CELLULOSE CHEMISTRY AND TECHNOLOGY

OPTIMIZATION OF TCF SINGLE-STAGE BLEACHING OF ABACA SODA PULP WITH A MIXTURE OF PERACETIC ACID AND SODIUM PERBORATE

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The influence of operating variables [*viz*: temperature 55-85°C, process time 30-120 min, pH 9-11,peraceticacid concentration 0.5-3.5% oven dried pulp (o.d.p.)., and sodium perborate concentration 1-5% o.d.p.] on the bleached pulp characteristics [*viz*: viscosity (VI), brightness (BR), kappa number (KN)], and resulting paper sheets properties [viz: breaking length (BL), stretch (ST), tear (TI), and burst index (BI)] was studied. The factorial experimental design of central composition was used to derive polynomial equations that reproduce experimental results with errors less than 5%. The most appropriate bleaching conditions were determined as: temperature 77°C; time 99min; pH 10.5; sodium perborate concentration 1% o.d.p., peracetic acid concentration 2.5% o.d.p. This set of operational variables provides pulp with high brightness (80.6%), good strength (breaking length: 4139 m, tear index: 17.64 mNm^2/g, stretch index: 4.82%, burst index: 3.36 kN/g) and pulp-related (viscosity: 1174 ml/g, kappa number6.84) properties, combined with cost and environmental benefits.

Keywords:TCF bleaching; peracetic acid; sodium perborate; abaca; non-wood pulp

INTRODUCTION

Global paper and paperboard production grew from 300 million to 401 million tons *per annum*,[1] between 1997 and 2012. Consequently, the constantly rising demand for the raw material of wood has led to its progressive scarcity and resulted in the gradual deforestation of some areas of the earth.[2] Facing the current situation, a variety of strategies have been suggested, such as changes in consumption patterns, or improving recovery rates.[3] Nevertheless, one of the most remarkable actions to confront the constantly increasing pulp consumption and conserve wood resources seems to be seeking an alternative source of cellulose fibers, capable of meeting market requirements. Given that only about 10% of today's pulp production is manufactured from alternative raw material, mostly in developing countries,[1] there is a lot of scope for improving and widening its utilization, especially taking into account that non-wood fibers are technically and chemically feasibleto replaceor supplement thewood supplyfor the pulp and paper production.[2,4,5,6,7]

Native to Philippines, abaca, also called Manila Hemp (*Musa textillisnee*), is from this standpoint an interestingnon-wooden plant of the *Musacea* family that provides high-quality fibers,[8]prized for its great mechanical strength, buoyancy, resistance to saltwater damage, and long fiber length – up to 3mm;suitable for manufacturing fishing nets and wrappings for electrical conductors, as well as specialized paper products, such as currency, cigarette filters, stencil papers, baby napkins, toilet paper, machine filters, hospital textiles (aprons, hats, gloves), tea bags, vacuum bags, etc., and more recently, used to produce methylcellulose oras a substitute of glass fiber in multiple automotive parts.[9,10]

In the recent past, the appearance of new environmental regulations that have placed restrictions on emission levels from cellulose industry, coupled with rising environmental awareness in wider society, havepromoted changes in the pulp bleaching techniques, which is precisely one of the most polluting sectors of the paper manufacturing industry, especially if elemental chlorine is used, thus leading to the introduction of Elemental Chlorine Free (ECF), and more recently Totally Chlorine Free (TCF) pulp bleaching technologies.[11,12,13] TCF bleaching employs oxidative chemicals (such as oxygen, hydrogen peroxide, ozone, sodium perborate,

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peroxyacids), and more recently biotechnological applications,[4,14,15] permitting the recovery of a larger part of dissolved organic material from bleaching, reducing the effluent load,[16] and enabling total closure of the recovery cycle.[17] Nevertheless, the TCF process carries a number of disadvantages in comparison with the conventional chlorine-based or ECF bleaching,[17,18] such as lower yield, cost-efficiency, and brightness, combined with a higher rate of pulp yellowing, among others, thus requiring the application of multi-sequential bleaching, longer time of retention, or alternatively, the use of chemically stronger bleaching stages, which may affect the fiber strength, and simultaneously, raise the chemicals load in the process effluents. Consequently, efforts are being made to improve the TCF bleaching selectivity, especially with respect to non-wooden fibers. For these reasons, TCF bleaching has been recently studied in terms of both wood and non-wood raw materials.[4,5,7,19,20] From this stand point, an interesting alternative to the conventional TCF peroxide-based bleaching seems to be the use of a mixture of an activated derivative of hydrogen peroxide, such as peracetic acid (PA), and peroxide precursors, such as sodium perborate (PB).

In the literature, various scientific works cover the application of peracteic acid during both wood and non-wood pulp bleaching,[5,16,21,22,23,24] showing its superior bleaching capacity and selectivity, while comparing to hydrogen peroxide. Nevertheless, its use in non-wooden fiber bleaching still lacks sufficient laboratory and industrial research.

Peracetic acid (PA) is the mono-acetyl derivative of hydrogen peroxide that can be prepared by the direct acid-catalysed reaction of hydrogen peroxide and acetic acid. What makes this oxidant especially attractive for the pulp and paper industry is its versatile nature; depending on the process conditions, it acts as bleaching or delignifying agent.[25] The oxidizing power of peracids is similar to that of chlorine dioxide and chlorine, with the obvious advantage of being chlorine-free.[17] In acidic media, PA reacts with lignin through the reaction of substitution/electrophilic addition, whereas in basic environment, the dominant form is the peroxyacetate ion with a strong nucleophilic character.[22,24]According to Bailey and Dence,[21]at pH from 7 to 9 the reduction in kappa number obtained with peracetic acid was essentially similar to that of an equimolar quantity of chlorine. Jablonsky *et al.*,[26] and more recently Shen *et al.*[16] reported that peroxyacetic acid improves the development of the pulp's degree of polymerization. However, for a charge above 1.5% o.d.p., a brightness ceiling was observed.[16] On the other hand, Jiménez *et al.*[5] point that a 4.5% PA charge, reduced temperature (55ºC), and long retention time (150 min) are the most favorable bleaching conditions.

