulosic pulps. Depending on the operational conditions, this acid can be used just like a bleaching agent or as a delignifying one. To modify as many chromophore groups as possible, bleaching with this acid under neutral conditions allows a minimized formation of small fragments and aromatic ring opening, which are the result of delignification. Other variables which need to be considered are temperature, consistency, time and chelating agents.[13,14]

The peroxy salts, because of their low cost and toxicity, have been used as bleaching agents in the paper industry. Perborates are peroxy salts obtained from borates and hydrogen peroxide, relatively soluble in water, releasing – when decomposed – hydrogen peroxide, sodium and borate hydroxide. The active bleaching agent is hydrogen peroxide, solubilized at the same time with the borosalt. The reaction conditions have to be selected within the range of optimal performance of the peroxide.[15-17]

An interesting raw non-wood material for obtaining bleached pulps is *Hesperaloe funifera*, which belongs to the Agavaceae family and comes from Mexico. Due to the unusual morphology of its fibers – high tensile index, stretch, burst index and tear index[18,19] – it presents favorable characteristics for producing pulps. Furthermore, it has low irrigation requirements, which makes it an optimal species for cultivation in areas with arid climates.[20] By controlling its flowering, an increase in the biomass production can be obtained, yielding about 20 tons of dry biomass per hectare per year, for a high planting density (27000 plants per hectare),[21] which recommends it for the production of paper pulp.[22]

In the present work, three experimental designs with hydrogen peroxide, peracetic acid and sodium perborate have been carried out under different operational conditions. The influence of the operational variables (temperature, time and hydrogen peroxide concentration in the first experimental design; temperature, time and concentration of peracetic acid – in the second experimental design; perborate concentration, time and concentration of peroxide – in the third experimental design) on the properties (yield, Kappa number, viscosity and brightness) of the bleached pulps was studied.

EXPERIMENTAL

Raw material

Hesperaloe funifera, a plant from the *Agavaceae* family, is up to 80 cm tall and 1.0-1.2 m wide, with long leaves – up to 5 cm wide and 2-3 cm thick. All species of its genus originate from Mexico and its neighbouring USA regions, where it is used mainly for ornamental purposes. *Hesperaloe* has very modest irrigation requirements, as it uses the acid metabolism of *Crassulaceans* (CAM) for photosynthesis. Its plants fix carbon dioxide and release water more intensely at night than during the day; also, because their coefficient of transpiration is lower at night, they use water highly efficiently. Based on these properties, *Hesperaloe* might be an effective cellulose raw material in arid zones, precluding the cultivation of other species,[22] or in areas with scarce water resources. The first crop takes 5 years to develop in full, the plant giving a new crop every three years afterwards. High-density plantations (27000 stem ha^{-1}) can yield 205 t of fresh biomass per hectare per crop, which amounts to approximately 20 tons of dry biomass per hectare, crop and year after the initial crop.[23] Such crop yields can be increased by careful control of plant flowering and use of higher planting densities.[22]

Following drying at room temperature, the raw material was cold ground in a Retsch SM 2000 mill, to homogenize the particle size. The ground product was sieved and the 0.25-0.40 mm fraction (sieves No. 60 and 40 in the Tyler series) was saved for analysis. In fact, particles larger than 0.40 mm are inefficiently attacked by chemical reagents, while the ones smaller than 0.25 mm can interfere with the filtering operations. The quantity of raw materials to be used is subsequently saved in plastic bags before cooking.

