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Leucaena diversifolia a new raw material for paper production by soda-ethanol pulping process

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ABSTRACT

Pulping and papermaking of *Leucaena diversifolia* by soda-anthraquinone-ethanol was studied using an experimental design in order to investigate the effects of cooking variables: temperature, time, soda concentration, ethanol concentration and wash-disintegrate temperature on the pulp yield and the physico-chemical characteristics of paper sheets (tensile index, burst index, tear index and brightness). Previously, in order to assess the potential of plants of this raw material grown over short periods, its results were compared with those of other leucaena varieties and the best crop among three grown for 1–3 years was selected. The results were evaluated using the response surface methodology with a view to identifying the most suitable operating conditions. In accordance with biomass production and the features of the raw materials and cellulose pulp obtained, the *L. diversifolia* grown for 2 years was found to be the most suitable choice for obtaining pulp and paper among the five leucaena varieties examined. Suitable physical characteristics of paper sheets (tensile index, burst and tear index) and acceptable yield pulping and brightness could be obtained by operating at medium temperature, active alkali concentration, pulping time, ethanol concentration and wash-disintegrate temperature.

Keywords: Pulping; Organosolv; *Leucaena diversifolia*; Paper

1. Introduction

Population growth and the increase in paper consumption have given rise to worldwide raw material shortages. According to the ASPAPEL information, paper production in Spain was about 6.35 million tons in 2006, with an increase in the production of 11.5% and consumption of raw materials for pulp and papermaking has also grown in parallel. Cellulose pulp production worldwide rose by 10.8% over the period 2003–2007 (192 million tons in 2008). Related to the increasing concern about environmental and economic issues, the need for alternative materials in substitution of conventional wood is evident. This is in agreement with the substantially increased use of non-wood raw materials (from 12,000 t in 2003 to 850,000 t in 2006) (FAO, 2009; EUROSTAT, 2009). Besides this, in the last decade, a great attention of the European agricultural research was focused on the search of new non-food and high-yield short-rotations crops with perspective for industrial utilisation (Shatalov and Pereira, 2005). Thus, high-yield fiber plants offer enormous potential to provide a productive new resource for the pulp and fiber manufacturing sector (Mansfield and Weineisen, 2007).

On this basis, *Leucaena diversifolia*, an example of an annually harvested high-yield and short-rotations fibers plant, was the raw material studied in this work, as potential pulping raw material and alternative source fibers. The interest in *L. diversifolia*, a leguminous tree, arises from the easy adaptability to Mediterranean ecological conditions (Rout et al., 1999; Ma et al., 2003), high biomass productivity, beneficial effects in the restoration of degrade soils (Vanlauwe et al., 1998; Sharma et al., 1998), and ability to intensive cultivation, combined with appropriate chemical composition for pulp and paper industry. References to the pulping of *L. diversifolia* are not found, however. Only three references of the same authors (Díaz et al., 2007; López et al., 2008; Alfaro et al., 2009) have been found. Other specie (*Leucaena leucocephala*) has been studied by Malik

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et al. (2004), González et al. (2008), Majumder and Ghosh (1985), Shibahare and Patel (2002), Khristova et al. (1988), Bhola and Sharma (1982), Jiménez et al. (2007) and Gillah and Ishengoma (1993, 1995).

Additionally, the pulping processes based on sulphur-free organic solvents could be considered as an important alternative to kraft and sulphite processes due to the use of less polluting and easily recoverable organic reagents (Mcdonough, 1993). Organosolv processes use either low- or high-boiling solvents that have been evaluated and revised by different authors (Muurinen, 2000; López et al., 2006; Rodríguez and Jiménez, 2008; Lavarack et al., 2005). In organosolv process is possible to break up the lignocellulosic biomass to obtain cellulosic fibers for pulp and papermaking, high quality hemicelluloses and lignin degradation products from generated black liquors, avoiding emission and effluents (Asiz and Sarkanen, 1989; Hergert, 1998; Paszner, 1998; Sidiras and Koukios, 2004). For pulp and papermaking, the method called the soda-ethanol process has been used by adding ethanol and anthraquinone to the alkaline liquor. Under this process, pulps with high-yield, low residual lignin content, high brightness and good strength properties can be produced (Shatalov and Pereira, 2004; Yawalata and Paszner, 2004). Moreover, valuable byproducts from hemicelluloses and sulphur-free lignin fragments useful for production of lignin-based adhesives and other products due to its high purity, low molecular weight, and abundance of reactive groups can be obtained (Dapía et al., 2002; Pan et al., 2005).

In this work the best year for harvest of *L. diversifolia* was selected for pulp and papermaking. This selection was made according biomass production, chemical properties of raw material and pulp and physical properties of paper sheets. Then a central composite factorial design was employed to examine the influence of the independent cooking variables (temperature, time, ethanol concentration, soda concentration and temperature of wash-disintegrate) on the pulping and papermaking of *L. diversifolia* using ethanol/soda/water mixtures. The resulting screened yield, tensile index, burst index, tear index and brightness of the paper sheets were then predicted with a view to identifying the most suitable operating conditions.

