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Title: Optimization the soda-AQ process for cellulose pulp production and energy content of black liquor from L. leucocephala K360

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Abstract: A commercial variety of Leucaena leucocephala K 360 was used for pulp production and papermaking employing the soda-anthraquinone process. Also, the chemical and energy contents of the resultant black liquors were determined to simultaneously optimize: pulp and paper production and energy generation. A process temperature of (185 °C), an operating time of (120 min) and an active alkali concentration of (21%) provided sheets of paper with good strength (tensile index of 12.12N m/g, burst index of 0.38 kPa m2/g, tear index of 1.29 mN m2/g and a Kappa number of 20.5) and black liquor with a greater calorific value (14.1 MJ/kg) than that obtained with higher active alkali concentrations.

However, reducing the active alkali concentration to a level in the low operation range led to less marked degradation of cellulose and allowed paper sheets with good properties to be obtained and energy to be optimally produced from the black liquor.

List the change

We agree with changes made by the editor. These changes have been highlight in yellow and new changes have been highlight in green.

The changes have been made about the file Word BITE-D-11-05292R2:

Page 7, line 1: "The chemical characterization is comparable to other Leucaena varieties and hardwoods.
Optimum results on the properties of viscosity and resistance of the sheets of paper
Black liquor with greater calorific value than to high active alkali concentrations" was changed by "The chemical composition of *Leucaena leucocephala* is comparable to that of other Leucaena varieties and hardwoods.
Optimum conditions for the production of sheet papers with optimal viscosity and resistance were determined.
Black liquor with greater calorific value was obtained at low active alkali concentration."

Page 8, line 1: "Optimization of *L. leucocephala* K360 use by soda-AQ process for cellulose pulp production and energy use of black liquor" was changed by "Optimization the soda-AQ process for cellulose pulp production and energy content of black liquor from *L. leucocephala* K360".

Page 9, line 5: Abtract changed until 150 words. "A commercial improved variety of *Leucaena leucocephala* inoculated with rhizobium was used for pulp production and papermaking by use a sodaanthraquinone process. Also, black liquors were characterized in chemical and energetic terms to simultaneously optimize both process: pulp and paper and energetic use.
The process to high process temperatures (185 °C), operating time intermediate (120 min) and low active alkali concentration (21%) provides sheets of paper with good strength properties of paper and black liquor with greater calorific value (14.1 MJ/kg) than to high active alkali concentrations.
Optimum results on the properties of viscosity and resistance of the sheets of paper (tensile index of 12.12N m/g, burst index of 0.38 kPa m2/g, tear index of 1.29 mN m2/g and Kappa number of 20.5) were obtained operating at high temperatures, high active alkali concentration and intermediate operating time. However, these conditions were low losses in cellulosic pulp yield (45.9%) and the fraction of glucan (39.6%)."
was changed by
"A commercial variety of *Leucaena leucocephala* K 360 was used for pulp production and papermaking employing the soda-anthraquinone process. Also, the chemical and energy contents of the resultant black liquors were determined to simultaneously optimize: pulp and paper production and energy generation. A process temperature of (185 °C), an operating time of (120 min) and an active alkali concentration of (21%) provided sheets of paper with good strength (tensile index of 12.12N m/g, burst index of 0.38 kPa m^2/g, tear index of 1.29 mN m^2/g and a Kappa number of 20.5) and black liquor with a greater calorific value (14.1 MJ/kg) than that obtained with higher active alkali concentrations.
However, reducing the active alkali concentration to a level in the low operation range led to less marked degradation of cellulose and allowed paper sheets with good properties to be obtained and energy to be optimally produced from the black liquor."

Page 11, Line 1: "an improved variety of Leucaena leucocephala" was changed by "the Leucaena leucocephala variety, which was selected in terms of its improved biomass yield"

Page 11, line 46: "2 and 10 mm in length" was changed by "2 and 10 mm in length by use in the reactor".

Page 11, line 49: “Samples were air-dried, homogenized stored at room temperature.” was changed by “Samples were air-dried, homogenized by mixing, and stored at room temperature”.

Page 12, line 11: “water up 4% H_2SO_4” was changed by “water to reduce H_2SO_4 content to 4%”.

Page 12, line 16: “by filtration” was changed by “by filtration through a Büchner funnel”.

Page 13, line 41: “from the liquor and disintegrated” was changed by “from the liquor by screening and disintegrated”.

Page 13, line 44: “high concentration pulper machine” was changed by “high concentration pulper machine (Metrotec S.A.).”

Page 14, line 24: “the variables was identified” was changed by “the variables were identified by t-student test (>2) and significace level p (< 0.5).”

Page 14, line 24: “and a lesser degree of substitution with arabinose” was changed by “Arabinose was less substituted than acetyl groups”

Page 19, line 35: “agricultural residues” was changed by “agricultural residues such as some some residues of fruit trees, fruit residues, gardening residues and sewage sludge (Feria et al., 2011b), cardoon, biomass residues of forest from poplar or pine (Gravalos et. al., 2010) or Arhar stalks (*Cajanus cajan*) and rice husk (Kumar et al., 2002)”.

And the references were added:

Kumar, A., Purohit, P., Rana, S., Kandpal, T.C., 2002. An approach to the estimation of the value of agricultural residues used as biofuels. Biomass Bioenerg. 22 (3), 195-203.

Gravalos, I., Kateris, D., Xyradakis, P., Gialamas, T., Loutridis, S., Augousti, A., Anastasios Georgiades, A., Tsiropoulos, Z. 2010. A study on calorific energy values of biomass residue pellets for heating purposes. FORMEC. Padova – Italy

Page 19, line 40: “The pH values were” was changed by “The pH values of black liquor were”.

