MODELING HYDROGEN PEROXIDE BLEACHING OF SODA PULP FROM OIL-PALM EMPTY FRUIT BUNCHES

Ana Ferrer,[a] Antonio Rosal,[b,]* Cristina Valls,[c] Blanca Roncero,[c] and Alejandro Rodríguez [a]

The influence of the variables soda (0.5-3.0%), hydrogen peroxide (1.0-6.0%) and time (1-5 h) in the bleaching of soda pulp of empty fruit bunches (EFB) from oil-palm, on the properties of bleached pulps, was studied. Polynomial and neural fuzzy models reproduced the results of brightness, kappa number, and viscosity of the pulps with errors less than 10%. By the simulation of the bleaching of pulp, using the polynomial and neural fuzzy models, it was possible to find optimal values of operating variables, so that the properties of bleached pulps differed only slightly from their best values and yet it was possible to save chemical reagents, energy, and plant size, operating with lower values of operating variables. Thus, operating with 1.13% soda concentration and 2.25% hydrogen peroxide concentration for 3 hours, a pulp with a brightness of 75.1% (8.1% below the maximum) and a viscosity of 740 mL/g (10.4% less than the maximum value), was obtained.

Keywords: Empty fruit bunches; Bleaching; Hydrogen peroxide; Polynomial model; Neural fuzzy model

Contact information: a: Chemical Engineering Department, University of Córdoba, Spain; b: Molecular Biology and Biochemical Engineering Department, University Pablo de Olavide, Seville, Spain; c: Textile and Paper Engineering Department, Technology University of Cataluña, Spain;
** Corresponding author: Antonio Rosal, e-mail: arosray@upo.es*

INTRODUCTION

In recent decades the increasing production of pulp for paper and other uses has led to a problem of inadequate supply of the classic raw materials (mainly hardwoods and softwoods) in some countries. For that reason there has been a growing emphasis on the use of alternative raw materials, mainly non-wood waste such as agricultural and food industry residues, forest residues, and fast-growing plants other than conventional woods (Jiménez *et al.* 2006).

One of the interesting non-wood resources is Empty Fruit Bunches (EFB), which consist of the lignocellulosic material residue from the palm oil industry. The value of these resources has been confirmed by several studies by various researchers. Several authors have studied the kraft process applied to these residues, of which the results presented by Ibrahim (2002) are the most relevant and recent. That publication compares the composition of EFB pulp obtained by the kraft, kraft-anthraquinone, soda, and soda-anthraquinone processes; the pulp obtained with the soda process had the highest content of lignin, holocellulose, and α-cellulose, as well as a higher viscosity. The soda process has also been studied by Law and Jiang (2001), producing fibers with more wall thickness, greater rigidity, higher solubilities in hot water and 1%-soda, and higher ash content. These pulps were bleached with hydrogen peroxide more easily than those of aspen; their paper sheets had lower tensile index, but greater stretch and tear index than those of aspen. Moreover, Daud *et al.* (1998) pulped the EFB with soda, sodium carbonate, and sodium sulfite processes, finding the first process to be the most efficient. Wanrosli *et al.* (2004), using a central composite experimental design, studied the influence of operating conditions (temperature, time, and alkali concentration) on the properties of EFB pulps (yield, kappa number, tensile index, and tear index). They obtained pulp yields in the range 30 to 45%. It was considered that the values of 160 °C, 60 to 120 minutes, and 20 to 30% of alkali are sufficient for the proper pulping. Jiménez *et al.* (2009a) also have studied the pulping of EFB with soda-anthraquinone, considering the influence of pulping variables and subsequent beating. Semi-chemical pulping for board by the soda-anthraquinone process also has been studied (Roliadi and Pasaribu 2004). Studies of thermomechanical pulp have also been made by several researchers, highlighting the results of Ghazali *et al.* (2006). Organosolv processes have also been studied: ethanol (Aziz *et al.* 2002), by modified IDE process (Quader and Lonnberg 2005), and high-boiling point organic solvents (Rodríguez *et al.* 2008a). Finally, biopulping has been investigated using a white fungus K14 (Goenadi *et al.* 1998).

The pulp bleaching plant, which is the most contaminating section in the paper manufacturing process, has gone through a number of changes intended to alleviate its adverse environmental impact. The need to reduce or eliminate the formation of organo-chlorinated compounds of high toxicity during the bleaching processes has led to the emergence of new products in the market, such as ECF (Elemental Chlorine Free) and TCF (Totally Chlorine Free) pulps (Ramos *et al.* 2008). TCF pulping processes avoid the formation of highly toxic organochlorine compounds (AOX) during bleaching. Usually TCF sequences include oxygen, hydrogen peroxide, and ozone-based stages (López *et al.* 2003; Roncero *et al.* 2003; Torres *et al.* 2004; Pedrola *et al.* 2004; Shatalov and Pereira 2005; Freire *et al.* 2006; Villaverde *et al.* 2009). Recently, enzyme stages involving xylanases or the laccase-mediator system have provided very promising results in pulp bleaching sequences (Valls and Roncero 2009; Valls *et al.* 2009, 2010a,b).

In the pulping of different materials, several authors have studied the influence of operating variables on the characteristics of the pulps obtained by the use of polynomial and neural fuzzy models. Polynomial models have also been used successfully for the study of operating variables in the bleaching of pulps (López *et al.* 2001, 2002, 2003; Pedrola *et al.* 2004; Jiménez *et al.* 2008; Valls and Roncero 2009; Valls *et al.* 2009, 2010b), but not studied in cases in which neural fuzzy models were used.

The aim of this work was to obtain a bleached EFB pulp with the best application conditions of the pressurized hydrogen peroxide stage (P_O). A P_O stage was performed after a W_AO_q sequence with EFB pulp (W_A, acid washing; O, oxygen delignification; q, chelating stage). For this reason this P_O stage was optimized following a sequential statistical plan of three variables (soda concentration, hydrogen peroxide concentration, and processing time). The results obtained were analyzed according to polynomial and neural fuzzy models.

EXPERIMENTAL

Raw Material

The research employed EFB from Malaysian oil palm (supplied by Palmor Corp. SDN BHD). Malaysia supplies 51% of the world's production of this oil (Malaysian Palm Oil Promotion Council). Each hectare of oil palm produces an average of 10 tons of fruits per year, and that amount of fruit yields 3000 kg of the oil (the main product) (http://www.arbolesornamentales.com).

