Chemical Engineering Journal 166 (2011) 22–29

Contents lists available at ScienceDirect

Chemical Engineering Journal

journal homepage: www.elsevier.com/locate/cej

Cellulosic pulp from *Leucaena diversifolia* by soda–ethanol pulping process

F. López, A. Pérez*, J.C. García, M.J. Feria, M.M. García, M. Fernández

Department of Chemical Engineering, Faculty of Experimental Sciences, University of Huelva, Campus of Carmen, Huelva, Spain

ARTICLE INFO

Article history:
Received 20 October 2009
Received in revised form 28 July 2010
Accepted 17 August 2010

Keywords:
Pulping
Organosolv
Leucaena diversifolia
Fiber cellulose
Experimental design
Optimisation

ABSTRACT

A selection of the best wood raw materials for cellulose pulp and papermaking from five varieties of the Leucaena has been made (*Leucaena diversifolia*, *Leucaena collinsii* and three varieties of *Leucaena leucocephala*) with growth periods of one, two and three years. In accordance with biomass production and the features of the raw materials and cellulose pulp obtained, *L. diversifolia* in its second year of growth was selected as the most suitable material for pulp and papermaking. Pulping of *L. diversifolia* by soda–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 chemical composition of the obtained pulps (yield, kappa number, viscosity, solubles substances, lignin, holocellulose and α-cellulose contents) and the physico-chemical characteristics of paper sheets (tensile index). The results were evaluated using the response surface methodology. The optimum pulping conditions were established for this lignocellulosic material, using the model predictions. The pulp obtained at these conditions has suitable chemical (pulp) and physical (paper sheets) characteristics: yield (46.5%), 1%NaOH solubles (3.04%), hot water solubles (0.63%), ethanol–benzene extractives (0.44%), holocellulose contents (96.7%), α-cellulose contents (75.8%), lignin contents (0.85%), viscosity (1367) kappa number (15.2) and tensile index (19.2 kN m/kg).

1. Introduction

Population growth and the increase in paper consumption have given rise to worldwide raw material shortages. According to the ASPAPEL information Spain paper production was about 6.35 million tons in 2006, with an increase in the production of 11.5%. On the other hand, under an EU directive, bio-fuels should have a 5.75% market share by 2010 and 20% in 2020. Besides the paper industry, wood is an important raw material employed for the bio ethanol or bio diesel production too.

Considering the shortage of conventional raw materials for pulping and the increasing demand of paper products and biofuels worldwide, systems of agricultural cropping and exotic tree varieties [1] have attracted renewed interest, especially in Mediterranean countries like Spain, Italy and Greece with insufficient forest resources [2].

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 utilization [3]. Thus, fast-growing high-yield fiber farms offer enormous potential to provide a productive new resource for the pulp and fiber manufacturing sector [4].

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 [5,6], high biomass productivity (43.7 t ha^{-1}) [7], beneficial effects in the restoration of degrade soils [8,9], and ability to intensive cultivation, combined with appropriate properties for pulp and paper industry.

The integral exploitation of lignocellulosic biomass is hindered by the inability to separate its main components without degrading the chemical structure of some. Extensive research in this field has focussed on a variety of highly specific issues and hindered systematic, comprehensive compilation of available fractionation methods. In dealing with such methods, Rijkens [10] discriminated between those based on delignification (i.e. the solubilization of lignin, joined with low effect on carbohydrate degradation and good selectivity in the delignification reaction) and those relying on hydrolysis. In addition, organosolv methods have attracted interest for development as commercial processes for reasons of environmental pollution, efficient utilization of the lignocellulosics feedstock, ease of bleachabil-

* Corresponding author at: Department of Chemical Engineering, Faculty of Experimental Sciences, University of Huelva, Campus of Carmen, Avda. 3 de marzo s/n, 21071 Huelva, Spain. Tel.: +34 959 21 99 88; fax: +34 959 21 99 83.
E-mail address: aperez.munoz@diq.uhu.es (A. Pérez).

1385-8947/$ – see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.cej.2010.08.039

ity, small-sized plants, and low capital and production costs [11].

Organosolv processes use either low-boiling solvents (e.g., methanol, ethanol, acetone), which can be easily recovered by distillation, or high-boiling solvents (e.g., ethyleneglycol, ethanolamine), that have been evaluated and revised by different authors [12].

In this work the anthraquinone–soda–ethanol was selected attending to its documented effect in increasing the delignification degree, the yield and the process selectivity in alkaline cooking [13–16].