Pulping

The operational conditions (170 ºC, 40 min, 15% NaOH o.d., 1% AQ o.d. and a liquid/solid ratio of 8) were selected from previous works,[24] for obtaining cellulose pulps with a good Kappa number/viscosity ratio. The raw material was introduced in a 15 L batch reactor heated by an outer jacket containing electrical wires, with soda-anthraquinone as reagent, fitting the total volume at the selected liquid/solid ratio. The reactor contents were stirred by rotating the reaction vessel *via* a motor connected through a rotary axle to a control unit including instruments for measurement and control of pressure and temperature. Once the reaction temperature is reached (heating rate = 10 °C/min), it is maintained during the time set, after which the cooked material is washed with water at room temperature, to remove the residual cooking liquor, and fiberized in a disintegrator at 1200 rpm for 30 min, at room temperature, 10% consistency. Pulp was then beaten in a Sprout-Bauer refiner operating at 0.5% pulp consistency, on using a disk spacing of 0.1 mm, and the fiberized material was passed through a Sommerville screen model K134 to remove the uncooked particles, while water was eliminated through centrifugation.

Experimental design

The experimental factorial design applied consisted of a series of points (tests) around a central composition point (central test) and several additional points (additional tests), used to estimate the quadratic terms of a polynomial model. The design met the general requirement of estimating all parameters in the mathematical model with a relatively small number of tests.[25]

The experimental design is defined by 3 parameters: number of variables, k; constant p, which takes values of 0 for $k < 5$ and 1 for $k \geq 5$, respectively; number of central points, n_c. These parameters originate three sets of points:

- 2^{k-p} points constituting a factorial design;
- 2*k axials points;
- n_c central points.

The total number of points (experiments) shall be given by the following expression:

$$n = 2^{k-p} + 2 \cdot k + n_c$$

When parameter p = 1, a considerable reduction occurs in the number of points of the factorial design, without affecting the determination of the first- and second-order parameters. According to the relationship:

$$x_k = \Gamma_{j=1,k-1}\, x_i$$

the normalized values of variable k-th coincide with the product of the normalized values of the k-1 variables, for the points of the experimental design.[26]

The total number of tests required for the 3 independent variables studied was 15.

The values of the independent variables were normalized to -1, 0 or +1, with equation [1], for facilitating the direct comparison of coefficients and for evidencing the individual effects of the independent variables on each dependent variable:

$$X_n = 2\frac{X - \bar{X}}{X_{max} - X_{min}} \qquad \text{[Eq. 1]}$$

where X_n is the normalized value of the 3 independent variables.

The experimental data were fitted to the following second-order polynomial:

$$Y = a_0 + \sum_{i=1}^{n} a_i X_{ni} + \sum_{i=1}^{n} a_j X_{ni}^2 + \sum_{i=1,\, j=1}^{n} a_l X_{ni} X_{nj} \qquad i<j \qquad \text{[Eq. 2]}$$

where Y denotes a pulp characteristic or property (yield, Kappa number, viscosity and brightness), and coefficients a_0, a_i, a_j and a_l are unknown characteristic constants estimated from the experimental data.

Bleaching

The cellulose pulp obtained under the above-mentioned conditions was introduced in heat-proof polystyrene bags placed in a thermostated bath. Once the reaction was performed under certain operational conditions for each experimental design, the pulp was washed with distilled water until neutral pH, then dried to humidity and turned to a centrifuge.

Bleaching with hydrogen peroxide

An experimental design of 3 variables (temperature – 60, 70 and 80 ºC, time – 30, 105 and 180 min, and hydrogen peroxide concentrations – 1, 3 and 5% o.d.) was carried out at constant 10% consistency, for each experiment, for 100 g of dried material.[12,27,28]

Bleaching with peracetic acid

An experimental design of 3 variables (temperature – 55, 70 and 85 ºC, time – 30, 90 and 150 min, and peracetic acid concentrations – 0.5, 1.5 and 2.5% o.d.) was carried out at constant 10% consistency, for each experiment, for 100 g of dried material.[14,29,30]

Bleaching with sodium perborate

An experimental design of 3 variables (concentration of perborate – 1, 3 and 5% on raw material dry, time – 60, 120 and 180 min and hydrogen peroxide concentration – 0, 1 and 2% o.d.) was carried out at constant temperature and consistency (70 ºC and 15%, respectively) for each experiment, for 100 g of dried material.[16,31]

Characterization of bleached pulps

After bleaching, the pulps were characterized by determining viscosity, Kappa number and brightness, according to TAPPI 230 om-94, TAPPI 236 cm-85 and ISO 5267-1, respectively. Pulp yield was determined by weighing.