The chemical properties of EFB were determined in accordance with the respective TAPPI standards for the different components, namely: T-222 for lignin, T-203 0S-61 for α-cellulose, T9m-54 for holocellulose, T-204 for ethanol-benzene extractives, and T-211 for ash. The analysis showed the following results: 24.5% lignin, 41.9% α-cellulose, 67.0% holocellulose, 1.2% extractives, and 3.2% ash.

The average fiber length of EFB (number average), determined by using a Visopan projection microscope, was found to be 0.53 mm, and the thickness or width 14 μm.

Pulping

Pulp was obtained by using a cylindrical 15-L batch reactor that was heated by means of electrical wires and attached to a rotary axle (to ensure proper agitation) to a control unit including a motor activating the reactor and the required instruments for measurement and control of pressure and temperature.

The raw material was cooked in the reactor, using 15% soda, 170 °C, a liquid/solid ratio of 10, and a processing time of 30 minutes, obtaining a pulp yield of 48%. These operating conditions were selected based on the results of other authors (Daud *et al*. 1998; Law and Jiang 2001, Jiménez *et al*. 2009b). Next, the cooked material was fiberized in a wet desintegrator at 1200 rpm for 30 min, and the screenings were separated by sieving through a screen of 0.14 mm mesh size. The pulp obtained was beaten in a Sprout-Bauer refiner.

Bleaching

The initial pulp properties of EFB were 38.4% ISO brightness, kappa number 9.7, and 797 mL g^{-1} viscosity. Before applying the hydrogen peroxide stage (P_O), the pulp was washed in acidic medium (W_A) and an oxygen delignification stage (O) was performed followed by a chelating stage (q) (W_AO_q sequence).

The pressurized peroxide bleaching stage (P_O) conditions, selected based on previous works (Moldes et al. 2010; Aracri and Vidal 2010), was carried out with 25 g odp (oven-dried pulp) in a 5 L reactor at 0.6 MPa O_2, with 0.5 % odp of Na_2SiO_3, 0.2 % odp of $MgSO_4$, at 5% consistency, at 105 ºC and 60 rpm with a blade stirrer. The soda concentration, hydrogen peroxide concentration, and processing time were the three variables of the experimental design, and were varied over the following ranges: 0.5-3% odp for soda concentration, 1-6% odp for hydrogen peroxide, and 1-5 h for processing time. After the Po stage, the liquors were recovered for pH measurement, and the pulp was efficiently washed for characterization.

Pulp Properties

Treated pulp samples were characterized in terms of kappa number, brightness, and viscosity according to ISO 302, ISO 3688, and ISO-5351-1, respectively. The kappa number was measured twice, and four measurements of brightness were obtained in order to calculate a relative standard deviation, which was found to be ≤0.1 for both properties. The viscosity was determined 4 times with a standard deviation of 5.

Experimental Design

The factorial design used (Montgomery 1991) consisted in a central experiment (in the centre of a cube) and several additional points (additional experiments being at the cube vertices and side centers).

Polynomial Model

Experimental data were fitted to the following second-order polynomial,

$$Ye = a_0 + a_1X_S + a_2X_P + a_3X_t + a_{11}X_S^2 + a_{22}X_P^2 + a_{33}X_t^2 + a_{12}X_SX_P + a_{13}X_SX_t + a_{23}X_PX_t \quad (1)$$

where Ye denotes the response variables [viz. Kappa number (KN), viscosity (VI) or brightness (BR)]; X_S, X_P, and X_t are the normalized values of the operational variables (soda concentration, hydrogen peroxide concentration, and time, respectively), and a_0 to a_{23} are constants.

Table 1. Normalized Values of Operational Variables and Experimental Values of the Properties of Bleached Pulp

Experiment Soda X_s, peroxide X_p, time X_t	Brightness, % ISO	Viscosity, mL/g	Kappa number
1 -1,-1,-1	63.7	814	4.86
2 -1,+1,-1	72.7	678	3.27
3 +1,+1,-1	77.0	637	3.15
4 +1,-1,-1	71.4	771	3.42
5 -1,-1,+1	71.5	774	3.57
6 +1,-1,+1	75.3	695	3.13
7 -1,+1,+1	80.1	580	1.14
8 0,0,0	77.7	671	3.00
9 +1,+1,+1	78.9	573	2.95
10 +1,0,0	78.2	641	2.74
11 0,0,+1	79.3	670	2.70
12 -1,0,0	76.0	731	3.05
13 0,-1,0	74.0	765	3.23
14 0,0,-1	74.4	703	3.60
15 0,+1,0	81.5	637	2.81
16 -0.5,-0.5,-0.5	72.7	745	3.83
17 +0.5,+0.5,+0.5	79.5	626	2.97

The values of the operational variables were normalized to values from -1 to +1 by using the following expression,

$$X_n = 2\,(X - \bar{X}) / (X_{max} - X_{min}) \tag{2}$$

where X_n is the normalized value of soda concentration (S), hydrogen peroxide (P), or time (t); X is the absolute experimental value of the variable concerned; $\bar{X}$ is the mean of X_{max} and X_{min}; and X_{max} and X_{min} are the maximum and minimum values, respectively, of such a variable.

The normalized values for the independent variables in the 15 experiments conducted are given in Table 1.

Neural Fuzzy Model

The integration of fuzzy systems and neural networks combines the advantages of the two systems and provides an especially powerful modelling tool, viz. the neural fuzzy system, which uses neural networks as tools in fuzzy systems (Jang et al. 1997). Thus, the variation of pulp properties as a function of the operational variables of the bleaching process can be predicted by using the following expression,

$$Ye = \frac{\sum_{l=1}^{m} y^l \left[\prod_{i=1}^{n} \mu^l_{Fi}(x_i,\theta^l_i)\right]}{\sum_{l=1}^{m} \left[\prod_{i=1}^{n} \mu^l_{Fi}(x_i,\theta^l_i)\right]} \tag{3}$$

where Ye is the estimated value of the property to be modelled, m the number of fuzzy rules applied, n that of independent variables, y^l the defuzzifier of a fuzzy rule and $\mu^l_{Fi}(x_i,\theta_i^l)$ the membership function of the independent variables within its range.