A selection of the best wood raw materials for cellulosic pulp and papermaking from five varieties of the Leucaena has been made (*L. diversifolia, Leucaena collinsii* and three varieties of *Leucaena leucocepha*) with growth periods of one, two and three years, together with the germination of the second year of plants already harvested following their first year of growth.

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 of *L. diversifolia* using ethanol/soda/water mixtures. The resulting yield, 1%NaOH solubles, hot water solubles, ethanol–benzene extractives, holocellulose lignin and α-cellulose contents, viscosity and Kappa number of the pulps, and tensile index 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 three month 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. Fertilizers were 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 one to two and three years, and the new sprouts of the plant after the first year cut, were collected (pruning was always made during winter).

Representation of foliage and branch wood samples was collected (varieties-wise, quadruplicate) 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), lignin (Tappi T 222 om-98) and holocellulose contents [17]. All treatments in this study were in a completely randomized design with five replications (variation coefficient less than 5%).

L. diversifolia wood trimming were used for pulp and papermaking, but only wood was considered as it contained the bark, which was very thin and difficult to strip off also, it accounted for only 1–2% of the overall mass.

Characterization experiments of pulp involved the following parameters: yield (Tappi 257 cm-85), 1% NaOH solubles (Tappi T 212 om-98), ethanol–benzene extractives (Tappi 204 cm-97), hot water solubles (Tappi 207 cm-93), α-cellulose (Tappi 203 om-93), holocellulose [17], lignin (Tappi T 222 om-98) contents, viscosity (Tappi T230 om-94) and kappa number (Tappi 236 cm-85). From paper sheets, gramage can be determined (T 220 sp-96), burst index (Tappi T 403 om-97), tear index (Tappi 414 om-98) and tensile index (Tappi 494 om-96). Also, for these determinations, a completely randomized design with five replications was made.

2.3. Pulping produce and formation of paper sheets

Cellulose pulps were obtained using a 1-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 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 (the process separating the pulp into a suspension of individual fibers in water in this study had been performed at different temperatures), without disturbing the fibers during 3 min, (2500 rpm), washed on a sieve of 16 mm mesh (the process of cleaning the dispersed fibers after cooking in this study had 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.

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:

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

where X is the absolute value of the independent variable concern $\overline{X}$ is the average value of the variable, and X_{max} and X_{min} are its maxi-

mum and minimum values, respectively. The pulping temperature, pulping time, soda concentration, ethanol concentration and wash-disintegrate temperature used in the different experiments of the design were 170 °C, 180 °C and 190 °C; 45 min, 60 min and 75 min; 12%, 17% and 22% NaOH; 30%, 45% and 60% EtOH (v/v) and 20 °C, 45 °C and 70 °C, respectively.

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-test and having a 95% confidence interval excluding zero).

3. Results and discussion

3.1. Selection of raw material for pulp and papermaking

In order to choose the most suitable specie of Leucaena and its best pruning year, different parameters from 5 different Leucaena varieties (*L. diversifolia*, *L. collinsii* and three *L. leucocephala* varieties) were evaluated. It can be observed from previous works [7] that depending on their biomass production (dry wood biomass) from one and two years harvests, *L. collinsii* was the specie that had the lowest biomass production from all the harvests; *L. diversifolia* was the one that presented highest biomass production on the second year harvest (28.3 (5.3) t ha^{-1} of woody biomass in two years and 43.7 (8.2) t ha^{-1} of total biomass) and *Leucaena leucocephala* from Indian variety the one with largest sprouts production after cutting (45.1 (10.2) t ha^{-1} one year after the first harvest). 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 *Leucaena leucocephala* [18]. Nevertheless, these are not conclusive data due to significant standard deviation. Length and diameter results from different Leucaena varieties were also presented [7]. Three *Leucaena Leucocephala* varieties show quite different lengths, higher than the other Leucaenas on their second year sprouts, but not the diameter. However, *L. diversifolia* shows a stalk length and diameter significantly higher and bigger than the other varieties on their second year harvest.

For this work, biomass production from third year harvest (three-year-old plants) has also been evaluated. *L. diversifolia* produced 11.73 (2.58) t ha^{-1} $year^{-1}$ of woody biomass (35.18 t (7.74) in three years and 50.48 (8.64) t of total biomass) and the rest of the Leucaena varieties between 6.53 and 8.54 t ha^{-1} $year^{-1}$, so it cannot be said that there is an increase in biomass production through next growing years. Third year sprouts production (i.e. the sprouting capacity after the second harvest) was approximately stable: 28.09 (7.27) t ha^{-1} $year^{-1}$ of woody biomass for *L. diversifolia* and between 10.2 and 31.94 t ha^{-1} $year^{-1}$ for the other Leucaena varieties.