RESULTS AND DISCUSSION

Properties of bleached pulp

The initial values of brightness, Kappa number and viscosity of the cellulosic pulp of *Hesperaloe funifera* were of 31.2, 13.6 and 693 mL/g, respectively.

Tables 1-3 show the experimental values of the bleached pulp properties, which differed less than 5% from their mean values – according to triplicate measurements.

The observed yield loss in the 3 processes was not very high (3% on the average, at 8.4% in the worst case – corresponding to sodium perborate). The hydrogen peroxide caused the minimum loss of yield in pulp, the perborate reagent being more aggressive with the fibers (Fig. 1). The largest decrease in Kappa number was obtained when hydrogen peroxide attained a 10.1 average value, representing a 25.7% fall, compared to 20.6 and 18.4% – obtained for the acid and perborate, respectively (Fig. 2). A similar behavior occurred with brightness, whose largest increase was obtained in the process with peroxide, 41.3% on the average, compared with 37.3 and 36.8% for acid and perborate, respectively (Fig. 3). Viscosity degradation was higher in the process with hydrogen peroxide, even if, in all three cases, the fall was not very noticeable in the initial value of pulp (693 mL/g) (Fig. 4), which agrees with the above observations, so that the highest values of selectivity were recorded for the pulps bleached with hydrogen peroxide (Fig. 5).

Table 1
Results of hydrogen peroxide bleaching of soda-AQ pulp from *Hesperaloe funifera*

Experimental temperature, time, peroxide concentration	Yield, %	Kappa number	Viscosity, mL/g	Brightness, % ISO	Selectivity, VI/KA
HP 1 70 ºC, 105´, 3%	97.5	9.7	599	44.5	61.8
HP 2 80 ºC, 180´, 5%	96.6	8.5	490	47.8	57.9
HP 3 60 ºC, 180´, 5%	98.1	9.2	529	45.0	57.6
HP 4 80 ºC, 180´, 1%	97.8	10.9	560	37.8	51.3
HP 5 60 ºC, 180´, 1%	99.7	10.8	656	38.0	60.9
HP 6 80 ºC, 30´, 5%	98.9	10.3	630	41.1	61.0
HP 7 60 ºC, 30´, 5%	99.7	10.8	497	38.5	45.9
HP 8 80 ºC, 30´, 1%	98.5	11.7	534	36.1	45.5
HP 9 60 ºC, 30´, 1%	98.6	11.0	589	35.2	53.5
HP 10 70 ºC, 180´, 3%	97.6	9.1	545	44.7	60.0
HP 11 70 ºC, 30´, 3%	96.7	10.1	577	40.2	57.1
HP 12 70 ºC, 105´, 5%	97.7	9.4	571	44.3	60.7
HP 13 70 ºC, 105´, 1%	99.2	10.4	691	38.8	66.8
HP 14 80 ºC, 105´, 3%	98.4	9.8	661	45.4	67.5
HP 15 60 ºC, 105´, 3%	97.5	9.6	647	42.2	67.3

Table 2
Results of peracetic acid bleaching of soda-AQ pulp from *Hesperaloe funifera*