Page 20, line 40: “Garcia Hortal” was changed by “Garcia-Hortal”. and the reference was changed too.

Page 23, line 40: “Although the effect was very limited in the case of viscosity ” was changed by “The effect of active alkali concentration on viscosity was very limited.”.

Page 23, line 52: “and in the fraction of glucan was excessive decreases.” was changed by “the glucan content was decreased to an excessive extent”.

Page 25, line 39: the conclusions were changed by: “Leucaena leucocephala is an interesting industrial crop for producing pulp, paper and energy. The paper sheets with the best properties were obtained by using a high active alkali concentration and temperature, and a medium operating time, in the alkaline delignification step. However, reducing the active alkali concentration to a level in the low operation range led to less marked degradation of cellulose and allowed paper sheets with good properties to be obtained and energy to be optimally produced from the black liquor."

Page 28, line 32: "Journal of Bangladesh Academy of Sciences" was changed by "J. Bangladesh Acad. Sci.".

Page 28, line 42: "Journal of Scientific and Industrial Research" was changed by "J. Sci. Ind. Res.".

Page 29, line 26: "414-415, pp. 231-243" was changed by "414-415, 231-243".

Table 1: "Chemical composition of *Leucaena leucocephala* and other raw materials." Was changed by "Chemical composition of *Leucaena leucocephala*, *Eucalyptus globulus*, and *Leucaena diversifolia* biomass."

Table 1: the footnote was changed to "[1] Bhola and Sharma,1982 [2] Majumer and Gosh,1985 [3] Jímenez et al.,2007 [4] Malik et al.,2004 [5] Garrote et al.,2004 [6] López et al.,2010b [7] Feria et al., 2011a [8] López et al.,2010a [9] Feria et al., 2009 [10] Telmo et al., 2010."

***Highlights (for review)**

The chemical composition of *Leucaena leucocephala* is comparable to that of other Leucaena varieties and hardwoods.

Optimum conditions for the production of sheet papers with optimal viscosity and resistance were determined.

Black liquor with greater calorific value was obtained at low active alkali concentration.

Optimization the soda-AQ process for cellulose pulp production and energy content of black liquor from *L. leucocephala* K360

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Abstract

A commercial variety of *Leucaena leucocephala* K 360 was used for pulp production and papermaking employing the soda-anthraquinone process. Also, the chemical and energy contents of the resultant black liquors were determined to simultaneously optimize: pulp and paper production and energy generation. A process temperature of (185 °C), an operating time of (120 min) and an active alkali concentration of (21%) provided sheets of paper with good strength (tensile index of 12.12N m/g, burst index of 0.38 kPa m^2/g, tear index of 1.29 mN m^2/g and a Kappa number of 20.5) and black liquor with a greater calorific value (14.1 MJ/kg) than that obtained with higher active alkali concentrations.

However, reducing the active alkali concentration to a level in the low operation range led to less marked degradation of cellulose and allowed paper sheets with good properties to be obtained and energy to be optimally produced from the black liquor.

Keywords

Soda anthraquinone process, energetic crops*, Leucaena leucocephala,* pulp, black liquor

1. INTRODUCTION

Non-wood plants offer several advantages over wood species as sources of papermaking fibers, including short growth cycles, moderate irrigation requirements and low lignin contents which help to alleviate energy and chemical requirements during pulping (Hurter and Riccio, 1998). The pulp and paper industry is the sixth largest industrial energy user in Europe and a major user of biomass. Usually black liquor generated during the Kraft process is burnt in a boiler to recover energy in the form of electricity, process utility steam, and pulping chemicals; however, black liquor could also be used as a source of biofuels.

The fast-growing, nitrogen-fixing tree/shrub *Leucaena leucocephala*, is cultivated as a fodder plant, for green manure, as a windbreak or as a biofuel crop. Leucaena has been widely introduced in Chine due to its beneficial qualities (Guo et al, 2012; Yu et al, 2012); but has become an aggressive invader in many tropical and sub-tropical locations. This tree can form dense monospecific thickets and is difficult to eradicate once established.

Leucaena species have a high production of biomass and re-sprout capacity of more than 50 tons/ha/year, (Sánchez et al., 2003, Feria et al., 2012). Pulping and papermaking from varieties of *L. diversifolia* and *L. leucocephala* by the soda-anthraquinone-ethanol process have already be explored (Díaz et al., 2007, López et al., 2008,López et al., 2010a, Feria et al., 2012).

In the present work, the *Leucaena leucocephala* variety, which was selected in terms of its improved biomass yield, was used for pulp production and papermaking by the soda-anthraquinone process and the process was optimized to obtain the best properties of paper and energy recovery from black liquor. Also, the black liquors were chemically and energetically characterized.

2. MATERIALS AND METHODS

2.1. Raw material.

Leucaena leucocephala K360 biomass. was harvested after seven years of growth in Huelva (southwestern Spain). The plants were grown in a nursery, in 300-cm^3 pots for three months, then planted in the field. Field experiments were carried out in two plots with a complete randomized block design with 4 replicates per plots. No fertilizers were added to the plots. The soil was sandy loamy with a pH of 6–8 at the experimental site and had moderate to substantial depths. The productivity of *L. Leucocephala* was 49.6 ± 10.67 ton/ha/yr of total dry weigh, and the harvested timber weighed 86 kg (Feria et al., 2011a), the *Leucaena leucocephala* samples were milled to pass an 8-cm screen, reduced to pieces between 2 and 10 mm in length by use in the reactor, and fines were removed by sieving through a 0.6-mm mesh. Samples were air-dried, homogenized by mixing, and stored at room temperature.