2. Materials and methods

2.1. Raw material

Plant was obtained from seed, for *L. diversifolia* and was used in this experiment. These plants were grown in a nursery, in 300 cm^3 pot holders; they were inured from bacterium Rhizobium and, when they were 3 months old, they were changed to the ground in La Rábida (Huelva, south-western Spain). Field experiments were carried out in two plots with a complete randomized block design with 4 replicates per provenance. Any fertilization was not added to plots. The soil at the experimental site was sandy loamy with a pH of 6–8 and having moderate to substantial depth. The sample, representing *L. diversifolia* provenance aged from 1 to 2 to 3 years, and the sprouts again of the plant after the first year cut, were collected (pruning was always made during winter). In this work, *L. diversifolia* samples from 3-harvest year were used for characterization, pulp and papermaking. *L. diversifolia* from 2-harvest year was evaluated for optimization of process conditions.

Representative foliage and branch wood samples were collected for moisture estimation and chemical analyses, in a random fashion. For yield estimation, four randomly selected plants per plot were cut at the base of the crown. The samples were immediately transferred to the laboratory in double-sealed polyethylene bags. After recording the fresh weights, they were dried to constant weights at 70 °C, and ground to pass through a 2 mm sieve. Estimates of dry weight biomass were obtained from the fresh weights of various plants types and their corresponding moisture contents. The average biomass of component parts per plant was multiplied by the number of plants per plot and extrapolated to a hectare.

2.2. Characterization of the raw material, pulp and paper

L. diversifolia wood trimming sample were milled to pass an 8 mm screen, since no diffusion limitations were observed for the particle size in preliminary studies. Samples were air-dried, homogenized in a single lot to avoid differences in composition among aliquots, and stored.

Characterization experiment involved the following parameters: 1% NaOH solubles (Tappi 212 om-98), hot water solubles (Tappi 207 cm-93), ethanol-benzene extractives (Tappi 204 cm-97), α-cellulose (Tappi 203-om-93), Klason lignin (Tappi T 222 om-98) and holocellulose (Wise et al., 1946) contents. All treatments in this study were in a completely randomized design with five replications (variation coefficient less than 5%. less than 1% for Kappa number, holocellulose and α-cellulose contents).

For determination of fiber length, 100 individual fiber were measured from each variety. Statistical analyses were performed using ANOVA and the differences among varieties were compared using Tukey's test. The means were separated on the basis of least significant difference at 0.05 probability level.

The superiors calorific values (constant volume) were determinate according "CEN/TS 14918:2005 (E) Solid biofuels—Method for the determination of calorific value" and UNE 164001 EX standards by using a Parr 6300 Automatic Isoperibol Calorimeter.

L. diversifolia wood trimming were used for pulp and papermaking. Characterization experiments of pulp involved the following parameters: same parameters than raw material, yield (Tappi 257), viscosity (Tappi T230 om-94.) and Kappa number (Tappi 236 cm-85). From paper sheets, grammage can be determined (T 220 sp-96), burst index (Tappi T 403 om-97), tear index (Tappi 414 om-98), tensile index (Tappi 494 om-96) and brightness (Tappi 525 om-92).

2.3. Pulping produce and formation of paper sheets

Cellulose pulps (1-, 2- and 3-year-old raw material; Table 1) were obtained using a 4-L bath cylindrical reactor that was heated by means of electrical resistances and linked to a control unit including the required instrument for measurement and control of the pressure and temperature. The control unit included temperature and pressure gauges as well as appropriate safety devices. The initial liquor to solid ratio was 8:1 (dry wt. basis); the aqueous soda concentration in the cooking liquor was 21% by weight; the ethanol concentration was 30% in volume and the anthraquinone concentration was 0.05% in weight. The reactor was then closed and simultaneously heated and activated to assure good mixing and uniform swelling of the wood. The temperature was set at 185 °C for 60 min and preheating was done for 30 min to reach

Table 1 – Energetic, physical and chemical characterization of the first year *Leucaena diversifolia* and sprouts, after prunings, with one year, second and third year and pulp and paper obtained.

Leucaena diversifolia, raw material	Hot water solubles (%)	1% NaOH solubles (%)	Ethanol–benzene extractives (%)	Holocellulose (%)	Klason lignin (%)	α-Cellulose (%)	Fiber length (mm)	Superior calorific value (constant volume. Over dry basis) (cal/g)
First year and sprouts[a]	3.2 (0.1)	17.4 (0.8)	4.4 (0.3)	77.9 (6.1)	19.0 (2.5)	40.1 (2.4)	0.81 (0.09)	
Second year[a]	2.7 (0.1)	15.9 (1.1)	3.8 (0.4)	75.2 (1.3)	21.0 (4.8)	41.6 (3.5)	0.82 (0.42)	
Third year	4.1	16.4	1.7	65.8	24.8	38.0		4529.7 (7.9)