In this paper, $[\prod \mu^l_{Fi}(x_i,\theta^l_i)]$ will be denoted by R_l which is known as a fuzzy rule. In this sense, R_l is defined by the product of n membership functions (one per independent variable). Then, equation (3) could be expressed as:

$$Y_e = \frac{\sum_{l=1}^{m} y^l \cdot R_l}{\sum_{l=1}^{m} R_l} \tag{4}$$

With three operational variables (our case), the use of a Singleton defuzzifier (a constant parameter: c_l) and a linear membership function for the independent variables allows equation (4) to be simplified to:

$$Y_e = \frac{\sum_{l=1}^{8} c_l R_l}{\sum_{l=1}^{8} R_l} \tag{5}$$

Linear membership functions were selected for independent variables with two levels. The mathematical equations which respond to linear membership functions are,

$$x_1 = x_{low} = 1 - (x - x_{low}) / (x_{high} - x_{low}) \tag{6}$$

$$x_2 = x_{high} = (x - x_{low}) / (x_{high} - x_{low}) \tag{7}$$

x_1 and x_2 denoting the values of S, P, and t for low and high levels; x_{high} and x_{low} the extreme values of the variable; and x the absolute value of S, P, or t.

With three independent variables one can establish the following eight fuzzy rules according to the extreme (high and low) values of such variables:

R1: low S, low P, and low $t = S_1. P_1. t_1$
R2: low S, low P, and high $t = S_1. P_1. t_2$
……………………
R7: low S, high P, and high $t = S_1. P_2. t_2$
R8: high S, high P, and high $t = S_2. P_2. t_2$

With a Gaussian membership function with three levels (low, medium, and high) for one of the variables and a linear membership function with two levels (low and high) for the other two, equation (5) would include 12 terms in the numerator and 12 in the denominator. The Gaussian membership function would be of the following type,

$$x_i = \exp\left[-0.5 \left((x - x_C) / L\right)^2 \right] \tag{8}$$

where x_i denotes the values of S, P, and t, for low, medium, and high levels; x is the absolute value of the variable concerned; x_c its minimum, central or maximum value; and L the width of its Gaussian distribution.

The parameters and constants in the previous equation were estimated by using the ANFIS (Adaptative Neural Fuzzy Inference System) Edit tool in the Matlab© 6.5 software suite.

RESULTS AND DISCUSSION

Based on the results of other researchers for pulps from other materials (Lopez *et al.* 2002 and 2003; Pedrola *et al.* 2004), and after a set of preliminary experiments, the following ranges were used for the operational variables during the hydrogen peroxide bleaching of EFB: 0.5 to 3% odp for soda concentration, 1 to 6% odp for hydrogen peroxide concentration, and 1 to 5 h for processing time.

Table 1 shows the experimental values of the bleached pulps properties of the EFB. During the hydrogen peroxide stage, the brightness increased, while the kappa number and viscosity decreased, depending on the application conditions. In fact, the bleaching effect of hydrogen peroxide has been attributed to its ability to react with various coloured carbonyl-containing structures in lignin (Ramos *et al*. 2008).

Polynomial Model

Table 2 lists the coefficients of the different terms in the polynomial equations, as well as the R^2 and the lowest Student's *t*-values for the terms. The predictions obtained with the previous equations reproduced the experimental results for the dependent variables with errors less than 2% for brightness, 4% for viscosity, and 10% for kappa number in 80% of cases (always below 16%) (Table 3).

Table 2. Polynomial Models for the Properties of Bleached Pulp (values of the constants in the polynomial equations)

Dependent variable	a_0	a_1	a_0	a_3	a_{11}	a_{22}	a_{33}	a_{12}	a_{13}	*t* *	R^2
Brightness	78.6	1.7	3.4	2.6	-1.7	-1.1	-2.0	-1.1	-1.2	2.3	0.99
Viscosity	689	-26	-71	-31	-	-	-	9	-	1.5	0.96
Kappa number	3.11	-	-0.49	-0.48	-	-	-	0.45	0.37	4.2	0.92
* Student's *t* value for the least significant term											

The proposed models were validated by conducting two pulping experiments (entries 16 and 17 in Table 1). The errors made in predicting pulp properties by using the polynomial models were quite small (see Table 3). This testifies to the accuracy of such models.

The values of the operational variables providing the best bleached pulp properties (kappa number, viscosity, and brightness) were identified by using multiple non-linear programming. Table 4 shows the optimum values of the dependent variables and those of the operational variables required to obtain them. In all the cases low or medium soda concentration are required.

Comparing the maximum values of the results of brightness (81.7%), kappa number (1.32), and viscosity (826 mL/g) with those obtained by Jimenez et al. (2009b) for EFB pulps obtained by soda-anthraquinone and diethanolamine processes, bleached by A_1OpA_2ZRP sequence (A is an acid treatment, Op an oxygen and peroxide stage, Z an ozone stage, R a reductive treatment, and P a peroxide stage), it may be seen that in both cases, the kappa number was greater (2.8 and 5.5), the brightness lower (77.5% and 71.3%), and the viscosity lower (653 mL/g and 783 mL/g). These discrepancies can be explained by more severe treatment of the pulps in applying the compared sequence, as well as the different nature of the unbleached pulps (pulping with diethanolamine).

Table 3. Values of the Dependent Variables as Estimated with Polynomial and Neural Fuzzy Models, and Deviations (in %) from their Experimental Counterparts (in brackets)