Experimental temperature, time, acetic concentration	Yield, %	Kappa number	Viscosity, mL/g	Brightness, % ISO	Selectivity, VI/KA
PA 1 70 ºC, 90´, 1.5%	97.9	10.6	606	39.7	57.0
PA 2 85 ºC, 150´, 2.5%	95.2	9.6	565	41.8	58.7
PA 3 55 ºC, 150´, 2.5%	95.1	10.5	618	37.4	58.7
PA 4 85 ºC, 150´, 0.5%	97.5	11.0	562	35.1	51.1
PA 5 55 ºC, 150´, 0.5%	97.6	11.3	614	34.2	54.4
PA 6 85 ºC, 30´, 2.5%	97.1	10.2	666	38.1	65.0
PA 7 55 ºC, 30´, 2.5%	95.7	11.4	631	36.6	55.3
PA 8 85 ºC, 30´, 0.5%	97.4	11.4	623	35.9	54.8
PA 9 55 ºC, 30´, 0.5%	98.0	11.2	638	34.2	57.0
PA 10 70 ºC, 150´, 1.5%	96.9	10.6	584	38.5	55.0
PA 11 70 ºC, 30´, 1.5%	97.0	11.4	640	36.6	56.3
PA 12 70 ºC, 90´, 2.5%	95.0	10.2	614	39.4	60.4
PA 13 70 ºC, 90´, 0.5%	99.4	10.5	630	36.8	60.0
PA 14 85 ºC, 90´, 1.5%	96.1	10.9	615	38.3	56.6
PA 15 55 ºC, 90´, 1.5%	96.8	11.9	626	36.9	52.7

Table 3
Results of sodium perborate bleaching of soda-AQ pulp from *Hesperaloe funifera*

Experimental perborate concentration, time, peroxide concentration	Yield, %	Kappa number	Viscosity, mL/g	Brightness, % ISO	Selectivity, VI/KA
SP 1 3%, 120´, 1%	97.9	11.1	623	38.2	56.2
SP 2 5%, 180´, 2%	91.6	11.2	588	40.1	52.4
SP 3 1%, 180´, 2%	95.0	10.9	585	38.2	53.5
SP 4 5%, 180´, 0%	95.5	10.2	564	39.6	55.4
SP 5 1%, 180´, 0%	96.5	12.3	690	34.7	56.0
SP 6 5%, 60´, 2%	95.5	11.8	605	38.6	51.1
SP 7 1%, 60´, 2%	95.0	12.6	623	34.4	49.6
SP 8 5%, 60´, 0%	96.2	11.9	651	35.0	54.8
SP 9 1%, 60´, 0%	96.2	10.7	615	33.9	57.2

SP 10 3%, 180´, 1%	96.8	9.6	555	38.1	57.6
SP 11 3%, 60´, 1%	97.8	12.4	593	35.6	48.0
SP 12 3%, 120´, 2%	98.1	10.5	616	38.2	58.9
SP 13 3%, 120´, 0%	96.8	9.9	591	37.1	66.3
SP 14 5%, 120´, 1%	95.7	9.4	606	38.2	64.7
SP 15 1%, 120´, 1%	96.4	11.3	599	35.0	48.1