Pulp from *Leucaena diversifolia*	Hot water solubles (%)	1% NaOH solubles (%)	Ethanol-benzene extractives (%)	Holocellulose (%)	Klason lignin (%)	α-Cellulose (%)
First year and sprouts[a]	0.7 (0.1)	2.8 (0.4)	1.9 (0.1)	94.5 (6.3)	1.74 (0.4)	81.4 (2.5)
Second year[a]	1.0 (0.2)	1.6 (0.1)	0.7 (0.1)	94.5 (6.0)	1.4 (0.1)	79.9 (4.5)
Third year	0.48	2.47	0.30	92.9	5.70	772

Paper from *Leucaena diversifolia*	Yield (%)	Kappa number (pulp)	Viscosity (pulp) (cm^3/g)	Tensile index (kN m/kg)	Burst index (kN/g)	Tear index ($mN\,m^2/g$)
First year and sprouts[b]	41.0	10.7	725	13.8	0.56	0.85
Second year[b]	46.4	17.4	881	20.3	0.80	1.20
Third year	39.7	23.7	675	10.8	0.32	0.81

Leucaena diversifolia biomass production (t/ha)

First year		Second year		Third year	
WDW	TDW	WDW	TDW	WDW	TDW
4.83 ± 0.94	7.45 ± 1.46	28.25 ± 5.33	43.58 ± 8.22	35.18 ± 7.74	50.48 ± 8.64

Percentages with respect to initial raw material (100 kg o.d.b.). Data for third harvest year have been obtained in this work. TDW: Total dry biomass; WDW: woody dry biomass.

[a] Díaz et al. (2007), the values in parentheses are standard deviation.

[b] López et al. (2008).

Table 2 – Values of the independent variables yield and the physical properties of the paper sheets.

Normalized values of temperature (X_T), time (X_t), active alkali concentration (X_A), ethanol concentration (X_E) and was/disintegrate temperature (X_{WD})	Screened yield (%)	Tensile index (kN m/kg)	Burst index (MPa m^2/kg)	Tear index (N m^2/kg)	Brightness (%ISO)
+1 +1 +1 +1 +1	38.2	15.0	0.59	0.83	40.4
+1 +1 +1 −1 −1	39.4	14.2	0.51	0.87	40.3
+ 1 +1 −1 +1 −1	54.9	15.3	0.59	0.99	24.4
+1 +1 −1 −1+1	52.7	16.4	0.62	0.94	21.3
+ 1 −1 +1−1 −1	42.6	15.4	0.63	0.84	42.9
+ 1 −1 +1 −1 +1	42.7	14.0	0.51	0.93	44.6
+ 1 −1 −1 +1 +1	56.5	11.8	0.45	0.83	25.7
+ 1 −1 −1 −1 −1	54.5	13.1	0.50	0.88	21.7
−1 +1 +1 +1 −1	47.5	13.1	0.47	0.73	43.9
−1 +1 +1 −1 +1	49.9	15.1	0.52	0.88	45.4
−1 +1 −1 +1 +1	57.9	8.7	0.31	0.65	26.0
−1 +1 −1 −1 −1	59.3	14.2	0.24	0.67	25.4
−1 −1 +1 +1 +1	51.9	13.2	0.43	0.71	39.4
−1 −1 +1 −1 −1	61.2	6.2	0.30	0.74	27.4
−1 −1 −1 +1 −1	63.1	7.3	0.28	0.72	25.3
−1 −1 −1 −1 +1	65.0	7.2	0.31	0.64	24.6
+1 0 0 0 0	47.4	17.9	0.74	1.00	36.3
−1 0 0 0 0	55.3	16.9	0.57	0.87	38.2
0 +1 0 0 0	47.3	18.4	0.71	0.99	40.8
0 −1 0 0 0	51.1	15.8	0.67	0.96	39.2
0 0 +1 0 0	45.4	15.6	0.56	1.00	46.4
0 0 −1 0 0	57.9	14.6	0.50	1.06	28.2
0 0 0+1 0	49.9	15.5	0.71	0.99	39.2
0 0 0 −1 0	50.4	16.3	0.71	0.94	39.2
0 0 0 0 +1	50.2	17.0	0.68	1.03	42.1
0 0 0 0 −1	50.8	18.7	0.71	1.04	39.4
0 0 0 0 0	49.7	17.4	0.68	1.03	41.0

the temperature mentioned. Finally, to open the reactor, the liquor was quickly refrigerated by internal heat exchanger to obtained low-pressure levels. Following cooking, the pulp was separated from the liquor and disintegrated, without disturbing the fibers during 3 min (2500 rpm), washed on a sieve of 16 mm mesh (the process separating the pulp into a suspension of individual fibers in water and the process of cleaning the dispersed fibers after cooking in this study have been performed at different temperatures). The pulp was defibered on a Sprout–Waldron refiner and passed again thought a Strainer filter (0.4 mm mesh) in order to isolate the uncooked material (<0.5%).

Paper sheets were prepared with an ENJO-F-39.71 sheet machine according to the Tappi 205 sp-95 standard.