Experi-ment	Polynomial model			Neural fuzzy model		
	Brightness, %	Viscosity, mL/g	Kappa number	Brightness, %	Viscosity, mL/g	Kappa number
1	63.8 (0.16)	826 (1.47)	4.90 (0.82)	64.0 (0.47)	820 (0.74)	4.97 (2.26)
2	72.8 (0.14)	666 (1.77)	3.02 (7.65)	73.1 (0.55)	684 (0.88)	3.38 (3.36)
3	77.4 (0.78)	632 (0.78)	3.18 (0.95)	77.4 (0.52)	642 (0.78)	3.22 (2.22)
4	71.8 (0.56)	756 (1.95)	3.26 (4.68)	71.8 (0.56)	776 (0.65)	3.49 (2.05)
5	71.4 (0.14)	764 (1.29)	3.20 (10.36)	71.9 (0.56)	775 (0.13)	3.68 (3.08)
6	74.6 (0.93)	694 (0.14)	3.04 (2.88)	75.7 (0.53)	696 (0.14)	3.20 (2.24)
7	80.4 (0.37)	604 (4.14)	1.32 (15.79)	80.5 (0.50)	580 (0.00)	1.25 (9.65)
8	78.6 (1.16)	689 (2.68)	3.11 (3.67)	77.3 (0.51)	674 (0.45)	3.20 (6.67)
9	79.2 (0.38)	570 (0.52)	2.96 (0.34)	79.3 (0.51)	574 (0.17)	3.02 (2.37)
10	78.6 (0.51)	663 (3.43)	3.11 (13.50)	79.2 (1.28)	643 (0.31)	2.77 (1.09)
11	79.2 (0.13)	658 (1.79)	2.63 (2.59)	76.8 (3.15)	656 (2.09)	2.94 (8.89)
12	75.2 (1.05)	715 (2.19)	3.11 (1.97)	74.6 (1.84)	722 (1.23)	3.32 (8.85)
13	74.1 (0.14)	760 (0.52)	3.60 (11.46)	71.5 (3.38)	730 (4.58)	3.47 (7.43)
14	74.0 (0.54)	720 (2.42)	3.59 (0.28)	75.4 (1.34)	706 (0.43)	3.63 (0.83)
15	80.9 (0.74)	618 (2.98)	2.62 (6.76)	80.1 (1.72)	627 (1.57)	3.23 (14.95)
16	73.0 (0.41)	755 (1.34)	3.80 (0.79)	72.6 (0.14)	729 (2.15)	3.76 (4.70)
17	80.7 (0.16)	627 (0.16)	2.83 (4.95)	78.1 (1.76)	638 (1.92)	3.23 (8.75)

Table 4. Optimal Properties in Bleached Pulp

Dependent variable	Optimum (maximum or minimum*) value of the dependent variable	Values of the operational variables required to obtain the optimum values of the dependent variables		
		X_s	X_P	X_t
Brightness, %	81.7	-0.05(1.69%)	1(6%)	0.68(4.36h)
Viscosity, mL/g	826	-1(0.5%)	-1(1%)	-1(1h)
Kappa number	1.32*	-1(0.5%)	1(6%)	1(5h)

López et al. (2002 and 2003) applied an experimental design of peroxide bleaching to kraft pulp from olive prunings, finding that the minimum values of the kappa number of the bleached pulp and the maximum values of the brightness and the viscosity were achieved when operating at 5% peroxide and 210 min. Moreover, Pedrola *et al*. (2004) used an experimental design to the P stage of the sequence OXZP (where O is an oxygen stage, X an enzymatic treatment, Z an ozone stage, and P a hydrogen peroxide stage) applied to eucalyptus kraft pulp, with 4 independent variables: hydrogen peroxide concentration, soda concentration, processing time, and temperature.

The models obtained in the cited research predict values for brightness and viscosity ranging from 84.6% to 90.5% and 890 mL/g to 919 mL/g, respectively, with the best results when the processing time and peroxide concentration were the highest and the temperature and soda concentration were the mean values, with the peroxide concentration being the most influential variable.

Reported results only partially coincide with those obtained in this work, which may be due to the different nature of the treated materials (pruning of olive and eucalyptus wood being compared relative to a non-wood: EFB), which had undergone different pulping procedures (kraft pulping being compared with soda pulping).

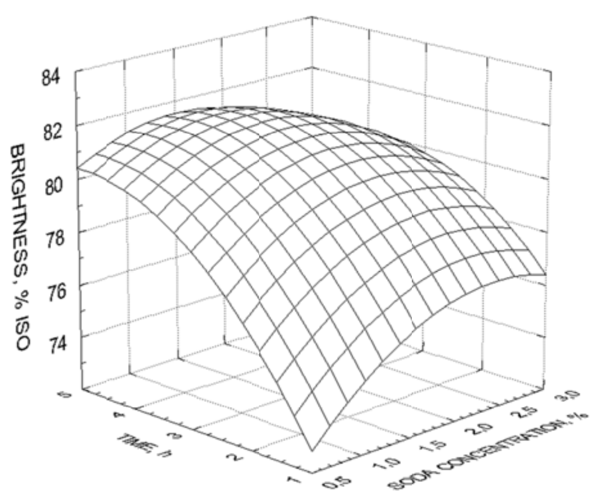

Figure 1. Variation of brightness of bleached pulps of EFB with soda concentration and processing time, for a hydrogen peroxide concentration of 6%

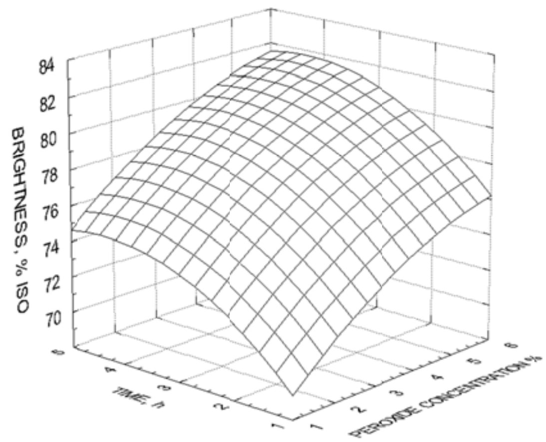

Figure 2. Variation of brightness of bleached pulps of EFB with hydrogen peroxide concentration and processing time, for a soda concentration of 1.69%