In previous work [7,19] these five Leucaena varieties were physic-chemically characterized as well as cellulose pulps and paper sheets obtained. Differences in fiber length were not significant, except for the case of *L. collinsii* that turned out to be much smaller than the other varieties. Considering the soluble content in hot water, 1% NaOH and ethanol–benzene extractives that *L. diversifolia* turned out to be the best material for cellulose pulp production due to its little content in substances, even though results showed no significant differences. Based on holocellulose, lignin and α-cellulose contents, and once *L. collinsii* was removed because of its low biomass production and fiber length. The variety of *L. diversifolia* was the best first year harvest. Nevertheless, this was not the same on the second year harvest, where it is difficult to obtain conclusions from the analysis in order to determine the most appropriate variety for obtaining cellulose pulp. Moreover, the fibers of two years old of *Leucaena leucocephala* are immature and consist of more non-fibrous elements i.e. vessels and parenchymatous cells [20].

Once *L. diversifolia* has been selected as the most interesting one for obtaining cellulose pulps and paper sheets, and based on all these previous works, the material has been analysed one year later and cellulose pulp and paper sheets have been obtained. On the *L. diversifolia* third year harvest, soluble substances content on hot water was 4.1%, 16.4% in 1% NaOH and in ethanol–benzene 1.7%. Holocellulose and α-cellulose contents went down up to 65.8% and 37.9%, respectively and the lignin content went up to 24.8%. It seems clear that an intense material lignification from the first to the second year and above all to the third one, with little decreases in holocellulose content to 3.5% and 12.5%, α-cellulose content to −3.7% and 8.8% and lignin content to −9.4% and −15.3%, respectively. Strong *L. diversifolia* lignification between the second and third year seems to suggest use the second year harvest for harvests of short rotation.

In Table 1, results from cellulose pulp and paper sheets characterization from one, two and three years old *L. diversifolia* are shown:

Lignification process is much more intense on second year than on third one, with relative little decreases of holocellulose content in pulps to 0.05% and 1.7%, for α-cellulose 1.8% and 3.3% and for lignin to 21.3% and −76.0%, respectively. 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.

3.2. Experimental design, modelization and optimization

Cellulose 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 five (chemical pulp properties) or twelve (tensile index) 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.

We can see that the 1% NaOH soluble substances, the α-cellulose content and tensile index of cellulosic pulp and paper sheets from *L. diversifolia* (second year harvest. Table 2) is better than those obtained using the proposed experimental design (Table 3). This is sufficiently explained by the absence in the use of anthraquinone in the second case. In spite of the commercial cost involved, we believe this application is useful and it is obvious that the values provided in Table 3 could be improved [21,22].

In a first approximation, the results of holocelulose, α-cellulose and lignin contents are similar or better than results reported by Serrano et al. [23] for soda, ethanol and soda–ethanol delignification process applied on Miscanthus, Palm oil empty fruit bunches and Rice straw (hollocelulose, α-cellulose and lignin contents between 61.6% and 85%, 54.9% and 75%, 12.5% and 18% respectively) but de operation conditions in delignification were very differents.

Identifying the independent variables with the strongest and weakest influence on the dependent variables in Eqs. (1)–(10) is not so easy since the former contain quadratic terms and other factors involving interactions between two independent variables, although here we would like to highlight the following.

Table 1
Chemical characterization of the first year *Leucaena diversifolia* and sprouts, after prunings, with one year, second and third year pulp obtained. And physico-chemical characterization of the first year *Leucaena diversifolia* and sprouts, after prunings, with one year, second and third year paper obtained.

Pulp from *Leucaena diversifolia*	Hot water solubles (%)	1% NaOH solubles (%)	Ethanol–benzene extractives (%)	Holocellulose (%)	Lignin (%)	α-Cellulose (%)
First year and sprouts[a]	0.71	2.78	1.90	94.5	1.74	81.4
Second year[a]	1.04	1.63	0.65	94.5	1.37	79.9
Third year	0.48	2.47	0.30	92.9	5.70	77.2

Paper from *Leucaena diversifolia*	Yield (%)	Kappa number	Viscosity (cm^3/g)	Tensile index (kNm/kg)	Burst index (kN/g)	Tear index (mNm^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

[a] Ref. [7].
[b] Ref. [19].