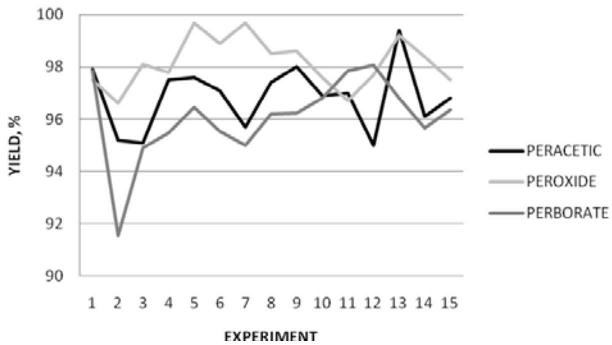

Figure 1: Yield values in the three bleaching processes

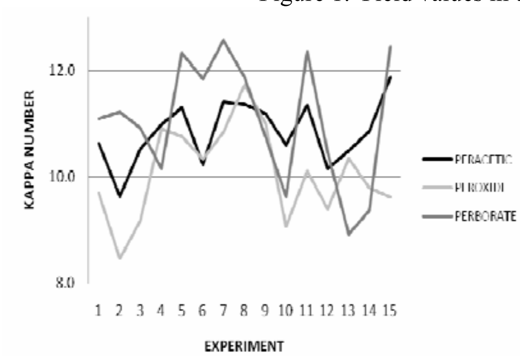

Figure 2: Kappa number values in the three bleaching processes

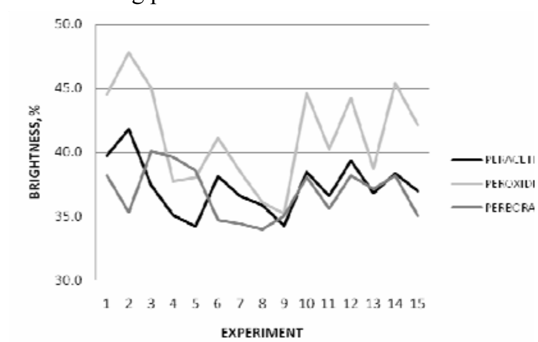

Figure 3 Brightness values in the three bleaching processes

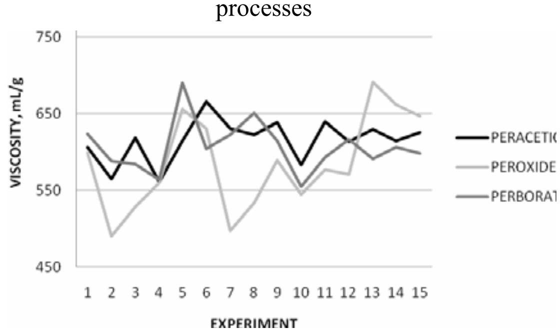

Figure 4: Viscosity values in the three bleaching processes

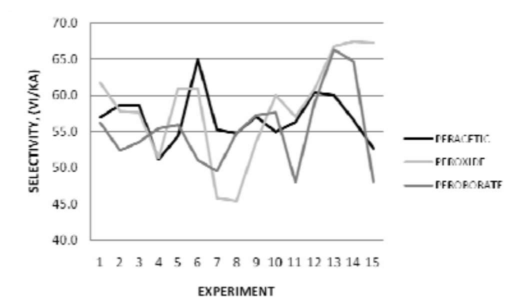

Figure 5: Selectivity values in the three bleaching processes

Experimental design

The experimental results were fitted to a polynomial model by multiple regressions, using the BMDP© software. The terms possessing a Snedecor *F*-value higher than 2.0 and a Student *t*-value higher than 1.5 were deemed statistically significant. Table 4 lists the coefficients of the different terms in the equations, as well as the highest *p* and lowest Student *t*-values for the terms.

The derived equations reproduced the experimental results with errors below 9, 4 and 8%, for all dependent variables (yield, Kappa number, viscosity and brightness) involved in the hydrogen peroxide, peracetic acid and sodium perborate bleaching processes, respectively.

The method of More and Toraldo,[32] an algorithm combining standard active set strategies with the gradient projection method, was applied for the solution of quadratic programming problems subjected to bounds in combination with non-linear programming, to identify the optimum value for each dependent variable (Table 5). This revealed that maximization of pulp yield and viscosity permits mild operating conditions, for avoiding an excessive dissolution of cellulose, hemicellulose and lignin, and for assuring a more effective preservation of fiber integrity, thereby producing smaller amounts of fines. Conversely, minimizing Kappa number and brightness obviously permits extreme operating conditions, for boosting the dissolution of both lignin and chromophores.

The polynomial equations obtained (Table 4) allowed to identify the specific independent variables, most strongly affecting the dependent variables.

Hydrogen peroxide bleaching shows that temperature is the most influential variable in the case of yield and viscosity (Fig. 6) while, for Kappa number and brightness, essential are the time and concentration of peroxide, respectively (Table 6).