Samples of the homogenized wood (10 g) were characterized with respect to acetone extractives (TAPPI T 280 wd-06 "Acetone Extractives of Wood and Pulp"), hot water solubles (TAPPI T 207 cm-08) and holocellulose contents (Wise et al., 1946). The samples were subjected to moisture determination by drying at 105 ºC to constant weight (TAPPI T-264-cm-07) and to quantitative acid hydrolysis with 5 mL of 72% sulphuric acid at 30º C for 1 h, followed by adding water to reduce H_2SO_4 content to 4% to perform a posthydrolysis at 121 ºC for 60 min, (TAPPI T 249 cm-09). The solid residue after hydrolysis was recovered by filtration through a Büchner funnel and considered as Klason lignin (TAPPI T 222 om-06). Acid-soluble lignin was determined following the standard method (TAPPI T 250 wd-96). The monosaccharides (glucose, xylose, arabinose) and acetic acid contained in the hydrolysates were quantified by high performance liquid chromatography (HPLC), using an ion exchange column (Aminex HPX-87H) at 30ºC; 0.05 M H_2SO_4 as mobile phase at a flow rate of 0.6 mL/min. Ashes were determined by calcinations (TAPPI T 244 cm-99).

The gross calorific values (constant volume) were determinate according to CEN/TS 14918:2005 (E) and UNE 164001 EX standards by using a Parr 6300 automatic Isoperibol calorimeter.

2.2. Pulp and black liquor characterization

Acetone extractives, hot water soluble, holocellulose contents, Klason lignin, soluble lignin, glucan and xylan contents were determined as stated in section 2.1., Pulping yield, Kappa number and viscosity were determined according to TAPPI T 257 cm-02, TAPPI T 236 om-06 and TAPPI T 230 om-04, respectively.

The characterization of black liquor was carried out by determining: pH, residual alkali (titrated according to TAPPI T 625 wd-99), and % total dry matter content (TAPPI T 650 om-09). The solid contents of black liquor were obtained after freeze-drying in a CRYODOS 22960 and determined as described in section 2.1.

2.3. Pulp production

Wood chips, water, soda and anthraquinone were mixed in the desired proportions and reacted in a 10-L stainless steel, reactor (MK-systems Inc.) fitted with recirculation. The operating conditions were 169, 177 and 185ºC; 90, 120 and 150 min operating time, and 21, 25 and 29% NaOH and 0.1% anthraquinone and a liquid/solid ratio of 8 kg water per kg of raw material on a dry basis (the moisture content of the material was considered to be water). Previous studies demonstrated that the influence of the variation of the liquid/solid ratio was negligible between 7 and 10 kg water per kg of raw material (Garrote et al., 2001).

The reactor was closed and simultaneously heated and actuated to assure good mixing and uniform swelling of the Leucaena chips. Once the pulping time had elapsed, the reactor was cooled to 25 ºC. Following cooking, the pulp was separated from the liquor by screening and disintegrated, without breaking the fibers, for 20 min in a high concentration pulper machine (Metrotec S.A.).

2.4. Paper sheet formation

Paper sheets were prepared with an ENJO-F-39.71 sheet machine according to TAPPI T 205 sp-06. Grammage, and burst, tear index and tensile indexes, Schopper-Riegler degree and ISO brightness were determined according to TAPPI T 220 sp-06, TAPPI T 403 om-10, TAPPI T 414 om-04, TAPPI T 494 om-06, (ISO 5267/1, TAPPI T 525 om-06, respectively.

2.5. Experimental design for pulping process

In order to relate the dependent (yield, soluble lignin, calorific value, glucose, xylose, kappa number, viscosity, acetone extractives, holocellulose, Klason lignin, hot water, soluble lignin, brightness, and tensile, burst and tear indexes) and independent variables (temperature, time and soda concentration) in the pulping process with the minimum possible number of experiment, a 2^n central composite factor experimental design was used, making it possible to construct a second-order polynomial. The statistical significance in the variables were identified by t-student test (>2) and significace level p (< 0.5) . Independent variables were normalized by using the following equation.

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

Where *X* is the absolute value of the independent variable concern $\overline{X}$ is the average value of the variable, and Xmax and Xmin are its maximum and minimum values respectively. Temperature and operation time have the highest influence. The range of variation of independent variables was determined according to previous experiments (data not show) and other studies (Alfaro et al., 2009, López et al., 2010).

The number of tests required was calculated as $N = 2^n + 2 \cdot n + n_c$, 2^n being the number of points constituting the factor design, 2n that of axial points, and n_c that of central points. Under the conditions used, N = 10.

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

$$Y = a_o + \sum_{i=1}^{n} b_i X_{ni} + \sum_{i=1}^{n} c_i X_{ni}^2 + \sum_{i=1; j=1}^{n} d_i X_{ni} X_{nj} \quad (i < j)$$

3. RESULTS AND DISCUSSION

3.1. Raw material characteristics

The chemical characterization of *Leucaena leucocephala* K360 and of other wood types is shown in Table 1. The major fraction was cellulose (analyzed as glucan) at 37.2% (or 41.0% as α-cellulose TAPPI T 203-om-93), followed by the Klason lignin at 24.1% (after quantitative acid hydrolysis) and hemicelluloses fraction (calculated as the sum of xylan, araban and acetyl groups) at 19.9%. This composition is similar to that found by other authors for *Leucaena leucocephala* and other varieties of Leucaena, and is comparable to that of other raw materials such as *Eucalyptus globulus* (Table 1). With regard to hemicelluloses, the principal fraction affected by hydrothermal treatments, the molar relation between the different monomers was as follows:

Xylose: Acetyl groups: Arabinose = 17.1:9.9:1

The predominant monomer was xylose, with a similar degree of acetyl groups substitution (up to 10 xylose molecules for each 5.7 monomer with acetyl groups) as that of other lignocellulosic materials. Arabinose was less substituted than acetyl groups. This composition is typical of O-acetyl glucuronoxylans, present in hardwoods (Tunc and Van Heiningen, 2008).