Observing the linear terms of the equations in Table 3, we can reach the most obvious conclusions on how independent variables would affect dependant variables. For example, to achieve the best yields and α-cellulose contents we advise, as a general rule, operation at low values for independent variables, but in order to achieve the best Kappa numbers, soluble compounds, lignin and holocellulose contents and tensile index, as a general rule, we recommend operation of independent variables at high values. It is more relevant to observe one of the quadratic terms that either totally or partially correct the main tendency observed by the influence of linear terms. The yield terms $+X_TX_T$ or $+X_AX_A$ show that greater yields can be achieved at low temperatures or alkali concentration (−1) that with intermediate values (0). In the case of viscosity, the terms $-X_TX_T$ or $-X_{WD}X_{WD}$ would show greater viscosity at low pulping and wash-disintegration temperatures, against the trend determined by the linear term ($+T$). For the kappa number and lignin content the "linear" trend at which work is most convenient, at high temperature and alkali concentration, could be corrected by terms $+X_TX_T$ and $+X_AX_A$ that would show the possibility of working at intermediate temperature and alkali concentration levels. In the case of holocellulose and α-cellulose contents and tensile index, the existence of the term $-X_AX_A$ and its relatively high coefficient in all three cases provides an important correction of the linear trend and shows the convenience of operating at intermediate alkali concentration levels.

As far as interaction terms are concerned, we can see the recurrence of term X_TX_t in almost all equations in Table 3 with a similar effect to the general effect of the quadratic terms. The linear operation trend is corrected or modulated under the most thorough operating conditions. The terms X_TX_A and X_tX_A also appear in almost all models, corroborating the importance of alkali concentration over independent variables although the effects were the opposite. Although the $+X_T$ and $+X_A$ interaction effect brings a decrease in soluble substance content and the kappa number, this may be due to a cellulose degradation process. In fact, term $-X_TX_A$ of Eq. (9) (α-cellulose) and $+X_TX_A$ of Eq. (7) (lignin) suggest the combination of low operation temperatures with high alkali concentrations or vice versa, and this shows that cellulose chain degradation is higher under more thorough operating conditions. The following most recurrent interaction terms are X_AX_E and X_AX_{WD}, which as a general rule show it is convenient to use intermediate ethanol concentration values and high wash-disintegration temperature. Additional information on the equations in Table 3 can be viewed in 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. Methodology for obtaining Fig. 1 is described in previous works from [24,25], an example, if the independent variables different from those plotted had no effect on the dependent variable considered. Then, the difference between the maximum and minimum values of the dependent variable in question would be zero (a point in the graphs of Fig. 1); also, if the influence was absolute (i.e. if the independent variable plotted had no effect), then, the previous difference would coincide with the height of the rectangle having the range of values of the independent variable plotted, $[(X_{ni})_{max} - (X_{ni})_{min}]$, and the maximum possible difference between the maximum and minimum values of the dependent variable considered, $\{Z[(X_{ni})_{max}]_{max} - Z[(X_{ni})_{min}]_{min}\}$, as its bases.

Because the influence of the other variables on the dependent variable considered can vary with each value of the independent variable plotted, the average change in the dependent variable will be given by:

$$\frac{\int_{(X_{ni})_{min}}^{(X_{ni})_{max}} [Z(X_{ni})_{max} - Z(X_{ni})_{min}]\, dX_{ni}}{[(X_{ni})_{max} - (X_{ni})_{min}]}$$

The change in the dependent variable with that in the independent variable plotted can be assimilated to the difference between $[Z[(X_{ni})_{max}]_{max} - Z[(X_{ni})_{min}]_{min}$ and the previous expression:

$$DZ_i = \left\{[Z(X_{ni})_{max}]_{max} - [Z(X_{ni})_{min}]_{min}\right\} - \frac{\int_{(X_{ni})_{min}}^{(X_{ni})_{max}} [Z(X_{ni})_{max} - Z(X_{ni})_{min}]\, dX_{ni}}{[(X_{ni})_{max} - (X_{ni})_{min}]}$$

These values allow one to weight the relative influences, as percentages, of each independent variable on the variation of each dependent variable.