Bleaching with peracetic acid shows that the most influential variable for Kappa number and brightness is the concentration of peracetic acid, while temperature has the highest impact on yield and time, as well as on viscosity. In bleaching with sodium perborate, the concentration of hydrogen peroxide is the most influential variable in the 4 dependent variables studied: yield, Kappa number, viscosity and brightness.

The values of the operational variables providing near-optimal pulp properties may be selected for saving chemicals, energy and immobilized capital, by using lower values of the operational variables. In hydrogen peroxide bleaching, it is possible to operate under medium values of temperature and time, at low peroxide concentration (70 ºC, 105 min and 1% o.d., respectively), good values of yield (9.5%), Kappa number (9.9), viscosity (585 mL/g) and brightness (44% ISO) being thus obtained. In bleaching with peracetic acid, operating under medium conditions of temperature and time, at a low concentration of peracetic acid (70 ºC, 90 min and 0.5% o.d., respectively), a pulp with good values of Kappa number (10.9), and viscosity (616 mL/g) is obtained, although the yield is slightly lower (96.4% and brightness – 37.9% ISO). Finally, bleaching with sodium perborate permits to obtain a pulp with values of yield (96%), Kappa number (10.8), viscosity (607 mL/g) and brightness (37.5% ISO) not far from the optimal ones, when operating under mild conditions of perborate concentration (3% o.d.) and time (120 min), and a low peroxide concentration (0%).

CONCLUSIONS

If considering its values of brightness, viscosity and Kappa number, the cellulosic pulp of *Hesperaloe funifera* obtained with soda-anthraquinone seems appropriate to be bleached under mild conditions, as shown in the present work.

Out of the 3 processes studied, the one using hydrogen peroxide is the best, showing lower yield losses, higher values of brightness and selectivity, and higher decrease in Kappa number, while viscosity suffers a higher loss compared with the other processes.

The polynomial model used allows obtaining of equations that relate the dependent variables with the independent ones, and reproduce the experimental results with errors below 9, 4 and 8% for bleaching with hydrogen peroxide, peracetic acid and sodium perborate, respectively. The application of the More and Toraldo method to the equations found shows that temperature is the most influential variable in the bleaching with hydrogen peroxide, while temperature and the concentration of peracetic acid are influencial in the bleaching with peracetic acid and, finally, the concentration of peroxide – in the bleaching with sodium perborate.

In the three bleaching pulp processes, bleached pulps with good values of yield, Kappa number, viscosity and brightness operating under medium and low conditions can be obtained, thus capital savings being possible when not operating under extreme conditions.

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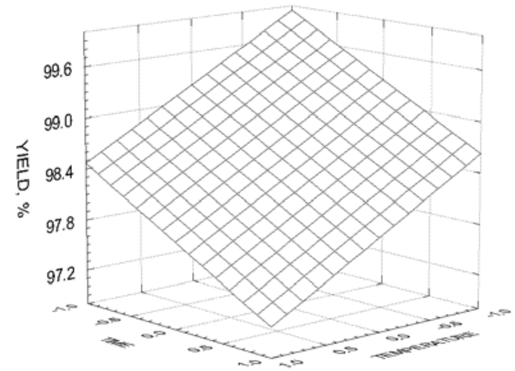

Figure 6: Variation of peroxide bleached pulp yield with temperature and processing time, at low hydrogen peroxide concentration

Table 4
Polynomial models for properties of pulps obtained by hydrogen peroxide, peracetic acid and sodium perborate bleaching of *Hesperaloe funífera*