Sodium perborate, in aqueous solution, undergoes a reaction of hydrolysis that results in hydrogen peroxide generation, which is the former bleaching agent, thus the process condition should be selected within the optimal range of peroxide performance.[7] Nevertheless, sodium perborate provides better stability and more convenient handling than hydrogen peroxide, which makes it extensively used as a component of detergents or disinfectants.[27] The action mechanism of perborate indicates that each mole of sodium perborate liberates two moles of hydrogen when dissolved in water.[28]

Only a few scientific references seem to exist in relation to TCF bleaching of abaca "soda" pulp.[5,29] Simultaneously, no mathematical models have been used in order to predict the most favorablebleaching process conditions conducted with the mixture of peracetic acid and sodium perborate.

For all the above mentioned reasons, the overall objective of thiswork was tostudy thefeasibility and synergy of the use of one-stage TCF bleaching with mixtures of peracetic acid and sodium perborate of abaca "soda" pulp. The factorial experimental design of central composition was applied in order to assess the influence of the operating variables on the pulp and resulting paper sheets quality.

EXPERIMENTAL

Raw material

Abaca fibers used in bleaching experiments was characterized by the following composition: 2.45% ethanol–benzene extractives, 1.35% ash, 67.85% α-cellulose, 0.37% lignin and 87.91% holocellulose, determined according to international standards TAPPI T-204, T-211, T-203 OS-61, T-222, and Wise *et al.* method.[30]

Pulping

The raw material pulped in a15 L cylindrical batch reactor wrapped in a heating wire jacket was used for this purpose. The reactor was connected, via a rotary axle, to the control unit, which included an engine actuating the reactor stirring (by turnover), temperature and pressure measurement and control instruments. The reactor was loaded with abaca at a liquid/solid ratio of 6:1, the material was cooked with 10% soda at 160ºC for 30 min.[8] After cooking, the reactor contents were filtered and the solid fraction washed with tap water. The fibers and the uncooked material were separated by screening through a sieve of 1 mm mesh to determine pulp yield (by weight) at the level of 77.6%, which corresponds to semi-chemical pulp. The pulp obtained was characterized by: brightness (55.7%); kappa number (17.90); viscosity (1624 mL/g); breaking length (4216 m); and burst index (5.45 kN/g).

Bleaching

The range of independent variables examined were based on the previous experience and results of TCF bleaching of non-wood pulpspreviously reported in the scientific literature.[5,31,32]

The power of each bleaching solution: peracetic acid, and sodium perborate, was separately determined by standard *iodine-thiosulfate* titration. The pulp was placed in heat-proof double plastic bags and immersed in a thermostatic bath pre-heated to the desired temperature, which was varied according to the experimental design applied (55, 70, 85°C), similarly as concentrations of peracetic acid (0.5, 2.0, 3.5% o.d.p.), sodium perborate (1, 3.5% o.d.p.), pH (9, 10, 11) and bleaching times (30, 75, 120 min). The following parameters were constant for all experiments: 10% consistency adjusted with distilled water, magnesium sulphate (0.2%o.d.p.), and diethylenetriaminepentaacetic acid(0.5% o.d.p.).

The pH adjustment of the bleaching liquor was made with 1.8% NaOH solution. To provide homogenous reaction between pulp and bleaching liquor, manual blending was conducted inside the thermostatic bath every 30 minutes. After process ending, the bleached pulp was thoroughly washed with tap water and left toair dry before proceeding with further characterization.

Characterization of bleached pulp and paper sheets

Bleached pulp samples were obtained in accordance with TAPPI T 257 Test Method, andtheirkappa number and intrinsic viscositywere determined, following TAPPI um 246, and UNE 57039-1standards, respectively.

Paper sheets were produced by using an EJO-F-39.71 sheet former,according to UNE-EN ISO 5269-1, and after appropriate preparation, were characterized following the respective international standards in terms of brightness (UNE57062), tear index (UNE-EN 21974), and burstindex (UNE-EN 2758), breaking length, and stretch index (UNE-EN 1924-2).

Experimental design

The factorial experimental design of central composition was used in order to analyze the influence of fiveoperating variables used in the single-stage TCF bleaching of abaca "soda" pulp [*viz*: temperature (T), time (t), pH (pH), sodium perborate (PB) and peracetic acid (PA) concentrations], on the properties of bleached pulp [*viz*: viscosity (VI), brightness (BR), kappa number (KN)], and of the resulting paper sheets[(*viz*: breaking length (BL), stretch (ST), tear (TI), and burst index (BI)].

The total number of tests required by the experimental design for 5 independent variables analyzed was found to be 27. The experimental design used accommodated 26 testing points placed on the cube vertices and side centers around 1 central composition point (central test that represents medium values of five independent variables) to assess the quadratic terms of a polynomial model and meeting the general requirement concerning the estimation of every parameter in the mathematical model in a relatively small index of tests.[33]

In order to facilitate direct comparison of the coefficients and visualization of the effects of the individual independent variables on the response variable considered,[8] the independent variables were normalized between -1, 0, and 1, as indicated in Table 1, using equation (1):

$$X_n = 2(X-\overline{X})/(X_{max} - X_{min}) \quad (1)$$

where: X_n is the normalized value of temperature (T), time (t), pH (pH), peracetic acid (PA), and sodium perborate (PB) concentrations. X is the absolute experimental value of the variable concerned; $\overline{X}$ is the mean of the extreme values of X; and X_{max} and X_{min} are its maximum and minimum values, respectively.