2.4. *Experimental design for the pulping conditions*

To be able to relate the dependent and independent variables with the minimum possible number of experiment, 2^n central composite factor design that enabled the construction of second-order polynomial in the independent variables and the identification of statistical significance in the variables was used. Independent variables were normalized by using the following equation:

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

where X is the absolute value of the independent variable concern, $\bar{X}$ is the average value of the variable, and $X_{\max}$ and $X_{\min}$ are its maximum and minimum values, respectively. The pulping temperature (X_T), pulping time (X_t), soda concentration (X_A), ethanol concentration (X_E) and wash-disintegrate temperature (X_{WD}) used in the different experiments of the design were 170, 180 and 190 °C; 45, 60 and 75 min; 12%, 17% and 22% NaOH; 30%, 45% and 60% EtOH (v/v) and 20, 45 and 70 °C wash/disintegrate temperature, respectively. First column in Table 2 shows the experimental matrix of runs, factors with their levels and central points.

The independent variables used in the equations relating to both types of variables were those having a statistical significant coefficient (viz. those not exceeding a significance level of 0.05 in the student's *t*-test and having a 95% confidence interval excluding zero).

3. Results and discussion

L. diversifolia was selected among 6 different Leucaena varieties (*Leucaena colinsii, L. diversifolia, Leucaena salvadorensis*, and three varieties of *L. leucocephala*: India, Honduras and K360) examined in previous studies (Díaz et al., 2007; López et al., 2008). In Table 1 results from energetic, physical and chemical characterization of raw material and the results from cellulose pulp and paper sheets characterization from 1-, 2- and 3-year-old *L. diversifolia* are shown. Total dry biomass and woody dry biomass results in 3 years are shown.

For this work, this biomass production from third year harvest (3-year-old plants) has also been evaluated. *L. diversifolia* produced 11.73 ± 2.58 t ha^{-1} year^{-1} of woody dry biomass (35.18 ± 7.74 t) in 3 years and 50.48 ± 8.64 t of total biomass, so it cannot be said that there is an increase in biomass production through next growing years. From the first and second year the biomass production were 4.83 ± 0.94 and 14.13 ± 2.68 t ha^{-1} year^{-1}. It is according with the idea of "fast growing and high pulp yielding trees, which can be grown in all types of soils like semi and arid regions" for *L. leucocephala* (Malik et al., 2004). Also, the "potential use as energetic crop"

Table 3 – Equations yielded for each dependent variable.

Eq.	Equation	r^2	F	% Error
1	$YI = 50.00 - 5.72X_A - 4.57X_T - 2.31X_t - 0.70X_E - 0.46X_{WD} + 1.33X_AX_A + 1.03X_TX_T - 1.31X_TX_A + 1.12X_TX_E + 0.97X_TX_t - 0.87X_AX_E - 0.57X_tX_A - 0.52X_AX_{WD}$	0.99	124.6	4.3
2	$TI = 17.34 + 1.83X_T + 1.46X_t + 0.75X_A - 2.79X_AX_A - 1.97X_EX_E - 0.94X_tX_E + 0.94X_AX_E + 0.90X_AX_{WD} - 0.66X_TX_t$	0.93	26.5	4.6
3	$BI = 0.729 + 0.095X_T + 0.040X_A + 0.027X_t + 0.013X_E - 0.158X_AX_A - 0.068X_TX_T - 0.031X_{WD}X_{WD} - 0.038X_TX_{WD} - 0.038X_EX_{WD} - 0.032X_TX_A + 0.022X_AX_E + 0.014X_tX_{WD}$	0.99	101.0	8.7
4	$TEI = 1.03 + 0.083X_T + 0.017X_t - 0.100X_TX_T - 0.070X_EX_E - 0.060X_tX_t - 0.034X_TX_A - 0.031X_EX_{WD} - 0.023X_AX_E + 0.023X_AX_{WD}$	0.97	64.5	5.3
5	$BR = 41.24 + 8.23X_A + 1.04X_{WD} + 0.96X_E + 0.95X_t - 4.71X_TX_T - 3.39X_AX_A - 2.03X_TX_t - 1.63X_EX_{WD} + 1.27X_TX_A - 1.27X_TX_{WD} - 1.12X_tX_{WD} + 0.99X_tX_A + 0.91X_AX_{WD} - 0.79X_tX_E$	0.99	107.2	4.4

where YI denotes yield (%), TI the tensile index (kN m/kg), BI the burst index, TEI the tear index, BR the brightness and X_T, X_t, X_A, X_E and X_{WD} the value of the temperature, time, active alkali concentration, ethanol concentration and wash/disintegrate temperature respectively. The differences between the experimental values and those estimated by using the previous equations never exceeded 10% of the former (15% for tensile index).

is another interesting idea. The superior calorific value of *L. diversifolia* is comparable with other wood raw materials like Eucaliptus globulus (4590 cal/g).