		Values of constants in polynomial equations										Values of *p*, Student-*t* test, R^2		
Chemical reagents	Dependent variable	a_0	a_1	a_2	a_3	a_4	a_5	a_6	a_7	a_8	a_9	$<p$	$>t$	R^2
Hydrogen peroxide	Yield, %	98.16	-0.74	-0.66	-0.38	-	-	-	-	-	-	0.0253	2.63	0.83
	Kappa number	9.88	-0.59	-0.63	-0.51	-	-	-	0.44	-0.26	-	0.1545	1.55	0.87
	Viscosity, mL/g	585	-43.9	-39.3	-29.5	-	-	-	-	-	-	0.0085	3.14	0.63
	Brightness, %	44.03	0.93	2.21	3.09	-	0.59	1.09	-	-1.58	-2.52	0.1670	1.49	0.88
Peracetic acid	Yield, %	96.85	-0.94	-0.63	-0.59	-	-	-	-	-	-	0.0193	2.74	0.76
	Kappa number	10.87	-0.32	-0.25	-0.34	-	-0.24	-0.15	-0.50	-	-0.54	0.0974	1.91	0.93
	Viscosity, mL/g	616	-23.2	-16.2	-9.9	-	-	7.25	-	-	-	0.1181	1.71	0.87
	Brightness, %	38.61	0.98	0.55	1.71	-	0.42	0.67	-0.93	-1.04	-	0.1995	1.42	0.92
Sodium perborate	Yield, %	95.98	-1.02	-0.99	-0.74	-	-	-0.73	-	-	-	0.0253	2.63	0.83
	Kappa number	10.78	-0.77	-0.55	-0.51	-	-0.25	-	-	-	0.41	0.1545	1.55	0.87
	Viscosity, mL/g	607	-22.70	-21.50	-	-	-	-	-	-	-	0.0085	3.14	0.63
	Brightness, %	37.44	1.53	1.32	0.92	-	-	-	-0.67	-	-	0.1670	1.49	0.88

Table 5
Values of operational variables required to ensure optimal properties of pulps obtained in the three bleaching processes

Reagent	Dependent variable	Optimum value of dependent variable	Values of operational variables required to obtain optimum values of dependent variables		
			X_T	X_t	X_P
Hydrogen Peroxide	Yield, %	99.9	-1	-1	-1
	Kappa number	8.3	1	1	1
	Viscosity, mL/g	697	-1	-1	-1
	Brightness, %	47.8	1	1	1
			X_T	X_t	X_A
Peracetic Acid	Yield, %	99.0	-1	-1	-1
	Kappa number	9.5	1	1	1
	Viscosity, mL/g	672	-1	-1	-1
	Brightness, %	41.0	1	1	1
			X_{Pb}	X_t	X_P
Sodium Perborate	Yield, %	98.0	-1	-1	-1
	Kappa number	9.1	1	1	1
	Viscosity, mL/g	651	-1	-1	
	Brightness, %	40.5	1	1	1

Table 6
Maximum changes in dependent variables with changes in one operational variable on constancy of the others in hydrogen peroxide, peracetic acid and sodium perborate bleaching

Equation	Variation with the operational variable								
	Hydrogen peroxide			Peracetic acid			Sodium perborate		
	Temperature, ºC	Time, min	Hydrogen peroxide, %	Temperature, ºC	Time, min	Peracetic acid, %	Hydrogen peroxide, %	Time, min	Sodium perborate, %
Yield, %	1.48	1.32	0.76	1.89	1.27	1.19	2.07	0.53	0.029
Kappa number	14.79	15.76	12.86	11.84	8.44	15.89	22.39	12.07	16.68
Viscosity, mL/g	12.58	11.26	8.45	6.90	6.97	5.10	6.97	6.6	-
Brightness, %	6.34	13.78	19.93	6.86	5.98	13.71	7.54	6.51	4.53

REFERENCES

[1] B. Pratima, in "Environmentally Benign Approaches for Pulp Bleaching", Elsevier, 2005, p. 177.

[2] L. Jiménez, "Pastas celulósicas de materias primas alternativas a las convencionales", Ed. Gráficas Sol, S. A. Spain, 2005.

[3] M. Sarwar Jahan, D. A. Nasima Chowdhury and M. Khalidul Islam, *Ind. Crop. Prod*., **26**, 324 (2007).