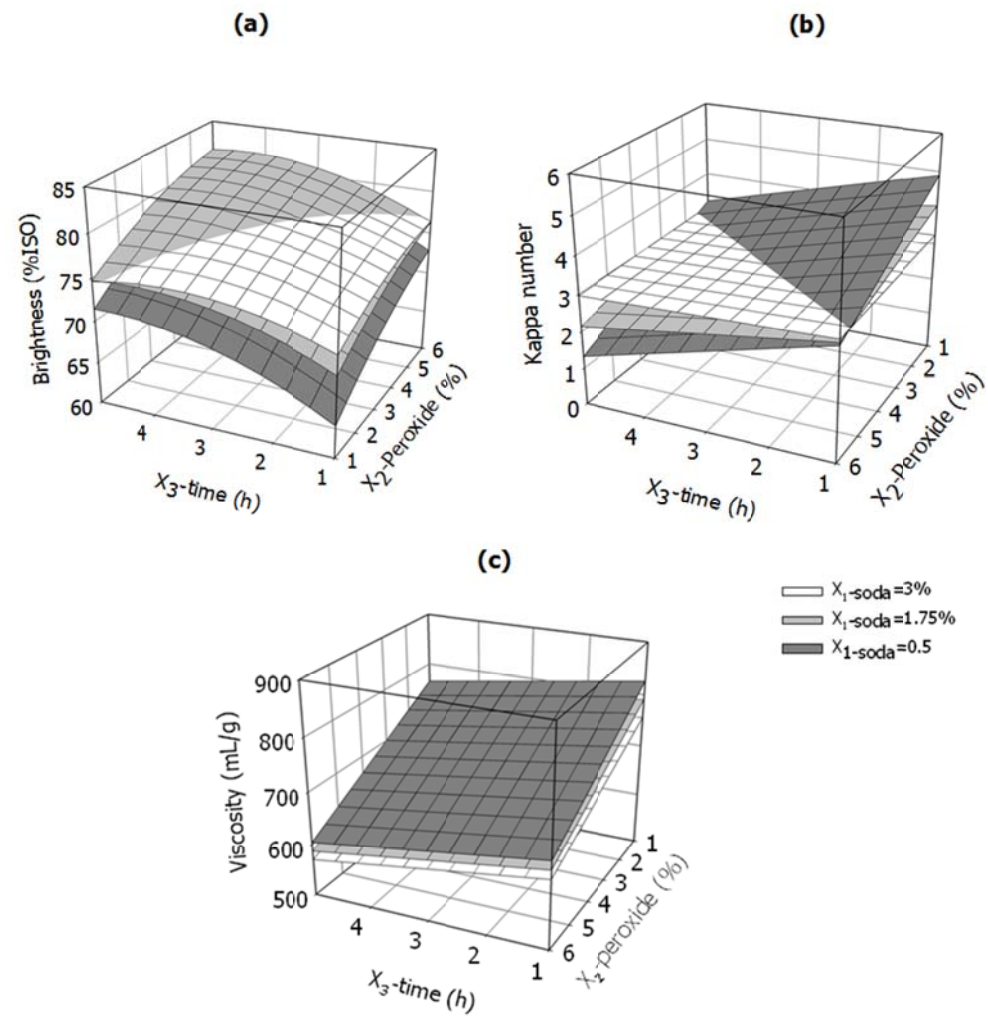

Figure 3. Surfaces estimated for brightness (a), kappa number (b), and viscosity (c) at different soda concentrations (0.5%, 1.75% and 3%)

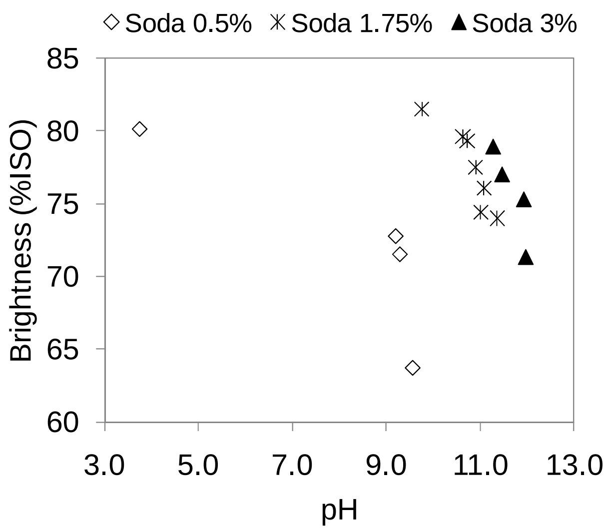

Figure 4. Representation of pH vs. brightness of all the experiences performed at different soda concentrations

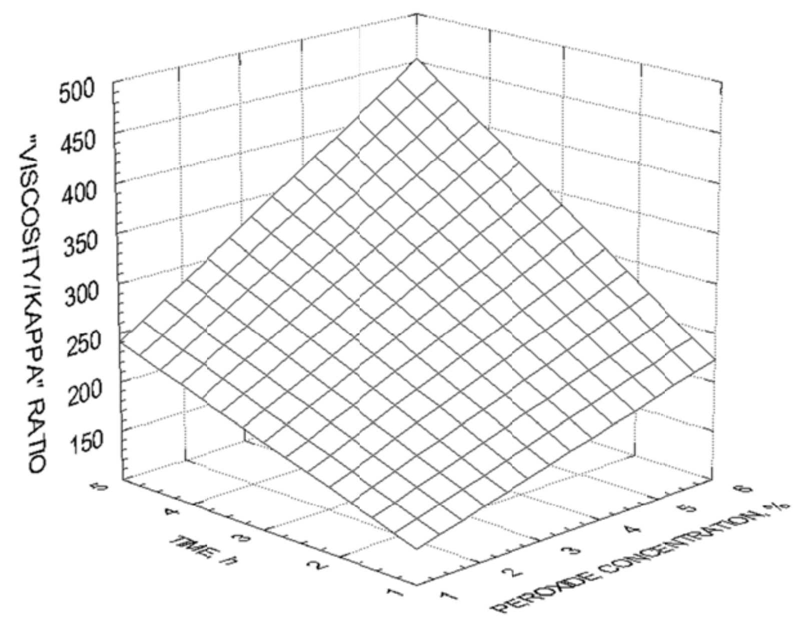

Figure 5. Variation of "viscosity/kappa number" ratio with the hydrogen peroxide concentration and processing time, for a soda concentration of 0.5%

The polynomial equations (Table 2) allow one to identify the operational variables most markedly influencing the bleached pulp properties. The maximum variations in the dependent variables with changes in the operational variables over the studied range were obtained by altering one independent variable at a time while keeping all others constant; the results are shown in Table 5 together with the maximum percentage differences in the dependent variables from their optimum values over the studied variation ranges. As shown in Table 5 and Figs. 1 and 2, the most influential operational variable on the brightness of bleached pulps is the hydrogen peroxide concentration, the soda concentration being less influential. These results are consistent with those obtained by Pedrola *et al*. (2004) for the case of eucalyptus kraft pulp bleaching, but not with those obtained for kraft pulp from olive pruning (López *et al*. 2002 and 2003), where the most influential variable was processing time. Based on Table 5 and similar to Figs. 1 and 2, it follows that for the viscosity, also the hydrogen peroxide concentration was the most influential variable, processing time being less influential; these results are consistent with those of López *et al*. (2002 and 2003) and those of Pedrola *et al*. (2004). It was also found that, for kappa number, the most influential variable was the hydrogen peroxide concentration, coinciding with the results obtained for the bleaching of kraft olive pruning pulp (López *et al*. 2002 and 2003) and kraft eucalyptus (Pedrola *et al*. 2004), and the soda concentration variable was the least influential, in agreement with the results of Pedrola *et al*. (2004).