Table 1

Process conditions used in the experimental design of abaca PA/PB single-stage bleaching together with their normalized equivalents

Independent variable	Factors	Normalized values		
		-1	0	1
Temperature (°C)	X_T	55	70	85
Time (min)	X_t	30	75	120
pH	X_{pH}	9	10	11
PA (% o.d.p.)	X_{PA}	0.5	2	3.5
PB (% o.d.p.)	X_{PB}	1	3	5

The experimental results obtained were adjusted to the second order polynomial equation (2), which relates each operational variable, their square and mutual interaction, with the experimental data obtained for the response (dependent) variable analyzed.

$$Y= a + bX_T+cX_t +dX_{pH} +eX_{PA} +fX_{PB}+ gX^2_T+ hX^2_t+ iX^2_{pH}+ jX^2_{PA} +kX^2_{PB} +lX_TX_t+ mX_TX_{pH}+ nX_TX_{PA}+oX_TX_{PB} + pX_tX_{pH} +qX_tX_{PA} + rX_tX_{PB} + sX_{pH}X_{PA} + uX_{pH}X_{PB} + vX_{PA}X_{PB} \qquad (2)$$

where *Y* denotes the dependent variables [*viz*: kappa number (KN), viscosity (VI), brightness (BR),breaking length (BL), burst index (BI), stretch index (ST), and tear index (TI)], X_T, X_t, X_{pH}, $X_{PA}$and $X_{PB}$are the normalized values of temperature, time, pH, peracetic acid, and sodium perborate concentrations, respectively, simultaneously, letters from *a* to *v*denote constant parameters.

The Sigma Plot v.11 software was used to examine multiple non-linear regressions involving all the terms fromequation (2), eliminating by the use of the stepwise method those with Snedecor's F value smaller than 2 and a Student-t value smaller than 1.5. The confidence interval for coefficient sand model constant parameters was set at 95%; zero was excluded.

RESULTS AND DISCUSSION

Table 2 containsthe experimental results that characterize the bleached pulp and paper sheets obtained from 27 tests conducted together with their respective coded independent variables.

The mathematical equations able to relate independent variables with the resulted pulp and paper sheets properties, together with their R^2, adjusted R and the smallest Sneadecor's F values are set in Table 3. The values of the dependent variables estimated through the aforementioned equations, when contrasting with the experimental results from Table 2, reproduce the latter with errors less than1% for viscosity and breaking length; 2%for brightness and stretch index; 4% for tear index; and 5% for burst index and kappa number.

Using non-linear programming, as implemented in the More and Toraldo method,[34] allows identifying the values of operational parameters, which reproduce the optimum results of the dependent variables that characterize bleached pulp and paper sheets, as shown in Table 4. As can be seen from this table, no specific set of bleaching conditions leads to the optimal values of all dependent variables studied, therefore different process variables should be considered to fulfill particular final product requirements. Notwithstanding these differences, it is still possible to look for some group of similarities, i.e. achieving pulp of both the highest possible brightness (84.65%) and the lowest kappa number(5.56) entitles the use of the maximum values of all independent variables (normalized 1), except for sodium perborate concentration that should remain low (-1) in order to maximize pulp brightness.

Table 2
Values of normalized variables of tests conducted together with corresponding experimental results that characterize bleached pulp and paper sheets

Test	X_T, X_t, X_{pH}, X_{PB}, X_{PA}	VI (mL/g)	KN	VK	BR (%)	*TI* (mNm^2/g)	*ST* (%)	*BL* (m)	*BI* (kN/g)
1	1,1,1,1,1	355	5.70	62	84.50	13.74	4.29	4048	3.03
2	1,1,1,-1,-1	1400	6.92	202	77.03	16.88	5.93	4678	3.21
3	1,1,-1,1,-1	1337	7.11	188	78.66	18.78	3.17	3170	3.97
4	1,1,-1,-1,1	1237	7.33	169	82.48	17.12	2.96	2394	3.78
5	1,-1,1,1,-1	1345	8.05	167	75.55	16.61	3.99	3571	3.62
6	1,-1,1,-1,1	1221	6.70	182	81.03	18.33	3.04	2548	3.76
7	1,-1,-1,1,1	1108	7.87	141	77.87	18.17	4.79	3287	3.76
8	1,-1,-1,-1,-1	1457	8.30	176	72.00	18.64	3.40	2819	3.88
9	-1,1,1,1,-1	1344	9.09	148	77.13	16.52	3.90	3230	3.32
10	-1,1,1,-1,1	946	6.62	143	81.90	16.62	3.81	3170	3.53
11	-1,1,-1,1,1	1329	7.92	168	78.44	19.08	2.72	2332	3.79
12	-1,1,-1,-1,-1	1405	7.85	179	71.70	18.88	3.18	2532	3.73
13	-1,-1,1,1,1	1181	7.49	158	77.40	17.87	2.48	2238	4.11
14	-1,-1,1,-1,-1	1312	7.72	170	71.60	19.11	5.59	4123	3.45
15	-1,-1,-1,1,-1	1481	8.17	181	71.08	16.78	4.67	3720	3.67