It seems clear that strong material lignification occurs from the first year to the second and, especially, the third, with simultaneous small reductions in holocellulose (3.5% between the first and second year, and 12.5% between the second and third). Simultaneously, the lignin content can increase by 9.4% and 15.3%, respectively, over these periods. The contents in α-cellulose evolve similarly. Based on the standard deviations and coefficients of variation for the results, the differences between some were statistically insignificant; however, the results of the subsequent characterization tests for the pulp and paper samples confirmed the hypothesis that lignification was more marked between the second and third year, which suggests that 2-year-old plants can be used as a short-rotation crop.

Accurately determining the contents in lignin, cellulose and various other components of cellulose pulp is quite difficult. Variability in the raw material, and the high complexity of pulping processes and analytical methods themselves, add an intrinsic difficulty. The results of the chemical characterization of the pulp samples, shown in Table 1, exhibited scarcely significant differences. There were some isolated significant differences such as an increase in lignin from the first and second year to the third (more than 70%), and also in α-cellulose content from the first year to the third (5.4%). As a rule, lignification was stronger during the second year, with slight reductions in the holocellulose and α-cellulose contents, but substantial increases in lignin content, of the pulp from the first year to the third, consistent with the variation of lignin in the raw material. Paper characteristics development in pulps obtained from first, second or third *L. diversifolia* harvest are much more clear about advisable to select the second pruning material for paper manufacture. The tensile, burst and tear index are maximum for second year material. Cellulose pulp yield and viscosity have also been highest for second year harvest and Kappa number shows a growing tendency.

Cellulose chemical-pulp and paper sheets have been obtained from second year harvest *L. diversifolia* with different experimental conditions and anthraquinone was not used. The normalized values of independent variables and properties of the pulp and paper sheets obtained in the pulping process, using the proposed experimental designs are shown in Table 2. Each value in experimental results is an average of two (pulp yield) or twelve (tensile, burst, tear index and brightness) samples. The deviations for these parameters from their respective means were all less than 5%. Substituting the values of the independent variables for each dependent variable in Table 2 into the polynomial expression used yielded the equations shown in Table 3. The difference between the three replicates of the central point (the mean value is shown in each case) was less than 5%.

As can be seen, the tensile, burst and tear index of paper sheets from *L. diversifolia* plants harvested the second year (Table 1) were better than those obtained with the proponed experimental design (Table 2). This was a result of using no anthraquinone in the later case. Despite its commercial cost, however, its use would no doubt improve on the results of Table 2 (Loewendahl and Samuelson, 1978; Francis et al., 2006).

Identifying the independent variables with the strongest and weakest influence on the dependent variables in Eqs. (1)–(5) is not so easy since the former contain quadratic terms and other factors involving interactions between two independent variables. In any case, these results warrant some comment.

Thus, the temperature was individual variable with the strongest linear influence on the physical properties of the paper sheets (tensile, burst and tear index). The treatment time and alkali concentration influenced the properties to a different extent, but invariably increased them in proportion. The active alkali concentration was the most influential variable on yield and brightness. Also, except for the linear temperature, which was the sole independent variable lacking statistical significance in the modelling equation for brightness (Eq. (5)), all linear coefficients for the independent variables were statistically significant and reflected a favourable effect on brightness development and an adverse effect on yield growth.

The analysis of quadratic terms reveals that both the lower and upper bounds of the variation ranges for the dependent variables would be inappropriate to obtain good paper properties. With the tensile index, for example, the negative, relatively large coefficients of the quadratic terms for the active alkali and ethanol concentrations suggest the need to use conditions near the central point in the design in their respective ranges of variation. Thus, too low active alkaline and ethanol concentrations would fail to provide adequate delignification, whereas too high concentrations of both chemicals would favour delignification of fibers and have a negative impact on the tensile index as a result. A similar comment can be made as regards the quadratic terms for the treatment temperature, disintegration temperature and, again, active alkali concentration ($-X_AX_A$) as regards burst index, and also for the treatment time and ethanol concentration ($-X_EX_E$) as regards tear index. Brightness also exhibits high, statistically significant coefficients for the temperature ($-X_TX_T$) and active alkali concentration. The influential quadratic terms for pulp yield are identical to those for brightness, albeit positive and much less significant.

Regarding interactions, the wash-disintegration temperature exhibits a substantial influence that was barely significant in the linear and quadratic terms. Worth special note in this respect is its positive interaction with the active alkaline (X_AX_{WD} term) concentration on the tensile strength, tear index and brightness, which suggests that using a high active alkali concentration would preclude efficient removal of degradation products at low wash-disintegration temperatures, thereby having an adverse impact on paper strength indices and brightness. The interaction of the wash-disintegration temperature with the ethanol concentration ($-X_EX_{WD}$ term) was negative and statistically significant in Eqs. (3)–(5) (burst and tear index and brightness). If we accept the need to use intermediate ethanol concentrations owing to the presence of the $-X_EX_E$ quadratic term in some of our models, then it would also be advisable to employ intermediate wash-disintegration temperatures. This assumption is additionally supported by the presence of $-X_TX_{WD}$ interaction terms in Eqs. (3) (burst index) and (5) (brightness), and $-X_tX_{WD}$ terms in Eq. (5) (brightness), consistent with our previous comments on linear and quadratic terms as regards avoiding the extremes of the variation ranges for the independent variables temperature and treatment time.