Table 5. Maximum Changes in the Dependent Variables with the Changes in One Operational Variable (Constant Value of the Others)

Dependent variable	Variation with the operational variable *		
	Soda (0.5 to 3.0%)	Peroxide (1.0 to 1.6%)	Time (1 to 5 h)
Brightness, %	1.9(2.33%)	6.9(8.45%)	5.5(6.73%)
Viscosity, mL/g	70(8.47%)	160(19.37%)	62(7.51%)
Kappa number	1.64(124.24%)	1.88(142.42%)	1.70(128.79%)

* The percent differences from the changes are given in parentheses.

The increase of soda concentration from 0.5 to 3% caused the brightness to increase (Fig. 3-a). However, the effect of soda concentration on pulp brightness was affected by peroxide and the processing time, since at low values of these variables the effect was more appreciable. At a high processing time with high soda concentration the variation of pulp brightness decreased. According to Dence and Reeve (1996), for each peroxide concentration there exists an optimum soda concentration. At a soda concentration above the optimum, the effectiveness of hydrogen peroxide is reduced and brightness reversion is observed. On the other hand, the hydrogen peroxide concentration and the processing time both increased brightness, with their effects being more apparent at low soda concentration.

Kappa number (Fig. 3-b) was strongly decreased by peroxide and the processing time at low soda concentration. However, this effect was not appreciable at medium and high soda concentrations. In general, the increase of soda concentration had a detrimental effect on kappa number. Only at a low peroxide concentration and a short processing time did the increase of soda concentration decrease kappa number.

Finally, the pulp viscosity (Fig. 3-c) was negatively affected by all the variables, being the hydrogen peroxide concentration the most influential independent variable. In contrast to kappa number and brightness, no interactions between variables were found. The decrease of viscosity was produced because cellulose may undergo depolymerization by reaction with hydroxyl radicals (Dence and Reeve 1996).

In general, it was observed that an increase of soda concentration had a detrimental effect on all of the properties. As expected, the pH of the effluent was strongly influenced by the soda concentration (Fig. 4). At high soda concentration (X_S=+1; 3%) the pH oscillated between 11.3 and 12.0; at medium soda concentration (X_S=0; 1.75%) the pH oscillated between 9.8 to 11.4; and at low soda concentration (X_S=-1; 0.5%) the pH was around 9.0. The pH around 10.5 has been judged to be the most appropriate for an optimal bleaching of a P stage (Ramos *et al.* 2009). Surprisingly at low soda concentration and maximum peroxide concentration and processing time (experiment 7 in Table 1) the pH strongly diminished (3.75). Under these conditions, the soda was consumed by the inorganic compounds present in the pulp and it was not possible to maintain the pH. Moreover, in this set of tests a high value of brightness (80.1% ISO) and a low value of kappa number (1.14) were obtained. However, the viscosity was significantly affected (580 mL g^{-1}). In fact, in Dence and Reeve (1996) it is reported that in acidic media there is a greater viscosity drop produced by hydrogen peroxide.

Neural Fuzzy Modeling

Table 6 shows the values of the constants in the neural fuzzy models, c_i, as obtained by using the brightness and viscosity values of Table 1, which was constructed with a Gaussian membership function for the variable time processing and a linear membership function for the other two (soda concentration and hydrogen peroxide concentration).

Table 6. Values of the Constants c_i in the Neural Fuzzy Model for the Bleached Pulp Properties

Rule	Soda (%), peroxide (%), time (hours)	Brightness, %	Viscosity, mL/g	Kappa Number
1	0.5,1.0,1	62.9	827	5.11
2	0.5,1.0,5	71.4	780	3.76
3	0.5,6.0,1	73.1	680	3.34
4	3.0,1.0,1	70.8	786	3.54
5	0.5,6.0,5	81.2	571	1.11
6	3.0,1.0,5	75.1	702	3.25
7	3.0,6.0,1	77.3	641	3.17
8	3.0,6.0,5	79.4	569	2.99
9	1.75,1.0,1	-	-	2.85
10	1.75,1.0,5	-	-	2.41
11	1.75,6.0,1	-	-	4.00
12	1.75,6.0,5	-	-	3.51
9	0.5,1.0,3	77.1	678	-
10	0.5,6.0,3	72.4	766	-
11	3.0,1.0,3	83.2	575	-
12	3.0,6.0,3	77.9	666	-
R^2		0.92	0.96	0.95

Table 6 also shows the values of the constants in the neural fuzzy models, as obtained by using the kappa number values of Table 1. This was constructed with a Gaussian membership function for the variable soda concentration and a linear membership function for the other two (peroxide concentration and processing time).

The predictions obtained with the previous models reproduced the experimental results for the dependent variables with errors less than 3% for the brightness, 5% for the viscosity, and 10% for the kappa number in 93% of cases (always below 15%) (Table 3).

The constants obtained in the neurofuzzy model make it possible to see the influence of operating variables separately on the characteristics of the pulps. Thus, at low soda and hydrogen peroxide concentrations, increasing the time processing would increase the brightness (from 62.9% to 71.4%) as per rules 1 and 2 in Table 6. Also, increasing the hydrogen peroxide concentration at a low soda concentration and time would increase the brightness from 62.9% to 73.1% as per rules 1 and 3.

As in the case of polynomial model, the neural fuzzy model could be validated by the use of experiments 16 and 17 (Table 1). It was found that by using the neural fuzzy model, the errors in the prediction of the results of the experiments 16 and 17 are minor (Table 3), which confirms the model tested.

As can be seen, these errors committed in the simulation model using the neural fuzzy model were similar to those found by applying the polynomial model, even somewhat lower in the case of kappa number. In view of this, it follows that both models (polynomial and neural fuzzy) are suitable for simulating the process of bleaching of EFB pulp, and therefore may be useful to determine the optimal operating conditions. Similar matches in the application of polynomial and neural fuzzy models have been found for the pulping of different materials using different processes: vine shoots with ethanolamine (Jiménez et al. 2007), paulownia with ethanol (Caparros et al. 2008), and *Leucaena leucocephala* and *Chamecytisus proliferus*, vine shoots and cotton stalks, with ethylene glycol (Rodriguez et al. 2008b).

Optimum Operating Conditions

First it seems reasonable to operate under such conditions so as to obtain a bleached pulp with low kappa number and high levels of brightness and viscosity. Such conditions may be characterized as having a high value of the ratio "viscosity over kappa number".