16	-1,-1,-1,-1,1	1386	7.80	178	75.88	16.10	4.91	3308	3.50
17	1,0,0,0,0	1066	6.85	156	80.37	17.23	4.38	4017	3.64
18	-1,0,0,0,0	1207	7.33	165	76.30	17.87	4.54	3899	3.71
19	0,1,0,0,0	1209	7.40	163	78.08	17.96	4.60	4062	3.45
20	0,-1,0,0,0	1346	7.70	175	75.82	18.02	4.83	4029	3.50
21	0,0,1,0,0	924	6.54	141	81.59	16.60	4.95	3985	3.37
22	0,0,-1,0,0	1143	8.20	139	77.15	17.60	4.68	3545	3.45
23	0,0,0,1,0	1127	7.15	158	78.20	18.06	4.56	4105	3.33
24	0,0,0,-1,0	1253	7.45	168	76.08	18.86	4.86	4042	3.42
25	0,0,0,0,1	670	7.25	92	78.70	19.13	4.53	3606	3.61
26	0,0,0,0,-1	977	7.74	126	75.74	19.54	5.29	4249	3.49
27	0,0,0,0,0	1061	7.64	139	78.38	18.30	4.96	4141	3.48

X_T, X_t, X_{pH}, X_{PB}, X_{PA} correspond to normalized values of temperature, time, pH, sodium perborate concentration, and peracetic acid concentration, respectively; VI: intrinistic viscosity, KN: kappa number; VK: relation viscosity/kappa number;BR: brightness; TI: tear index; ST: stretch index; BL: breaking length; BI: burst index

Table 3
Equations that relate independent variables with pulp and paper sheet properties studied, together with their R^2, adjusted R, and Snedecor's F distribution values

		R^2	$R_{adj.}$	F^1
VI=	$1056-59X_T-71X_t-103X_{pH}-56X_{PB}-146X_{PA}+81X_T^2+222X_t^2-22X_{pH}^2+135X_{PB}^2-232X_{PA}^2-29X_TX_t-91X_TX_{PB}-57X_TX_{PA}-56X_tX_{pH}-23X_tX_{PB}-58X_tX_{PA}-27X_{pH}X_{PB}-67X_{pH}X_{PA}-47X_{PB}X_{PA}$	0.99	0.99	726.24
KN=	$7.4800-0.29X_T-0.21X_t-0.32X_{pH}-0.35X_{PA}-0.26X_TX_t-0.15X_TX_{pH}-0.20X_TX_{PB}+0.16X_{pH}X_{PB}-0.30X_{pH}X_{PA}$	0.87	0.79	12.06
BR=	$78.06+1.56X_T+1.76X_t+1.25X_{pH}+0.51X_{PB}+2.65X_{PA}-0.94X_t^2-0.82X_{PB}X_{PA}$	0.94	0.92	43.13
TI=	$18.250.23_t-0.49X_{pH}-0.27X_{PB}-0.31X_{PA}-0.71X_T^2-1.16X_{pH}^2+1.07X_{PA}^2-0.40X_TX_t-0.40X_TX_{pH}-0.20X_TX_{PB}-0.77X_tX_{pH}-0.24_tX_{PA}-0.52_{pH}X_{PB}$	0.92	0.84	11.42
ST=	$4.93-0.17X_t+0.19X_{pH}-0.17X_{PB}-0.31X_{PA}-0.47X_T^2-0.21X_t^2-0.11X_{pH}^2-0.22X_{PB}^2+0.32X_TX_{ti}+0.16X_TX_{pH}+0.29X_TX_{PB}+0.13X_TX_{PA}+0.54X_{ti}X_{pH}-0.0500X_{ti}X_{PB}-0.29X_{pH}X_{PB}-0.42X_{pH}X_{PA}+0.12X_{PB}X_{PA}$	0.99	0.99	227.89
BL=	$4143+110X_T+249X_{pH}-287X_{PA}-185X_T^2-97X_t^2-378X_{pH}^2-69X_{PB}^2-215X_{PA}^2+268X_TX_t+144X_TX_{pH}+203X_TX_{PB}+37X_TX_{PA}+335X_tX_{pH}+74X_tX_{PA}-181X_{pH}X_{PB}-167X_{pH}X_{PA}+59X_{PB}X_{PA}$	0.99	0.99	473.29
BI=	$3.46-0.08X_t-0.08X_t-0.12X_{pH}+0.18X_T^2-0.09X_TX_{pH}-0.06X_TX_{PB}-0.07X_TX_{PA}-0.14X_tX_{pH}+0.08X_{pH}X_{PA}$	0.87	0.82	15.21

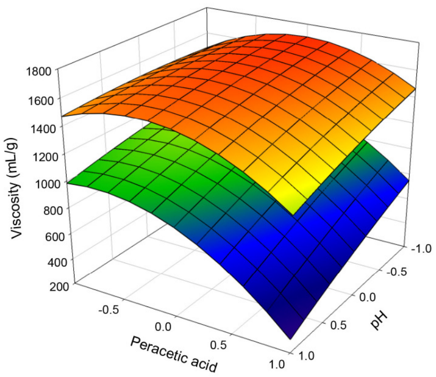
[1] Snedecor's F distribution; VI: intrinsic viscosity; KN: kappa number; VK: relation kappa number/viscosity;BR: brightness; TI: tear index; ST: stretch index; BL: breaking length; BI: burst index

The variability in the values of the analyzed dependent variables as a function of the independent variables can be obtained making use of previously given equations, by means of gradual change of one independent variable, whereas holding the others in their optimum values. Table 4 shows the maximum percentage deviation of the dependent variable considered in regard to its optimum. In this way, it is possible to determine the process parameters of greater or lesser influence on the value of each response variable. Simultaneously, the level of possible interaction between the independent variables considered could also be evaluated.