[4] P. Khristova, J. Tomkinson, I. Valchev, I. Dimitrov and G. Lloyd Jones, *Bioresource Technol*., **85**, 79 (2002).

[5] C. Freire, A. Silvestre, C. Neto and D. Evtuguin, *Bioresource Technol*., **97**, 420 (2006).

[6] R. Vicufia, E. Oyarztin and M. Osses, *J. Biotechnol*., **40**, 163 (1995).

[7] X. Sun, R. C. Sun, J. Tomkinson and M. S. Baird, *Polym. Degrad. Stabil*., **83**, 47 (2004).

[8] A. A. Shatalov and H. Pereira, *Bioresource Technol*., **99**, 472 (2008).

[9] L. Jiménez, L. Serrano, A. Rodríguez and A. Ferrer, *Bioresource Technol*., **100**, 1478 (2009).

[10] J. J. Villaverde, P. Ligero and A. de Vega, *Bioresource Technol*., **100**, 4731 (2009).

[11] L. Jiménez, E. Navarro, J. L. Ferrer, F. López and J. Ariza, *Process Biochem*., **35**, 149 (1999).

[12] F. López, M. J. Díaz, M. E. Eugenio, J. Ariza, A. Rodríguez and L. Jiménez, *Bioresource Technol*., **87**, 255 (2003).

[13] L. Jiménez, E. Ramos, M. J. de la Torre, I. Pérez and J. L. Ferrer, *Bioresource Technol*., **99**, 1474 (2008).

[14] Z. Yuan, Y. Ni and A. Van Heiningen, *Appita J*., **51**, 377 (1998).

[15] A. McKillop and W. R. Sanderson, *Tetrahedrom*, **51**, 6145 (1995).

[16] S. Varennes, C. Daneault and M. Perenteau, *Tappi J*., **79**, 245 (1996).

[17] C. Leduc, C. Sain, C. Daneault, R. Lanouette and J. Valade, *Tappi J*., **83**, 77 (2000).

[18] D. Guillot Ortiz and P. Van der Meer, *Botánica Complutensis*, **30**, 137 (2006).

[19] S. P. McLaughlin, in "Progress in new crops", ASHS Press, edited by J. Janick, Arlington, VA, 1996, pp. 395-402.

[20] J. Nelson and S. P. McLaughlin, *Ind. Crop. Prod*., **17**, 93 (2007).

[21] S. P. McLaughlin, *J. Arid Environ*., **55**, 143 (2003).

[22] S. P. McLaughlin, *Econ. Bot*., **54**, 192 (2000).

[23] A. Wong and S. P. McLaughlin, *Procs. Tappi Pulping Conference*, Boston, MA, 2000.

[24] R. Sánchez, A. Rodríguez, A. Requejo and A. Ferrer, *Bioresource Technol*., **101**, 7032 (2010).

[24] D. C. Montgomery, in "Design and analysis of experiments", Editorial Iberoamericana, Mexico, 1991, p. 303.

[25] S. Aknazarova and V. Kafarov, in "Experiment optimization in chemistry and chemical engineering", Mir Publisher, Moscow, 1982, pp. 3, 145-158.

[26] A. A. Shatalov and H. Pereira, *Bioresource Technol*., **96**, 865 (2005).

[27] J. Gierer, K. Jansbo and T. Reitberger, *J. Wood Chem. Technol*., **13**, 561 (1993).

[28] D. P. Chattopadhyay and J. K. Sharma, *Ind. J. Fibre Text. Res*., **24**, 120 (1999).

[29] J. Jäkärä, A. Parén and A. Peca, *Appita J*., **99**, 463 (1999).

[30] C. García, P. Poveda and J. C. Villar, *Investigación y Técnia del Papel*, **143**, 55 (2000).

[31] A. More and A. Toraldo, *Numer. Math*., **55**, 377 (1989).