Adjusting the experimental data of (viscosity / kappa number) to a second degree polynomial, the following equation can be used:

$$\text{Viscosity/kappa} = 237 - 26\,X_S + 27\,X_P + 39\,X_T - 48\,X_S X_P - 45\,X_S X_T + 31\,X_P X_T \qquad (R^2 = 0.84;\ t = 2.0) \qquad (9)$$

Figure 5 shows the changes in the "viscosity/Kappa number" ratio in terms of two operating variables (peroxide concentration and processing time), keeping constant the third independent variable (soda concentration). As shown, the highest "viscosity/ kappa number" ratio (453) corresponded to when one is operating with high levels of peroxide concentration and time and low concentration of sodium hydroxide. However, under these operating conditions, although they get good values for the kappa number and brightness, viscosity has a value far below the maximum (27% less). Therefore, it is more convenient to find the optimum operating conditions through simulation, using the polynomial and neural fuzzy models.

According to the experimental design carried out, the soda concentration has to be diminished, since it has a detrimental effect on all the properties. In addition, the hydrogen peroxide has to be kept at a minimum due to its negative effect on the pulp viscosity.

Thus, by applying the polynomial models to various combinations of values of the operational variables, one can identify those providing acceptable bleached pulp properties (*viz.* values close to the optimum ones of Table 3) while saving chemical reagents, energy, and challenges related to capital investments and facilities, through the use of lower concentrations of soda and peroxide as well as shorter processing times than those required to obtain the optimum bleached pulp properties. One such combination uses a soda concentration of 1.13% and a hydrogen peroxide of 2.25% for a time of 3 hours. Under these conditions it was possible to obtain a brightness of 75.1% (8.1% below the maximum) and a viscosity of 740 mL/g (10.4% less than the maximum value). Under these conditions it is possible to obtain a value of the ratio “viscosity/Kappa” of 213, well below the maximum, 453.

This brightness value (75.1%) is higher than that found by Law and Jiang (2001): 64.1% for when soda pulp bleaching of EFB with 5% hydrogen peroxide, 4.5% soda, at 70 °C and 1 h are considered. The difference found may be due to different operating conditions considered in both cases. Comparing the brightness and viscosity values obtained in this work with those reported by Jiménez et al. (2009b) to bleach soda pulp and diethanolamine pulp of EFB (653 mL/g and 783 mL/g and 77.5% and 71.3%, respectively), shows that the obtained values are intermediate between those reported by these authors. This can be explained by different pulping and bleaching processes used.

CONCLUSIONS

1. Based on the R^2 values they provided (greater than 0.92 in all cases), the proposed polynomial and neural fuzzy models can be used to accurately predict bleached pulp properties as a function of the operating conditions. Both models reproduced with similar accuracy (errors of 10%) the properties of bleached pulps of EFB.
2. Neural fuzzy models allow one to assess the influence of each operational variable on pulp properties. This allows one to compare any two rules involving identical levels of two variables and differing in the third in order to make reliable predictions by determining the influence of the third variable on each pulp property.
3. Polynomial models can additionally be used to establish the influence of each operational variable on bleached pulp properties (Table 5), albeit not in a direct manner as with constants c_i in the neural fuzzy models.
4. By simulating the process of bleaching pulp EFB, with the polynomial and neural fuzzy models, it is possible to find optimal values of operating variables, so that the properties of bleached pulps differ slightly from their best values and instead will save chemical reagents, energy and plant size, operating with lower values of operating variables. Thus, operating with a soda concentration of 1.13%, a hydrogen peroxide concentration of 2.25%, for a time of 3 hours, it was possible

to obtain a pulp with a brightness of 75.1% (8.1% below the maximum) and a viscosity of 740 mL/g (10.4% less than the maximum value).

ACKNOWLEDGMENTS

The authors are grateful to Spain's DGICyT and MICINN for funding this research within the framework of the Projects CTQ2007-65074-C02-01, TRA2009-0064, FUNCICEL-CTQ2009-12904, and ENZFIBRECELL-CTQ2010-20238-CO3-01.

REFERENCES CITED

Aracri, E., and Vidal, T. (2011). "Xylanase- and laccase-aided hexenuronic acids and lignin removal from specialty sisal fibres," *Carbohydr. Polym.* 83, 1355-1362.

Aziz, A. A., Husin, M., and Mokhtar, A. (2002). "Preparation of cellulose from oil palm empty fruit bunches via ethanol digestion: Effect of acid and alkali catalysts," *J. Oil Palm Research* 14(1), 9-14.

Caparrós, S., Díaz, M. J., Ariza, J., López, F., and Jiménez, L. (2008). "New perspectives for *Paulownia fortuni* L valorisation of the authohydrolysis and pulping processes," *Bioresource Technol*. 99, 741-749.

Daud, W. R. W., Law, K. N., and Valade, J. L. (1998). "Chemical pulping of oil palm empty fruit bunches," *Cell. Chem. Technol*. 32(1-2), 133-143.

Dence, C. W., and Reeve, D. W. (1996). *Pulp Bleaching. Principles and Practice*, TAPPI Press, Atlanta, USA.

Freire, C., Silvestre, A., Neto, C., and Evtuguin, D. (2006). "Effect of oxygen, ozone and hydrogen peroxide bleaching stages on the contents and composition of extractives of *Eucalyptus globulus* kraft pulps," *Bioresource Technol*. 97, 420-428.

Ghazali, A., Wanrosli, W. D., and Law, K. N. (2006). "Alkaline peroxide mechanical pulping (APMP) of oil palm lignocellulosics. Part 2. Empty fruit bunch (EFB) responses to pretreatments," *Appita J*. 59, 1, 65-70.

Goenadi, D. H., Away, Y., Suharyanto, P., Panji, T., Watanabe, T., and Kuwahara, M. (1998). "Bio-pulping of empty fruit bunches of oil palm by white rot fungi isolated from tropical plantation," International Conference on Biotechnology in the Pulp and Paper Industry, 7th, Vancouver, B.C., June 16-19, B, 49-51.

http://www.arbolesornamentales.com, acceded October 2010

Ibrahim, R. (2002). "Chemical composition of alkaline pulps from oil palm empty fruit bunches," *Oil Palm Bulletin* 44, 19-24.

Jang, J. S. R., Sun, C. T., and Mizutani, E. (1997). *Neuro-Fuzzy and Soft Computing: A Computational Approach to Learning and Machine Intelligence*, Prentice Hall

Jiménez, L., Angulo, V., Caparrós, S., and Ariza, J. (2007). "Comparison of polynomial and neural fuzzy models as applied to the ethanolamine pulping of vine shoots," *Bioresource Technol*. 98, 3440-3448.