The content of acetone extractive compounds in *L. leucocephala* (Table 1) *was* 1.1%, lower than that of eucalyptus wood (2.09%) and that of Leucaena found by other authors (1.64-8.19%)(Bhola and Sharma, 1982; Majumer and Gosh, 1985; Jímenez et al., 2007; Malik et al., 2004). These compounds could cause problems related to pitch deposits in the manufacturing of pulp (Gutiérrez et al., 2003).

The holocellulose content in *L. leucocephala* K360 was in the range of that of other Leucaena varieties (between 3.3% higher and 8.5% lower) and higher (5.5%) than that reported for *Eucalyptus globulus*. The Klason lignin values were higher than those for *Eucalyptus globulus* (Garrote et al., 2004) and those observed in previous studies on *L. leucocephala* (Majumer and Gosh, 1985; Malik et al., 2004). Glucan, xylan, araban and acetyl group values were similar to those from other Leucaena varieties and eucalyptus wood, but the ash content was higher than that of similar species of Leucaena (52.9%)(Malik et al., 2004).

The gross heating value for *L. leucocephala* was slight lower than that of *L. diversifolia* (2.0%) (Feria et al., 2009) and other solid biofuels such as willow and one-year-old poplar (Klasnja et al., 2002), but higher than that of *Populus euramericana* or *Eucalyptus globulus* (between 18.8 MJ/kg and 17.0 MJ/kg) (Telmo et al., 2010).

3.2. Pulp and paper production and characterization

Table 2 presents results for total pulp yield, acetone extractives, hot water soluble, holocellulose, Klason lignin, soluble lignin, glucan and xylan contents using the proposed experimental design. Each value is an average of results obtained with two (pulp yield) or four samples. Table 3 presents properties of black liquor from the *Leucaena leucocephala* pulping process (pH, residual alkali, % solid and gross heat of solid liquor). Each value is an average of three samples. Table 4 shows Kappa number, viscosity and results from the physical characterization of paper sheets (brightness, tensile index, burst index and tear index). Each value is an average of data obtained from twelve samples. The deviations for these parameters from their respective means were less than 5%. Substituting the values of the independent variables for each dependent variable in the polynomial expression yielded the equations shown in Table 5. The difference between the three replicates of the central point (the mean value is shown in each case) was less than 5 or 10% in all cases.

Identifying the independent variables with the strongest and weakest influence on the dependent variables in equations in Table 5 is not easy since the former contain quadratic terms and other factors involving interactions between two independent variables. The influential linear term of the temperature in the process was the most important in the development of strength properties of paper sheets, viscosity, and chemical properties of cellulose pulp with the exception of the fraction of hemicelluloses. Effectively, pulp yield, and hot water soluble, holocellulose, glucan and xylan content were more affected by the linear variation of the concentration of active alkali or the process time which indicates the importance of these variables on the hydrolysis of hemicellulose fraction in the range of temperatures considered. An increase in any of the three independent variables was always accompanied by a linear decrease in process yield. Pulp yields were between 36.6 and 51.7% (Table 2). A strong dependence of yield on concentration of active alkali in the pulping process can be concluded. Yields were significantly lower than those obtained in a similar soda-anthraquinone-ethanol process reported by López et al. (2011) with *Leucaena diversifolia* with yields between 38.2 and 65.0%.

Specifically, the concentration of alkali was the most influential linear term for the variation of yield and xylan content. Process time was the most influential term for variation in glucan and holocellulose. Process time, with a negative sign, suggest the use of a low or intermediate operating times to avoid excessive degradation of cellulose. Achieving a fixed Kappa number and efficiency in the cooking process were the two objectives of the experimental design, along with preserving yield and a requirement of only moderate consumption of reagents.

A large part of the wood (about 50%) is dissolved in the cooking liquor in a traditional Kraft pulp mill. The dry matter content of black liquor is typically 12 to 18 wt%. Kraft black liquor contains four main groups of organic constituents; 30-45 wt% ligneous material (polyaromatic), 25-35 wt% saccharinic acids (hydroxyl acids), about 10 wt% formic and acetic acid and 3-5 wt% extractives. It also contains about 1 wt% methanol and many inorganic elements, mainly sodium (17-20 wt%) and sulphur (3-5 wt%). The composition of black liquor varies considerably depending on the cooking process and the wood used (Wallberg et al., 2004). The properties of black liquor determined with the current study show a strong linear dependence on the active alkali concentration. A similar linear dependence was observed in the case of pH and residual alkali, (the soda remaining unreacted in the liquor. This observation suggests that the soda can be recovered in the process). The greater extraction of solids (mainly hemicellulose) at higher active alkali concentrations, could contribute to a decrease in the gross heat value because the hemicellulosic fraction was predominantly extracted. This fraction has a lower gross heat than the cellulosic fraction.The gross heating value for the black liquor from *L. leucocephala* is similar to that of cotton stalks or olive trimming residues and higher than that of agricultural residues such as some residues of fruit trees, fruit residues, gardening residues and sewage sludge (Feria et al., 2011b), cardoon, biomass residues of forest from poplar or pine (Gravalos et. al., 2010) or Arhar stalks (*Cajanus cajan*) and rice husk (Kumar et al., 2002) but it was not higher than that of wood (Table 1).