As in the interaction of the wash-disintegration temperature with the treatment temperature, the negative sign of the terms in the temperature-treatment time ($-X_TX_t$) and ethanol concentration-treatment time ($-X_tX_E$) terms present in Eqs. (2) (tensile index) and (5) (brightness) suggest the need to use medium levels of these independent variables.

The independent variable active alkali concentration is the most influential as regards the presence of interaction terms; however, it has contradictory effects on the dependent variables. Thus, the $+X_AX_E$ and $+X_TX_A$ terms in Eqs. (2)–(5) (tensile, burst and tear index and brightness) suggest the need to operate near the upper bounds of the active alkali concentration range; however, a negative sign in such terms would suggest the opposite and an effect of the variable difficult to quantify. The $-X_AX_E$ and $-X_TX_A$ terms are especially important – they have high coefficients – in Eq. (4) (tear index).

The equations of Table 3 can be used to derive additional information via Fig. 1. Fig. 1 shows a plot of each dependent variable against each independent one constructed by changing all the independent variables between the normalized values from −1 to +1. At a given value of an independent variable, the magnitude of the difference between the maximum and minimum values of the dependent variable is related to the influence of the independent variables other than that plotted on the variation of the dependent variable concerned.

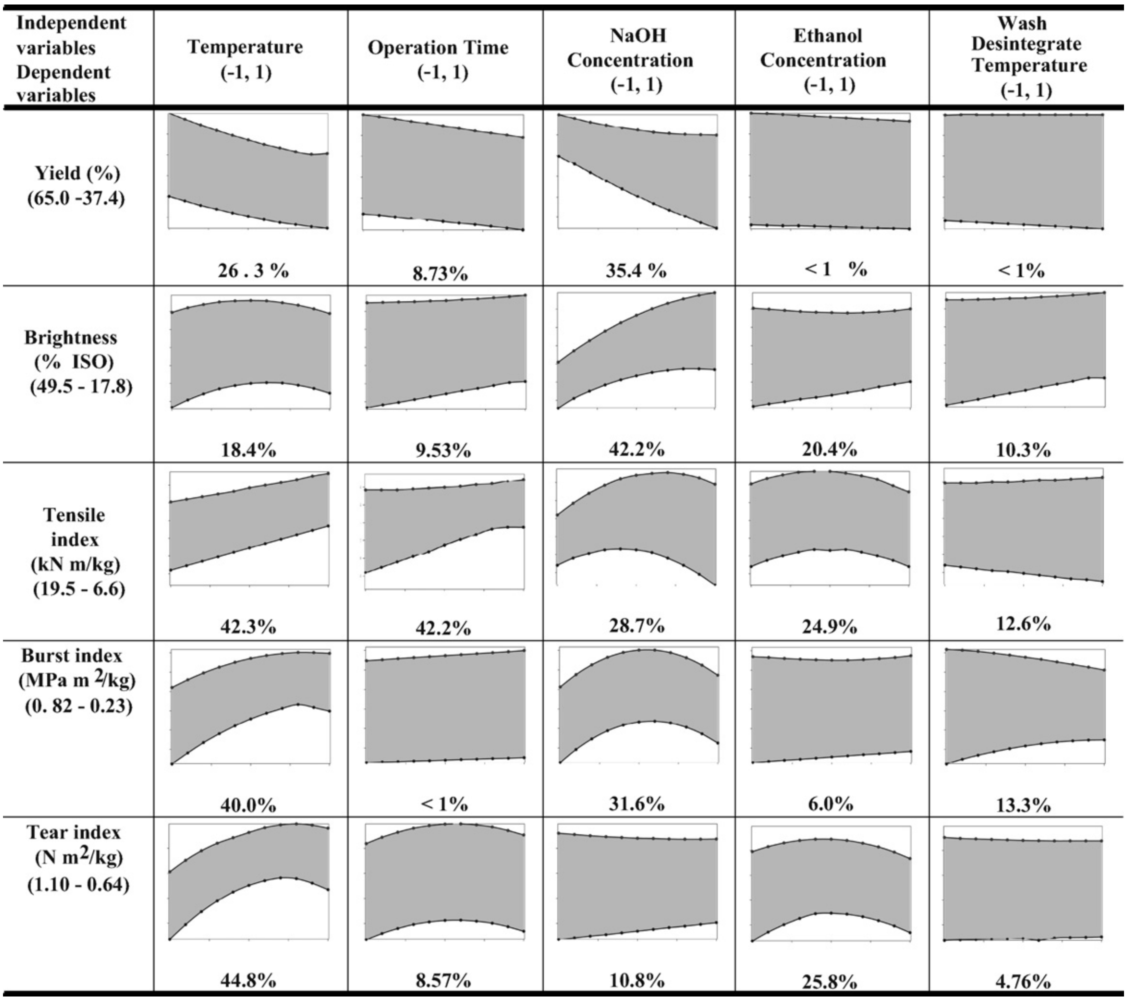

Fig. 1 – Variation of dependent variables as a function of normalized independent variables.