Pulp properties

Plotting previously established polynomial equations as a function of two interacting independent variables, while keeping the others in their respective optimums from Table 4, allows visualizing the magnitude of the resulting changes in the value of the analyzed dependent variable. Consequently, Figures 1 and 2 show the variation in viscosity (from300 to 1704mL/g), as a function of peracetic acid concentration and pH of bleaching liquor (Figure 1); and process temperature and peracetic acid concentration (Figure 2) to obtain the maximum value (upper plot) contrasted with the process conditions resulted in minimum viscosity (bottom plot).

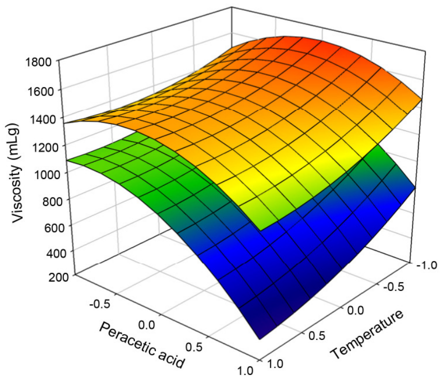
Max: T= -1; t = -1; PB=1



Min: T = 1; t = 0.53; PB = 0.87

Figure 1: Variation of viscosity as a function of pH (pH) and peracetic acid concentration (PA) on constancy of temperature (T), process time (t) and sodium perborate concentration (PB) to reach the minimum (bottom plot) and maximum (upper plot) value

Max: t = -1; pH = -1; PB = 1



Min: t = 0.53; pH = 1; PB = 0.87

Figure 2: Variation of viscosity as a function of temperature (T) and peracetic acid concentration (PA) on constancy of process time (t), pH (pH), and sodium perborate concentration (PB) to reach the minimum (bottom plot) and maximum (upper plot) value

Table 4

Optimal values of dependent variables

Dependent variable	Min. and max. value of analyzed variable	Normalized value of process variables to obtain min. or max. value* of dependent variable**				
		T	t	pH	PB	PA
KN*	Max:8.66	-1	1	1	1	-1
	Min: 5.56	1 *(32.37%)*	1 *(16.91%)*	1 *(15.03%)*	1 *(11.99%)*	1 *(17.67%)*
BR (%)	Max: 84.65	1 *(3.69%)*	0.93 *(4.16%)*	1 *(2.95%)*	-1 *(0.73%)*	1 *(8.20%)*
	Min: 68.57	-1	-1	-1	-1	-1
VI (mL/g)	Max: 1704	-1 *(14.38%)*	-1 *(13.47%)*	-1 *(15.04%)*	1 *(11.99%)*	-0.02 *(17.67%)*
	Min: 300	1	0.53	1	0.87	1
TI (mNm^2/g)	Max: 20.11	0.34 *(6.40%)*	-1 *(3.42%)*	0.28 *(5.72%)*	-1 *(4.87%)*	-1 *(7.00%)*
	Min: 15.08	-1	-1	-1	-1	0
ST (%)	Max: 6.31	0.08 *(8.43%)*	1 *(14.12%)*	1 *(28.92%)*	-1 *(17.64%)*	-1 *(26.60%)*
	Min: 2.46	-1	1	1	1	1
BL (m)	Max: 4721	1 *(18.93%)*	1 *(22.69%)*	1 *(23.93%)*	-0.19 *(2.07%)*	-0.82 *(18.00%)*
	Min: 2230	-1	-1	1	1	1
BI (kN/g)	Max: 4.12	1 *(11.39%)*	1 *(3.11%)*	-1 *(14.05%)*	-1 *(2.84%)*	-1 *(7.17%)*
	Min: 3.04	-0.2	1	1	-1	-1

*Kappa number minimum value is referenced as optimum, otherwise maximum value is considered for the rest of dependent variables; **in brackets: % deviation from optimum when changing one of the process variables on the constancy of the others;

T: temperature; t: time; pH; PB: sodium perborate concentration; PA: peracetic acid concentration;VI: viscosity, KN: kappa number; BR: brightness; TI: tear index; ST: stretch index; BL: breaking length; BI: burst index

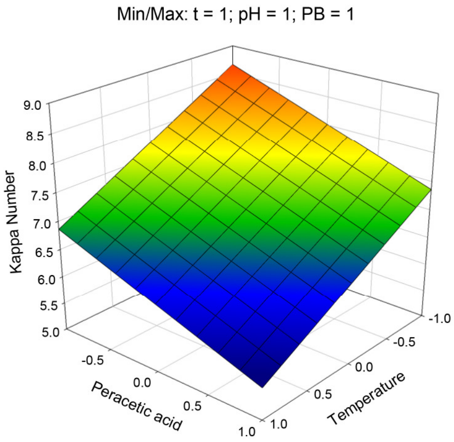


Figure 3: Variation of kappa numberas a function of temperature (T) and peracetic acid concentration (PA) on constancy of process time (t), pH (pH), and sodium perborate concentration (PB) to reach the minimum and maximum values

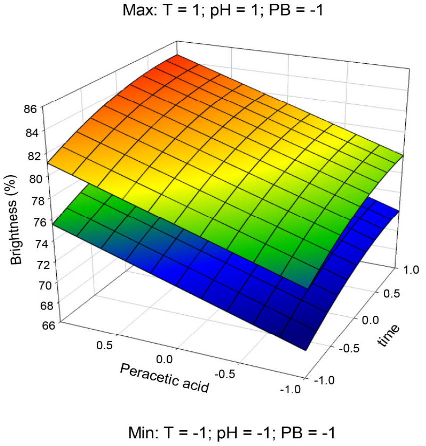


Figure 4: Variation of brightness as a function of time (t) and peracetic acid concentration (PA) on constancy of process temperature (T), pH (pH), and sodium perborate concentration (PB) to reach the minimum (bottom plot) and maximum (upper plot) value