The pH values of black liquor were similar to those obtained with traditional Kraft processes. Solids extraction (the total dry matter content was measured in the black liquor obtained from the reactor) was lower than that of the Kraft process. This result means that not all the solids were extracted from the pulp, because the liquid of the washing pulp was not recovered. The total dry matter contents were similar to those obtained by Wallberg et al., 2004.

The analysis of quadratic terms revealed that the lower and upper bounds, of the variation ranges for the dependent variables would be inappropriate to obtain good paper properties and pulp viscosity. With respect to the tensile index, for example, the negative sign and, relatively large coefficients of the quadratic terms for the process temperature and process time suggest the need to use conditions near the central point in the design in their respective ranges of variation. Thus, a process temperature or operation time too low would not provide an adequate delignification (see equations Y_{Ka} with high coefficients for X_TX_T and X_CX_C terms with positive sign). A worse kappa number at temperatures and alkali concentrations at high ranges of operation is obtained. Whereas values of time and temperature that are too high favor delignification of fibres and have a negative impact on the tensile index because the cellulose or hemicellulose fraction is degraded faster than the lignin fraction. The quadratic term of the active alkali concentration (X_CX_C) has a slightly positive effect on viscosity, the burst and tear indexes, considering that the hemicelluloses content is important to the physical properties of paper sheets (García-Hortal, 2007).

The contents of Klason lignin and viscosity depend mainly on the dependent variable, temperature. For lignin Klason, the value is similar to those obtained by López et al. (2011) for *Leucaena diversifolia*, ranging between 0.4 and 11.4%; but the kappa numbers are substantially better than those reported by López et al. (2011), ranging between 9.8 - 57.8, and those of cellulose pulp obtained from a Kraft process (20.5 to 40.3) using *L. leucocephala* (Khristova et al., 1988) or that obtained by Ghilla et al. (1995) of 28. The values for viscosity are lower than those obtained by López et al. (2011) for *Leucaena diversifolia* which ranged between 595 and 1504 cm^3/g.

The values for tensile, burst and tear indexes, and for brightness were similar to those obtained by López et al. (2010a) for *L. diversifolia* ranging between 6.2 and 18.7 N m/g, 0.24 and 0.74 kPa m^2/g, 0.64 and 1.06 mN m^2/g and 21.3 and 46.4%ISO, respectively , but were higher than those obtained by Jiménez et al. (2007) for *L. leucocephala* in an ethyleneglycol process (3.07 N m/g, 1.32 kPa m^2/g, 0.24 mN m^2/g and 37.56%ISO respectively). These properties improve significantly through a refined process, as has been shown in previously with on *Leucaena diversifolia* (Feria et al., 2012).

Although a sheet of paper can be formed by simple felting, the sheets do not have commercial interest because of their weakness and lack of resistance. The properties of different types of paper depend on process equipment, additives, and mixtures of pulp from different types of raw materials (www.paperonweb.com, 2012). The typical bond office and coated papers, test liners and newsprints have tensile indexes of 40 – 175 N m/g, burst indexes of 1.2 – 4.3 kPa m^2/g and tear indexes of 6.25 – 9.7 mN m^2/g. These properties are for bleached paper, but Leucaena unbleached pulp has similar properties.

The interactions terms, temperature and time interaction (X_TX_t) exhibited a substantial influence on the majority of properties studied, except for those related to black liquor, where the influence of the interaction term, X_TX_C, dominated. The influence of the X_TX_t term was to be expected in terms of higher solubilization of the fraction of polysaccharides and lignin.

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 and a fixed value of the two least influential variables (Fig. 1a to 1f).

The response surface corresponding to the variation of yield (Fig. 1a) shows a decrease in yield at high active alkali concentrations. Temperature and process barely affect the variation of yield except at a high temperatures and processing times. In fact, the holocellulose content (Fig. 1b) showed a sharp decline in the range of intermediate to high operating times, especially at elevated temperatures.

Similar influences were observed for hot water, acetone solubles and for xylan contents (data not shown), although in the last case, all independent variables had a significant influence on solubilization of hemicelluloses (evaluated as the fraction of xylan). The soluble lignin surface response suggests that an intermediate time and soda concentration should be used. The Kappa number decreased with a rise in temperature.

The glucan contents (Fig. 1c) suggest operations for low or intermediate times and at high temperatures. Overall, it could be argued that operating at intermediate operating times and temperatures favors lower fiber degradation and provides cellulose pulp from which sheets of higher strength could be obtained.

The surface responses corresponding to strength properties of paper sheets and viscosity showed a similar behavior as that of the glucan contents. High temperature had a favorable effect on the development of tensile, burst and tear indexes and viscosity. For example, the best tensile index (Fig. 1d) was obtained in the central interval of operating times and the effect of active alkali concentration was negligible. This behavior was analogous for the other four properties, although for the development of the burst index, the active alkali concentration had more of an influence. This outcome had already been observed in the quadratic term of the model $X_C X_C$ in Table 5 for Y_{BI} and Y_{vis}. The effect of active alkali concentration on viscosity was very limited.

Thus, the best results for viscosity and resistance of the sheets of paper were obtained at high operating temperatures and intermediate operating times. Furthermore, under these conditions, cellulose pulp losses were limited, the glucan content was decreased to an excessive extent.

Black liquor showed the expected behavior. Both, the residual alkali (data not shown) and solids content % (Fig. 1e) were greater at high alkali concentrations and temperatures, with negligible influence of operation time. The pH showed a similar behavior (data not shown).