Jiménez, L., Pérez, A., Rodríguez, A., and De la Torre, M. J. (2006). "New raw materials and pulping processes for production of pulp and paper," *Afinidad* 63, 525, 362-369.

Jiménez, L., Ramos, E., De la Torre, M. J., Pérez, I., and Ferrer, J. L. (2008). "Bleaching of soda pulp of fibres of *Musa textilis nee* (abaca) with peracetic acid," *Bioresource Technol*. 99, 1474-1480.

Jiménez, L., Serrano, L., Rodríguez, A., and Sánchez, R. (2009a). "Soda-anthraquinone pulping of palm oil empty fruit bunches and beating of the resulting pulps," *Bioresource Technol*. 100, 1262-1267.

Jiménez, L., Serrano, L., Rodríguez, A., and Ferrer, A. (2009b). "TCF bleaching of soda-anthraquinone and diethanolamine pulp from oil palm empty fruit bunches," *Bioresource Technol*. 100, 1478-1481.

Law, K. N., and Jiang, X. (2001). "Comparative papermaking properties of oil-palm empty fruit bunch," *Tappi J*. 84, 1, 95.

López, F., Ariza, J., Eugenio, M. E., Díaz, J., Pérez, I., and Jiménez, L. (2001). "Pulping and bleaching of pulp from olive tree residues," *Process Biochem*. 37, 1-7.

López, F., Díaz, M. J., Eugenio, M. E., Ariza, J., Rodríguez, A., and Jiménez, L. (2003). "Optimization of hydrogen peroxide in totally chlorine free bleaching of cellulose pulp from olive tree residues," *Bioresour. Technol*. 87, 255-261.

López, F., Eugenio, M. E., Díaz, M. J., Pérez, I., and Jiménez, L. (2002). "Bleaching of olive tree residues pulp with peractivc acid and comparative study with hydrogen peroxide," *Ind. Eng. Chem. Res.* 41, 3518-3525.

Malaysian Palm Oil Promotion Council (MPOPC), http://www.mpopc.org acceded October 2010

Moldes, D., Cadena, E. M., and Vidal, T. (2010). "Biobleaching of eucalypt kraft pulp with a two laccase-mediator stages sequence," *Bioresource Technol.* 101, 6924-6929.

Montgomery, D. C. (1991). *Design and Analysis of Experiments*, Grupo Editorial Iberoamericana, Mexico, México, pp. 303.

Pedrola, J., Roncero, M. B., Colom, J. F., Vidal, T., and Torres, A. L. (2004). "Application of an experimental design to modelling the hydrogen peroxide stage in TCF bleaching of eucalypt pulp," *Appita J*. 57, 141-145.

Quader, M. M. A., and Lonnberg, B. (2005). "Pulp and chemical cellulose obtained with oil palm empty fruit bunches by a modified IDE process," *JIRCAS Working Report* 39, 47-53.

Roliadi, H., and Pasaribu, R. A. (2004). "The posible utilization of empty oil-palm bunches as a substitute of pulp wood for the manufacture of corrugating-medium paperboard using semi-chemical soda-anthraquinone pulping," APPITA Annual Conference and Exhibition, 58th, 2, 335-341.

Ramos, E., Calatrava, S. F., and Jiménez, L. (2008). "Bleaching with hydrogen peroxide. A review," *Afinidad* 65, 537, 366-373.

Rodríguez, A., Serrano, L., Moral, A., Pérez, A., and Jiménez, L. (2008a). "Use of high-boiling point organic solvents for pulping oil palm empty fruit bunches," *Bioresource Technol*. 99, 1743-1749.

Rodríguez, A., Pérez, A., De la Torre, M. J., Ramos, E., and Jiménez, L. (2008b). "Neural fuzzy model applied to ethylene-glycol pulping of non-wood raw materials," *Bioresource Technol*. 99, 965-974.

Roncero, M. B., Torres, A. L., Colom, J. F., and Vidal, T. (2003). "TCF bleaching of wheat straw pulp using ozone and xylanase. Part A: Paper quality assessment," *Bioresource Technol.* 87, 305-314.

Shatalov, A. A., and Pereira, H. (2005). "*Arundo donax* L. reed: New perspectives for pulping and bleaching. Part 4. Peroxide bleaching of organosolv pulps," *Bioresour.Technol*. 96, 865-872.

Torres, A. L., Roncero, M. B., Colom, J. F., Martínez, J. A., and Vidal, T. (2004). "Application of an experimental design to modeling of ozone bleaching stage in TCF processes," *Ozone Sci. Eng.* 26, 443-451.

Valls, C., Molina, S., Vidal, T., Del Río, J. C., Colom, S. F., Martínez, A. T., Gutiérrez, A., and Roncero, M. B. (2009). "Influence of operation conditions on laccase-meduiator removed of sterols from eucalypt pulp," *Process Biochem*. 44, 1032-1038.

Valls, C., and Roncero, M. B. (2009). "Using both xylanase and laccase enzymes for pulp bleaching," *Bioresour.Technol*. 100, 2032-2039.

Valls, C., Vidal, T., Gallardo, O., Díaz, P., Pastor, F. I. J., and Roncero, M. B. (2010a). "Obtaining low-HexA-content cellulose from eucalypt fibres: Which glycosil hydrolase family is more efficient?" *Carbohydrate polymers* 80, 154-160.

Valls, C., Vidal, T., and Roncero, M. B. (2010b). "Boosting the effect of a laccase-mediator system by using a xylanase stage in pulp bleaching," *J. Hazard. Mater.* 177, 586-592.

Villaverde, J. J., Ligero, P., and Vega, A. (2009). "Bleaching *Miscanthus x giganteus* acetosolv pulps with hydrogen peroxide/acetic acid. Part 1: Behaviour in aqueous alkaline media," *Bioresource Technol.* 100, 4731-4735.

Wanrosli, W. D., Zainuddin, Z., and Lee, L. K. (2004). "Influence of pulping variables on the properties of *Elaeis guineensis* soda pulp as evaluated by response surface methodology," *Wood Sci. Technol*. 38(3), 191-205.

Article submitted: December 17, 2010; Peer review completed: February 19, 2011; Revised version received and accepted: March 1, 2011; Published: March 3, 2011.