The effect of cellulose degradation, expressed as reduction of pulp viscosity, was observed when incrementing process pH and temperature, indicating possible cellulose chain cleavage (Figures 1 and 2). According to previous findings,[35] the drop in viscosity could be attributed to excessive alkaline hydrolysis of the glycosidic linkages, which might result in a secondary peeling reaction. The viscosity reduction could, on the other hand, be also stimulated by the cellulose reaction with hydroxyl ions related to the rise in process alkalinity. Following the same line, the maximum prevention of pulp viscosity (1704mL/g) was reached at the minimum pH (pH = 9), and temperature considered (T=55ºC), high concentration of sodium perborate (PB=5% o.d.p.), and medium of peracetic acid (PA=2% o.d.p.), which simultaneously exert the major influence. The results obtained suggest that bleaching in the presence of peracetic acid and sodium perborate is less aggressive towards carbohydrates under lower temperature and moderately alkaline conditions. These findings are in concordance with the previous studies on peracid bleaching,[23,36] which showed that within a pH range close to neutral the pulp carbohydrate degradation depended mainly on peracid concentration (increase in PA concentration is related to a drop in intrinsic viscosity value). According to various authors,[25,37,38] the major process selectivity in peracetic bleaching was observed within the temperature between 50 and 70ºC.

By contrast, reaching the highest brightness and the lowest kappa numbervalues requires most severeprocess conditions (Table 4, Figures 3 and 4). From this standpoint, pH reduction (pH=9), while upholding the rest of process variablesin their most desirable conditions from Table 4, would deviate kappanumberand brightness by 15.03 and 2.95% with reference to their optimal values, respectively. Peracetic acid concentration and process temperature affect in a linear manner the change in kappa number value, as shown in Figure 3, whereas the rise in brightness value is proportional to the increase in peracetic acid charge (Figure 4).Table 4 shows that the kappa number value varies between 5.56 (min) and 8.66 (max). The constancy of time, pH, and sodium perborate concentration to achieve both minimum and maximum values give an overall idea that this variable couldbe principally controlled by process temperature and peracetic acid concentration. Bothminimum and maximum brightness value (68.57; 84.65%, respectively) correspond to the minimum sodium perborate concentration (1% o.d.p.), confirming its limited action in brightness development, which could be attributed to the higher oxidative power of peracetic acid as compared to that of hydrogen peroxide –product of sodium perborate hydrolysis.[17]

To further assess the single-stage PA/PB bleaching feasibility, the viscosity, kappa number, and brightness of 27 tests conducted (Table 2) were contrasted with the results previously determined in a separate bleaching with peracetic acid or sodium perborate of abaca soda pulp,[29] obtained under pulping conditions analogous to those stated in the present paper. Therefore, the reference unbleached pulp was characterized by identical values of brightness (55.70%); kappa number (17.90) and viscosity (1624 mL/g). Performing bleaching tests with the use of pulp characterized by equivalent, aforementioned parameters, confirms the reliability of such a comparison. Consequently, a series of approximate to common operational conditions were chosen as the reference factor (Table 5), indicating the existence of a synergistic effect of the PA/PB mixture, not only improves the pulp delignification degree, expressed as a decrease in kappa numberof 43 and 46%, but also enhances pulp brightness by 19, and 2%, compared to the corresponding PB or PA bleached pulps, respectively. The higher viscosity value of sodium perborate or peracetic acid bleached pulp gives a general concern that PA/PB bleached pulp might exhibit higher carbohydrates damage. Nevertheless, as shown in Table 5, contrasting viscosity/kappa index (VK) *vs.* pulp brightness proves higher PA/PB process selectivity.

Table 5

Comparison of kappa number, brightness and viscosity values obtained in one-stage PA/PB abaca soda pulp bleaching, with previously reported results of separate abaca pulp bleaching with sodium perborat or peracetic acid

Process conditions	VI(mL/g)	KN	BR(%)	VK
PA/PB (T = 70°C, t= 120 min, PB =3% o.d.p., pH =10, PA=2% o.d.p.)	1209	7.40	78.08	163.38
PB (T = 70°C, t = 120 min, PB = 3% o.d.p., pH = 10.5)[29]	1305	12.90	65.34	101.16
PA/PB (T= 55°C, t= 30 min, PA = 0.5% o.d.p., pH = 9; PB = 5% o.d.p.)	1481	8.17	71.08	181.27
PA (T = 55°C, t= 30 min, PA = 0.5% o.d.p., pH = 7)[29]	1506	15.22	69.90	98.95

PA/PB: TCF bleaching with the mixture of peracetic acid and sodium perborate in a single stage;
PB: TCF bleaching with sodium perborate; PA: TCF bleaching with peracetic acid

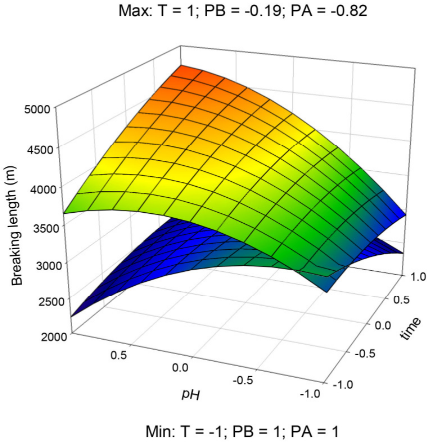


Figure 5: Variation of breaking length as a function of process time (t) and pH (pH) on constancy of temperature (T), sodium perborate (PB) and peracetic acid (PA) concentrations to reach the minimum (bottom plot) and maximum (upper plot) value