Fig. 1f, shows the gross heating values, and indicates that high process temperatures and low active alkali concentrations provided black liquor with a greater calorific value than high active alkali concentrations. This finding is in accordance with the hypothesis that operating conditions in the upper ranges of the intervals lead to excessive degradation of the fiber (thus, the resistance of the sheets of paper decrease) and also a loss of calorific value in the black liquors by the addition of an amount of the hemicellulose fraction of lower calorific value.

4. CONCLUSIONS

Leucaena leucocephala is an interesting industrial crop for producing pulp, paper and energy. The paper sheets with the best properties were obtained by using a high active alkali concentration and temperature, and a medium operating time, in the alkaline delignification step. However, reducing the active alkali concentration to a level in the low operation range led to less marked degradation of cellulose and allowed paper sheets with good properties to be obtained and energy to be optimally produced from the black liquor.

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Table

Table 1: Chemical composition of *Leucaena leucocephala*, *Eucalyptus globulus,* and *Leucaena diversifolia* biomass.

	L. leucocephala					*Eucalyptus globulus*	*L. diversifolia*		
Reference	[1]	[2]	[3]	[4]	This work	[5]	[6]	[7]	[8]
Holocellulose, %	76.6		68.3	76.6	70.6	66.9	65.8	76.3	72.8
Klasson lignin, %	26.1	21.5	18.4	19.6	24.1	22.9	24.8	24.8	23.7
Glucan, %	n.d.	41.8	-	58.7	37.2	46.8-53.4	-	38	32.2
Xylan, %	-	-	-	-	17.1	14.2-16.6	-	15.7	15.5
Araban, %	-	-	-	-	1.0	0.4-0.54	-	1.5	1.0
Acetyl groups, %	-	-	-	-	2.8	3.6	-	3.3	2.1
Acetone extractives, %	3.3	1.6	8.2	2.6	1.1	2.1	1.7	-	3.9
Ash, %	0.8	1.0	2.2	0.9	1.3	0.4 [9]	-	1.6[9]	1.4
Gross heating value, MJ/kg, o.d.b.					18.945	17.000 [10]	18.840	19.324 [9]	19.083

% on dry basis. [1] Bhola and Sharma,1982 [2] Majumer and Gosh,1985 [3] Jímenez et al.,2007 [4] Malik et al.,2004 [5] Garrote et al.,2004 [6] López et al.,2010b [7] Feria et al., 2011a [8] López et al.,2010a [9] Feria et al., 2009 [10] Telmo et al., 2010.

Table 2: Normalized Values of Independent Variables (X_C: Alkali concentration, X_t and X_T: time and temperature of operation) and chemical characterization of pulps using the proposed experimental design. (* relative to the raw material -dry mass-).

Normalized values of independents variable: X_T X_t X_C			**Yield, %**	**Acetone extrac-tives, %**	**Hot water soluble, %**	**Holoce-llulose, %**	**Klason lignin, %***	**Soluble lignin, %**	**Glucan, %***	**Xylan, %***
0	0	0	41.2	2.5	2.5	90.0	1.9	1.0	28.3	4.5
0	0	0	41.1	2.5	2.6	90.1	1.8	1.0	27.2	4.4
-1	-1	-1	51.4	2.8	1.7	89.1	3.2	0.9	33.7	6.3
-1	-1	+1	40.9	3.2	2.0	85.1	2.0	0.8	31.5	5.3
-1	0	0	44.0	2.5	3.0	91.4	2.1	1.4	31.9	5.1
-1	+1	-1	51.7	2.0	4.4	84.1	2.4	1.0	36.2	6.6
-1	+1	+1	42.3	2.5	3.0	87.5	2.5	0.8	26.7	4.4
0	-1	0	42.2	2.9	1.7	92.0	2.2	0.7	24.8	5.4
0	0	-1	47.9	2.2	2.4	91.3	2.8	0.8	32.2	5.3
0	0	+1	38.6	2.2	1.8	90.5	2.0	0.9	30.1	4.0
0	+1	0	38.8	2.5	3.5	82.0	1.6	0.7	20.1	4.2
+1	-1	-1	51.5	3.1	3.2	85.7	2.6	0.9	35.1	7.3
+1	-1	+1	40.8	2.9	3.0	87.7	0.6	1.0	36.2	6.5
+1	0	0	38.6	3.0	3.7	84.4	1.0	1.4	34.0	5.0
+1	+1	-1	39.4	3.0	4.1	83.5	1.3	0.8	27.9	5.3
+1	+1	+1	34.7	3.0	3.5	78.7	0.7	0.8	26.7	4.2

Table 3: Properties of black liquor from *Leucaena leucocephala* pulping process.

Normalized values of independent variables: X_T X_t X_c			pH	Residual alkali (g/l)	% solid	Gross Heat of solid liquor (MJ/kg)
0	0	0	13.0	12.1	8.9	14.1
0	0	0	13.0	12.1	8.9	14.1
-1	-1	-1	12.9	10.9	7.7	14.0
-1	-1	+1	13.1	17.9	9.1	12.3
-1	0	0	13.2	14.5	8.4	12.6
-1	+1	-1	12.8	9.3	8.4	14.1
-1	+1	+1	13.1	17.2	9.5	12.4
0	-1	0	13.1	12.1	8.9	14.3
0	0	-1	12.4	8.1	8.3	15.1
0	0	+1	13.0	14.1	10.1	13.8
0	+1	0	12.9	12.1	9.3	14.6
+1	-1	-1	12.5	7.3	9.0	14.7
+1	-1	+1	13.1	12.9	10.8	13.3
+1	0	0	12.7	10.9	9.4	13.5
+1	+1	-1	11.8	6.0	8.8	14.8
+1	+1	+1	12.8	11.7	11.0	13.8