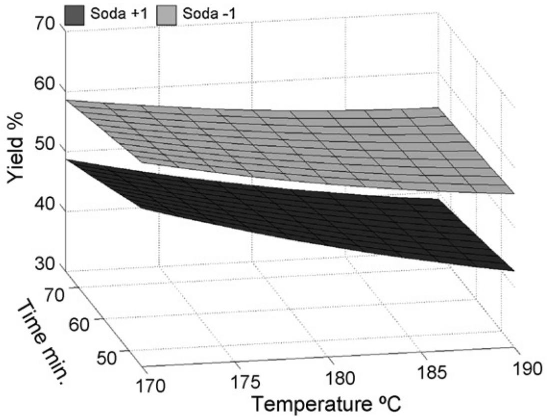

Fig. 2 – Yield variations as a function of temperature and time operation at two NaOH concentration levels.

Methodology for obtaining Fig. 1 is described in previous works from Díaz et al. (2005).

Very briefly, and consistent with the previous comments, the active alkali concentration and treatment temperature are the variables most strongly influencing all dependent variables (the strength-related properties of the paper sheets in the latter case, and pulp yield and brightness in the former).

In order to determine the values of the independent variables giving the optimum values of dependent variables, the response surfaces for each dependent variable were plotted at two extreme levels of the independent variable most strongly influencing each (Fig. 1) and a fixed value of the two least influential variables (Figs. 2–6).

As can be seen from Figs. 2 and 3, obtaining a high pulp yield or brightness entails using high active alkali concentrations and medium values of all other variables. On the other hand, Figs. 4–6, which show the variation of the strength-related indices, suggest the need to use a high treatment temperature and medium levels of the other variables. These conclusions are according with the previous analysis of linear and quadratic terms, and their interactions. For example, the decrease in yield (Eq. (1)) to be expected from using an alkali concentration of 17% (0) rather than 22% (+1) was less than 10% with respect to the experimental values for the central point in the experimental design (0 0 0 0 0 in Table 2). For brightness, the difference was 10.7%. Similarly, using a temperature of 180 °C (0) rather than 190 °C (+1), would result in tensile, burst and tear indices lower than those for the central point in the experimental design by 10.5%, 4.0% and −1.7%, respectively.

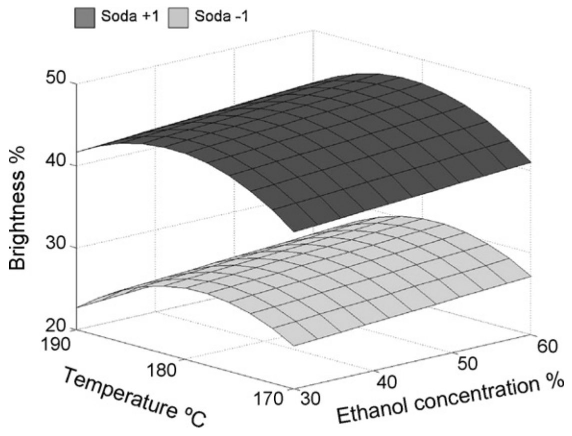

Fig. 3 – Brightness variations as a function of ethanol concentration and temperature operation at two NaOH concentrations levels.

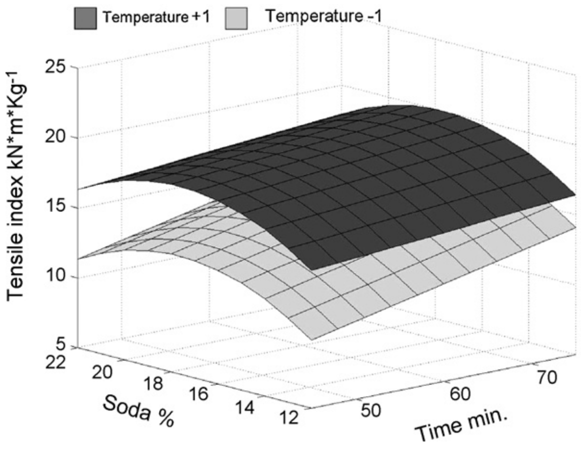

Fig. 4 – Tensile index variations as a function of NaOH concentration and time operation at two temperature levels.

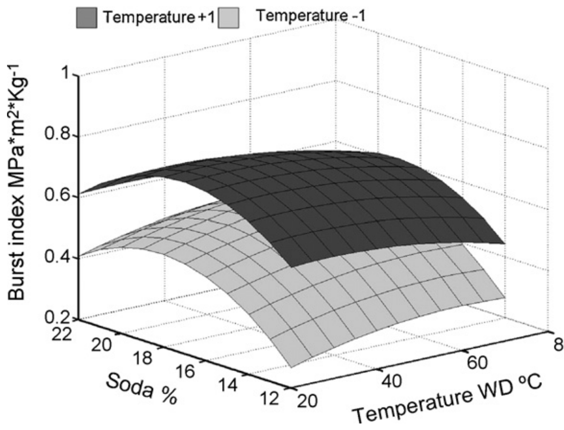

Fig. 5 – Burst index variations as a function of NaOH concentration and wash-disintegrate temperature at two temperature levels.