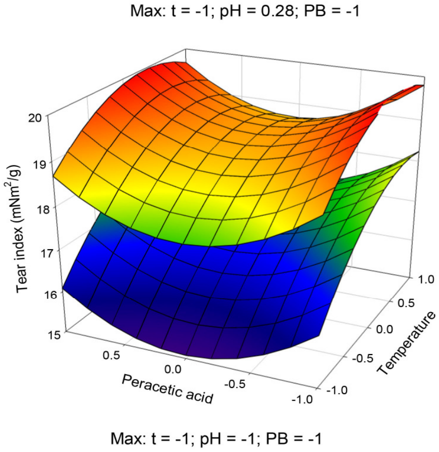


Figure 6: Variation of tear index as a function of process temperature (T) and peracetic concentration (PA) on constancy of time (t), pH (pH), and sodium perborate concentration (PB) to reach the minimum (bottom plot) and maximum (upper plot) value

Paper sheet characteristics

The analysis of the influence of independent variables on the strength propertiesof the resulted paper sheets (Table 4)clearly identifies the pH of the bleaching liquor as a crucial process parameter for 3 out of 4 analyzed dependent variables.

The breaking length value varies from 2230 to 4721m (minimum and maximum, respectively). Therise in pH appeared to play the major role in maximizing breaking length and stretch index values of the resulted paper sheets, reaching the optimum peak for the highest pH considered (*viz*: pH=11), as indicated in Figure 5.

It can be observed that the further increase in breaking length might be achieved by increment of bleaching time. Similar results were reported by Barros *et al.*,[36] demonstrating that the rise in pH during peracetic acid bleaching affected positively the bonding strength properties of the resulted paper sheets. However, as indicated in Figure 6, tear index development (between 15.08 and 20.11 mNm^2/g, minimum and maximum, respectively) depends mainly on peracetic acid concentration and bleaching temperature. The minimum value of tear index corresponds to medium peracetic acid concentration and low process temperature, therefore maximizing or minimizing peracid concentration coupled by an increase in the bleaching temperature wouldincrement the value of this dependent variable.

Optimized process conditions

Contrasting the experimental results of test 15 and 16 (Table 2), conducted under analogous conditions (-1) of time, temperature and pH, but with opposite oxidant concentration showed that the use of 1% o.d.p. of sodium perborate and 3.50% o.d.p. of peracetic acid, when referring to test 15, raised the final pulp brightness by 6.8%, and reduced kappa number by 4.50%, however, a drop in viscosity by 6.40% was also observed.The use of process variables of test 15 (T=55°C, t=30 min, pH=9, PB=5% o.d.p., PA=0.50% o.d.p.) provided quality bleached pulp, with the additional benefits of being carried out under conditions that resulted in considerable energy conservation, thus generating economic and environmental benefits.

Table 2 also shows that the pulp bleached with maximum values of operational conditions (test 1) provided the best experimental results of brightness (84.50%) and kappa number (5.70), but the lowest viscosity (355 mL/g), indicating considerable damage of carbohydrates. On the contrary, the best experimental value of viscosity/kappa index (VK) *vs.* pulp brightness was observed in the case of test 2, which simultaneously produced the best breaking length (4678m), and stretch index (5.93%) results. Whereas the highest experimentally obtained burst index (4.11 kN/g) and tear index (19.11 mNm^2/g) suited the particular conditions of test 13 and 14, respectively.

By using a set of specific values of operational variables in the polynomial equations given, through the mathematical simulation of the possible interaction between independent and dependent variables considered, the specified range of process conditions that provide pulp and paper sheets able to fulfill final product requirements can be proposed. As previously discussed, aiming at high and low values of brightness and kappa number, respectively, results in inconvenient reduction in pulp viscosity, thus different process scenarios should be considered. Not with standing these differences, a compromise between bleached pulp and resulted paper sheet characteristic (greatest values) can be proposed, thus the process conditions can be set as following: T=77°C; t=99 min; pH=10.5;PB=1% o.d.p., PA=2.5% o.d.p.; providing pulp and resulted paper sheets characterized bypredicted values of: 1174mL/g for viscosity, 6.84 for kappa number 80.60% for brightness, 17.64 mNm^2/g for tear index, 4.82% for stretch index, 4139m for breaking length, and 3.36kN/g for burst index. This operating mode supplies pulp and paper of fine quality, while saving chemical reagents, energy and immobilized capital by means of the temperature, time, pH, sodium perborate, and peracetic acid concentrations used, being less demanding than those required to maximize some properties. Additionally, reducing bleaching time and temperature improves theindustrial applicability of the bleaching sequence studied.

CONCLUSION

The use of the factorial design of central composition enabled to obtain equations that provide highly accurate predictions of the dependent variables as a function of the operating conditions, with errors less than 5%.

Within the studied range of operational variables, the peracid concentration and pH of bleaching liquor were in general identified as crucial process parameters.

Contrasting the results obtained with those resulted from separate PA or PB bleaching, the use of the PA/PB mixture provesthe existence of a synergistic effect between the oxidants used by the increase in pulp brightness and viscosity/kappa number relation.

The following bleaching parameters that meet a consensus between product quality, process environmental performance and economy, can be proposed: medium temperature (0.48) and peracetic concentration (0.30), medium to high process time (0.53) and pH (0.50), and low sodium perborate concentration (-1),*viz*: T

=77°C;t=99min; pH=10.5; PB=1% o.d.p., PA=2.5% o.d.p. This set of operational variables provides pulp with high brightness (80.6%), good strength (breaking length: 4139 m, tear index: 17.64 mNm^2/g, stretch index: 4.82%, burst index: 3.36 kN/g) and pulp-related (viscosity: 1174 mL/g, kappa number 6.84) properties, combined with cost and environmental benefits.