Table 4. Normalized values of independent variables and physical characterization of pulps and paper sheets obtained in the pulping process using the proposed the experimental design

Normalized values of independent variables: X_T X_t X_C			Schooper Riegler degree, ºSR	Kappa number	Viscosity, cm^3/g	Brightness, %	Tensile index, N m/g	Burst index, $MPa \cdot m^2/kg$	Tear index, mN m^2/g
0	0	0	20.0	17.4	597	33.1	13.6	0.42	1.33
0	0	0	19.5	17.7	600	33.2	13.4	0.38	1.29
-1	-1	-1	13.0	21.1	579	25.2	2.7	0.09	0.37
-1	-1	+1	15.5	21.1	683	31.1	4.0	0.14	0.49
-1	0	0	15.0	20.7	733	31.4	7.2	0.09	0.81
-1	+1	-1	16.0	22.6	820	27.9	6.0	0.17	0.75
-1	+1	+1	17.0	18.8	753	32.6	6.6	0.21	0.62
0	-1	0	19.0	16.1	522	32.9	11.2	0.38	0.84
0	0	-1	19.0	19.7	736	29.4	11.1	0.42	1.29
0	0	+1	21.5	17.3	679	35.0	15.4	0.63	1.53
0	+1	0	21.0	16.1	513	32.9	11.1	0.38	1.06
+1	-1	-1	17.0	18.9	612	28.7	11.0	0.30	0.78
+1	-1	+1	19.0	14.0	420	35.4	15.2	0.59	1.23
+1	0	0	19.5	16.1	472	33.9	14.4	0.38	1.39
+1	+1	-1	18.5	20.3	540	28.1	8.8	0.31	1.05
+1	+1	+1	21.0	12.9	292	32.4	12.3	0.52	1.25

Table 5. Equation obtained for each dependent variable of pulping process.

Equation	R^2	**F-Snedecor**
$Y_{Yl} = 40.98 - 2.53 X_T - 1.99 X_t - 4.46 X_C + 2.94 X_CX_C - 2.49 X_TX_t + 0.89 X_tX_C$	0.981	76
$Y_{Ka} = 17.33 - 2.21 X_T - 1.85 X_C + 1.20 X_TX_T - 1.12 X_tX_t + 1.26 X_CX_C - 1.06 X_TX_C - 0.79 X_tX_C$	0.985	74
$Y_{Acet} = 2.46 + 0.2 X_T - 0.19 X_t + 0.07 X_C + 0.32 X_TX_T + 0.27 X_tX_t - 0.23 X_CX_C + 0.19 X_TX_t - 0.14 X_TX_C$	0.980	43
$Y_{Holo} = 89.97 - 2.91 X_T - 3.17 X_t + 0.98 X_C - 2.10 X_TX_T - 2.80 X_tX_t - 1.19 X_TX_t$	0.991	169
$Y_{vis} = 607.2 + 123.2 X_T - 45.9 X_C - 103.1 X_tX_t + 86.7 X_CX_C - 63.8 X_TX_t - 59.5 X_TX_C - 28.3 X_tX_C$	0.982	62
$Y_{HW} = 2.53 + 0.34 X_T + 0.69 X_t - 0.25 X_C + 0.90 X_TX_T - 0.35X_CX_C - 0.27 X_tX_C - 0.29 X_TX_t$	0.963	30
$Y_{SL} = 1.02 + 0.37 X_TX_T - 0.33 X_tX_t - 0.18 X_CX_C + 0.05 X_TX_C - 0.05 X_TX_t$	0.967	59
$Y_{KL} = 1.91 - 0.614 X_T - 0.195 X_t - 0.451 X_C - 0.429 X_TX_T + 0.445 X_CX_C - 0.185 X_TX_c + 0.355 X_tX_C$	0.983	67
$Y_{GL} = 27.55 - 2.33 X_t - 1.39 X_C + 5.49 X_TX_T - 5.01 X_tX_t + 3.69 X_CX_C - 1.45 X_TX_C - 0.46 X_TX_t - 1.2 X_tX_C$	0.951	37
$Y_{XY} = 4.41 - 0.61 X_t - 0.64 X_C + 0.66 X_TX_T + 0.41 X_tX_t + 0.26 X_CX_C - 0.46 X_TX_t - 0.16 X_TX_C - 0.19 X_tX_C$	0.988	71
$Y_{pH} = 12.98 - 0.22 X_T - 0.13 X_t + 0.27 X_C - 0.23 X_CX_C + 0.14 X_TX_C - 0.11 X_TX_t - 0.06 X_tX_C$	0.985	77
$Y_{Alk} = 12.11 - 2.10 X_T - 0.48 X_t + 3.22 X_C + 0.57 X_TX_T - 1.03 X_CX_C - 0.45 X_TX_C$	0.993	205
$Y_{sol} = 8.97 + 0.57 X_T + 0.15 X_t + 0.83 X_C + 0.30 X_CX_C - 0.14 X_TX_t + 0.19 X_TX_C$	0.986	102
$Y_{GH} = 14.12 + 0.47 X_T + 0.11 X_t - 0.71 X_C - 1.08 X_TX_T + 0.32 X_CX_C + 0.32 X_tX_t + 0.13 X_TX_C$	0.993	160
$Y_{BR} = 33.49 + 0.97 X_T + 2.72 X_C - 1.23 X_TX_T - 0.68 X_tX_t - 1.38 X_CX_C - 0.45 X_tX_C - 0.98 X_TX_t$	0.996	291
$Y_{TI} = 13.42 + 3.51 X_T + 1.38 X_C - 2.71 X_TX_T - 2.35 X_tX_t + 0.72 X_TX_C - 1.37 X_TX_t$	0.992	182
$Y_{BI} = 0.41 + 0.14 X_T + 0.08 X_C - 0.19 X_TX_T - 0.04 X_tX_t + 0.1 X_CX_C - 0.03 X_TX_t$	0.986	81
$Y_{TeI} = 1.32 + 0.27 X_T + 0.1 X_t + 0.09 X_C - 0.22 X_TX_T - 0.37 X_tX_t + 0.09 X_CX_C + 0.08 X_TX_C - 0.06 X_tX_C$	0.997	141