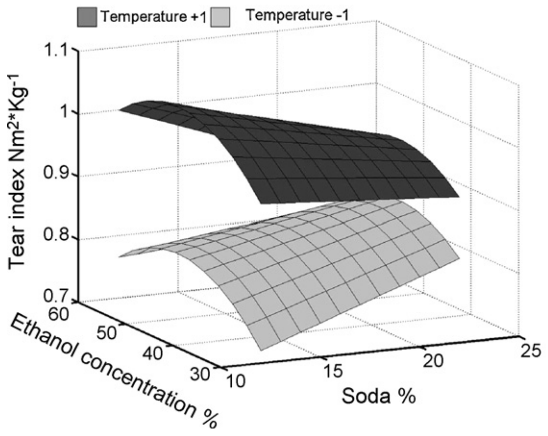

Fig. 6 – Tear index variations as a function of ethanol concentration and NaOH concentration at two temperature levels.

Relating to pulp and paper properties, Kappa number (17.4 with anthraquinone)/brightness (>40.0 ISO) are considerably good for an organosolv/soda paper and the other physical properties (without refining) are also acceptable (González et al., 2008; Caparrós et al., 2008) for a huge range of uses of the paper obtained. The mechanical properties of the papers are

Table 4 – Chemical characterization of *Leucaena leucocephala* and pulp and paper obtained.

Leucaena leucocephala	Holocellulose (%)	Klason lignin (%)	α-Cellulose (%)	Hot water solubles (%)	Ethanol-benzene extractables (%)	1% NaOH solubles (%)	Pulping yield	Kappa after pulping	Tensile index (kN m/kg)	References
NaOH pulping		21.5	57.7	2.5	1.6	17.6		18		Majumder and Ghosh (1985)
Kraft pulping with anthraquinone	67.5	24.9		10.5	3.8	24.9	30.3–32.9	25.8–32		Shibahare and Patel (2002)
Kraft pulping		21.4	41.8	9.4	5.1	21.3	42.5–47.7	20.5–40.3	5.3–8.4 (50° SR)	Khristova et al. (1988)
Kraft pulping	76.6	26.1		4.0	3.3	12.6 (0.1N soda)	47.8–56	22.2–51.9	1.9–3.5 (without refining); 6.2–7.7 (4000 PFI), 42.7 (without refining); 77.5–88.5 (1000 PFI)	Bhola and Sharma (1982)
Kraft pulping							49.5	28		Gillah and Ishengoma (1993, 1995)
Ethanol or ethylene glycol pulping	76.0	21.0	44.0	4.0	5.0	18.0	54–58	120.6–132.3	3.4 (41° SR)–3.7 (45° SR)	Jiménez et al. (2007), González et al. (2008)

acceptable and compare with those of good hardwood kraft pulps (Khristova et al., 1988).

Unlike previous work by Gillah and Ishengoma (1993, 1995) on *L. leucocephala* kraft pulp harvested in the tenth growth year (yield 49.5%, kappa number 28, average tensile strength with 2000 *H*-factor and 20% effective alkali content), better or at least comparable results have been obtained with lower active alkali needs and a lower tree production period. Similar comments could be made to respect previous works by other authors on *L. leucocephala* varieties (Table 4). Majumder and Ghosh (1985) indicate that strength properties of *L. leucocephala* have been found to be remarkably good and better than those other species.

This would support the hypothesis that the *L. diversifolia* is suitable as a material for papermaking in intermediate operation conditions within the selected variation range: around 15–19% of alkali concentration, 40–50% ethanol concentration, 55–65 min of operation time, wash-disintegration temperatures between 40 and 50 °C and with operation temperature between 175 and 185 °C. Applying these conditions to the models in Table 3, the results from central point in Table 2 would be obtained.

4. Conclusions

In accordance with biomass production (43.7 t ha^{-1} of total biomass in 2 years) and the features of the raw materials and cellulose pulp obtained (kappa number, 17.4; viscosity, 881 cm^3/g, α-cellulose, 79.9%, tensile index, 20.3 kN m/kg), the *L. diversifolia* specie in its second year of growth was the most suitable pulp and papermaking lignin cellulose material among the three harvest year studied.

Suitable physical characteristics of paper sheets (tensile index, burst and tear index) and acceptable yield pulping and brightness could be obtained by operating at medium temperature (180 °C), active alkali concentration (17%), pulping time (60 min), ethanol concentration (45%, v/v) and wash-disintegrate temperature (45 °C) by using a soda-ethanol-anthraquinone pulping process.

The pulp obtained at these conditions has suitable chemical (yield pulp) and physical (paper sheets) characteristics: yield (49.7%), brightness (41% ISO), tensile index (17.4 kN m/kg), burst index (0.68 MPa m^2/kg) and tear index (1.03 N m^2/kg).

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