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REFERENCES

[1] FAOSTAT: available online <http://faostat.fao.org>, last access: December, 2013.

[2] S. Hetsch, in Geneva Timber and Forest Discussion Paper 52,Geneve, United Nations Publications, 2009, pp. 1-44.

[3] A. Villanueva and P. Eder, in JRC Scientific and Technical Reports,Luxemburg, European Union Publication Office, 2011, pp. 1-97.

[4] U. Fillat, P. Montserrat, T. Vidal and M. B. Roncero, *Biomass Bioenerg*., **34**, 1896 (2010).

[5] L. Jiménez, E. Ramos, M. J. De la Torre, I. Pérez and J. L. Ferrer, *Bioresour. Technol*., **99**, 1474 (2008).

[6] A. Requejo, A. Rodriguez, J. L.Colodette, J. L. Gomide and L. Jimenez, *Bioresour. Technol*.,**117**, 117 (2012).

[7] A. Rodríguez, A. Requejo and Z. Gonzales, *Cellulose Chem. Technol*., **45**, 371 (2011).

[8] L. Jiménez, E. Ramos, A. Rodríguez, M. J. De la Torre, and J. L. Ferrer, *Bioresour. Technol*., **96**, 977 (2005).

[9] FAO: available online <http://www.naturalfibres2009.org/es/index.html>, last access: December 2013.

[10] D.Y. Ye and X. Farriol, *Ind. Crop. Prod*., **26**, 54 (2007).

[11] Joint Research Centre, European IPPC Bureau: available online<http://eippcb.jrc.ec.europa.eu/reference/BREF/PP_BREF_FD_07_2013.pdf>, last access December 2013.

[12] United Nations Environment Programme, in *Procs.The 2nd Meeting of the Expert Group*, Section Vc, Geneve, November 19-24, 2006, pp. 1-14, available online http://www.pops.int/documents/meetings/bat_bep/EGBATBEP2/meetingdocs/EGBATBEP2_3.pdf, last access September 2014.

[13] N.P. Cheremisinoff and P.E. Rosenfeld, in "Handbook of Pollution Prevention and Cleaner Production", vol. 2, Amsterdam, Elsevier Inc., 2010, pp. 261-291.

[14] R. Martín-Sampedro, A. Rodríguez, A. Ferrer, L. L. García-Fuentevilla and M. E. Eugenio, *Bioresour. Technol*., **110**, 371 (2012).

[15] P. Bajpai, *Crit. Rev. Biotechnol*., **24**,1 (2004).

[16] Y. Shen, X. Zhou and X. Lu, *Cellulose Chem. Technol*., **46**, 97 (2012).

[17] P. Bajpai, "Environmentally Benign Approaches for Pulp Bleaching", New York, Elsevier Science, 2005, vol. 1, pp. 177-192.

[18] P. E. G. Loureiro, D. V. Evtuguin, and M. G. V. S. Carvalho, *J. Chem. Tech. Biot*., **86**, 381 (2011).

[19] S. Hedjazia, O. Kordashiab, R. Patt, A. J. Latibarid, and U. Tschirnere, *Ind. Crop.Prod*., **29**, 27 (2009).

[20] A. A. Shatalov, and H. Pereira, *Carbohyd. Polym*., **67**, 275 (2007).

[21] C. W. Bailey and C. W. Dence, *Tappi J*.,**49**, 9 (1966).

[22] N. Liebergott, *Pulp-Pap. Can*., **97**, 73 (1996).

[23] K. Poppius-Levlin, A. S. Jääskeläinen, A. Seisto and A. Fuhrmann, *J. Am. Chem. Soc*.,**24**, 471 (2000).

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

[25] L. B. Brasileiro, J. L. Colodette and D. Pilo-Veloso, *Quim. Nova*, **24**, 819 (2001).

[26] M. Jablonsky, M. Vrska, S. Suty and G. Szeiffova, *Wood Res.-Slovakia*, **50**, 51 (2005).

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

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

[29] E. Ramos,PhD Thesis, Universidad de Córdoba, 2003.

[30] L.E. Wise, M. Murphy, A. D'Adieco, *Paper Trade J*., **122**, 35 (1946).

[31] M.J. Díaz, M.E. Eugenio, F. López, J. Ariza and T. Vidal, *Cellulose Chem.Technol*.,**40**, 245 (2006).

[32] F. López, M. E. Eugenio, M. J. Díaz, I. Pérez and L. Jiménez, *Ind. Eng. Chem. Res*.,**41**, 3518 (2002).

[33] D. C. Montgomery, "Design and Analysis of Experiments", Grupo Editorial Iberoa-mericana, 1991, pp. 303.

[34] J. Moreand G. Toraldo, *Numer. Math*., **55**, 377 (1989).

[35] C. P. Leh, W. D. Wan Rosli, Z. Zainuddin, and T. Tanaka, *Ind. Crop. Prod*., **28**, 260(2008).

[36] D. P. Barros, V. L. Silva, H. Hämäläinen, and J. L. Colodette, *BioResources*, **5**, 881 (2010).

[37] L. Kham, Y. Le Bigot, M. Delmas and G. Avignon, *Ind. Crop. Prod*., **21**, 9 (2005).

[38] D. Danielewicz, B. Surma-Slusarska, *Fibres Text. East. Eur*., **14**, 89 (2006).