Where: Y_{Yl} denotes solid yield (%), Y_{ka} Kappa number; Y_{Acet}, acetone extractives in pulp; Y_{Holo}, Holocellulose in pulp; Y_{vis}, viscosity; Y_{HW}, hot water soluble in pulp; Y_{SL}, soluble lignin contents in pulp; Y_{KL}, Klason lignin in pulp; Y_{GL}, glucan content in solid phase relative to the content in the raw material (dry basis); Y_{XY}: xylan content in solid phase relative to the content in the raw material (dry basis); Y_{pH}, pH in black liquor; Y_{Alk}, residual alkali in black liquor; Y_{sol}; solid percent in black liquor; Y_{GH}: gross heat value in black liquor; Y_{BR}, Brightness; Y_{TI}, Tensile index; Y_{BI}, Burst index and Y_{TeI}, Tear index.
X_T, X_t and X_C denote normalized pulping temperature, time and soda concentration, respectively. The differences between the experimental values and those estimated by using the previous equations never exceeded 10% of the former.

Figure

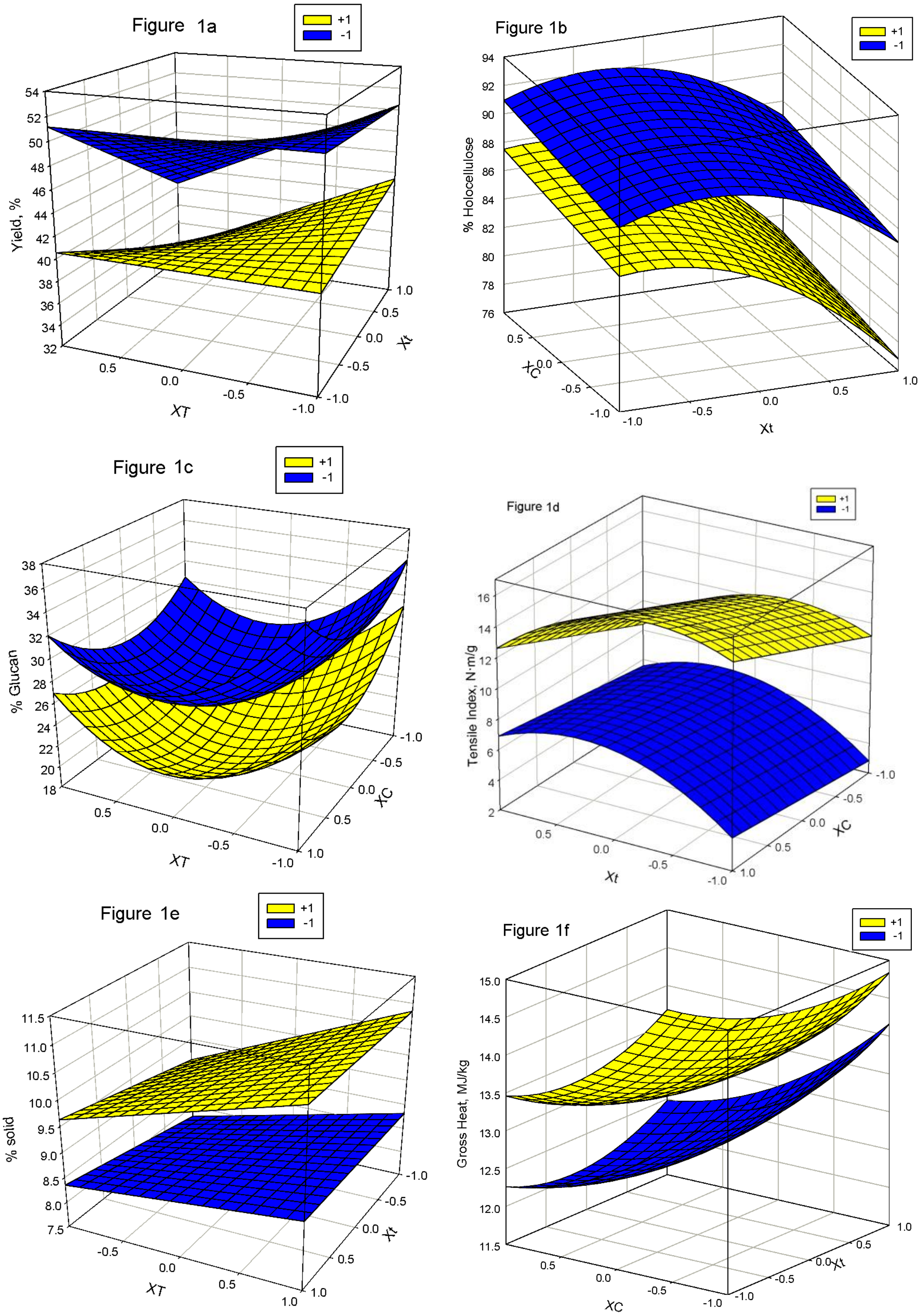

Fig. 1. Variations of properties as a function of temperature alkali active concentration and time of process. (+1 and -1 response surfaces),