As can be seen in Fig. 1, the active alkaline concentration or operation temperature are the variables with the strongest influence among all dependent variables except ethanol–benzene extractives and α-cellulose contents where ethanol concentration is the most powerful independent variable.

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 and 3).

An example of the above is Fig. 2 that shows that low lignin content may be obtained at high pulping temperature and intermediate active alkali concentration and pulping time. This partly confirms the prior analysis of the quadratic terms and the effect of excessive cellulose degradation in combination with high alkali concentrations and the excessive operation time if the temperature is high. The response surface for the kappa number (no show) also shows it is convenient to operate at high temperature with the

Table 2
Values of the independent variables and the physico-chemical properties of the pulp and paper sheets obtained in the pulping process by using the proposed experimental design.

Normalized values of temperature, time, active alkali concentration, ethanol concentration and wash temperature					Yield (%)	Viscosity (cm^3/g)	Kappa number	NaOH 1% solubles (%)	Ethanol–benzene extractives (%)	Hot water solubles (%)	Lignin (%)	Holocellulose (%)	α-Cellulose (%)	Tensile index (kN m/kg)
1	1	1	1	1	38.2	1224	15.4	2.2	0.40	0.20	4.5	96.5	55.5	15.00
1	1	1	−1	−1	39.4	1365	11.1	3.7	0.27	0.25	2.6	96.5	72.4	14.2
1	1	−1	1	−1	54.9	1143	44.3	5.6	1.79	0.57	5.8	90.5	70.2	15.3
1	1	−1	−1	1	52.7	1504	43.7	3.0	1.02	0.76	5.3	92.0	73.9	16.4
1	−1	1	−1	−1	42.6	1308	11.9	2.6	0.19	0.68	1.3	95.9	57.4	15.4
1	−1	1	−1	1	42.7	726	9.8	2.3	0.34	0.25	1.8	96.7	73.3	14.0
1	−1	−1	1	1	56.5	1521	43.3	5.1	0.52	1.40	5.0	90.6	71.3	11.8
1	−1	−1	−1	−1	54.5	1508	43.4	3.7	1.22	0.75	5.7	90.1	71.9	13.1
−1	1	1	1	−1	47.5	691	13.9	3.3	0.11	1.04	0.4	95.4	72.7	13.1
−1	1	1	−1	1	49.9	1057	14.6	2.2	0.21	0.32	0.8	96.3	78.9	15.1
−1	1	−1	1	1	57.9	760	54.0	4.4	0.42	1.02	7.0	87.1	67.0	8.7
−1	1	−1	−1	−1	59.3	983	48.3	3.3	0.94	0.80	6.3	88.3	70.1	14.2
−1	−1	1	1	1	51.9	1375	24.1	2.9	0.37	0.70	3.0	94.4	77.3	13.2
−1	−1	1	−1	−1	61.2	696	57.5	3.8	0.44	1.11	11.4	91.9	68.9	6.2
−1	−1	−1	1	−1	63.1	595	57.8	5.1	0.17	1.78	9.8	82.6	59.7	7.3
−1	−1	−1	−1	1	65.0	608	55.7	4.0	0.50	0.89	10.2	85.0	65.3	7.2
1	0	0	0	0	47.4	1387	15.2	3.0	0.43	0.64	0.9	95.6	76.4	17.9
−1	0	0	0	0	55.3	1022	48.6	3.1	0.12	0.95	3.0	93.1	77.1	16.9
0	1	0	0	0	47.3	1325	13.3	2.8	0.30	0.93	0.6	95.1	74.7	18.4
0	−1	0	0	0	51.1	1468	22.8	2.8	0.15	1.22	2.3	93.9	73.9	15.8
0	0	1	0	0	45.4	1011	16.2	3.1	0.08	0.88	1.7	96.1	76.6	15.6
0	0	−1	0	0	57.9	1119	41.7	4.6	0.60	1.27	6.0	88.7	73.5	14.6
0	0	0	1	0	49.9	1089	20.4	2.9	0.27	0.91	1.1	94.8	73.0	15.5
0	0	0	−1	0	50.4	1179	18.6	2.5	0.40	0.72	1.7	94.8	77.8	16.3
0	0	0	0	1	50.2	1126	16.8	2.9	0.10	0.88	0.6	95.3	79.3	17.0
0	0	0	0	−1	50.8	1274	16.9	3.7	0.26	0.98	1.4	97.6	77.3	18.7
0	0	0	0	0	49.7	1081	17.0	3.0	0.15	1.07	1.5	94.9	77.0	17.4

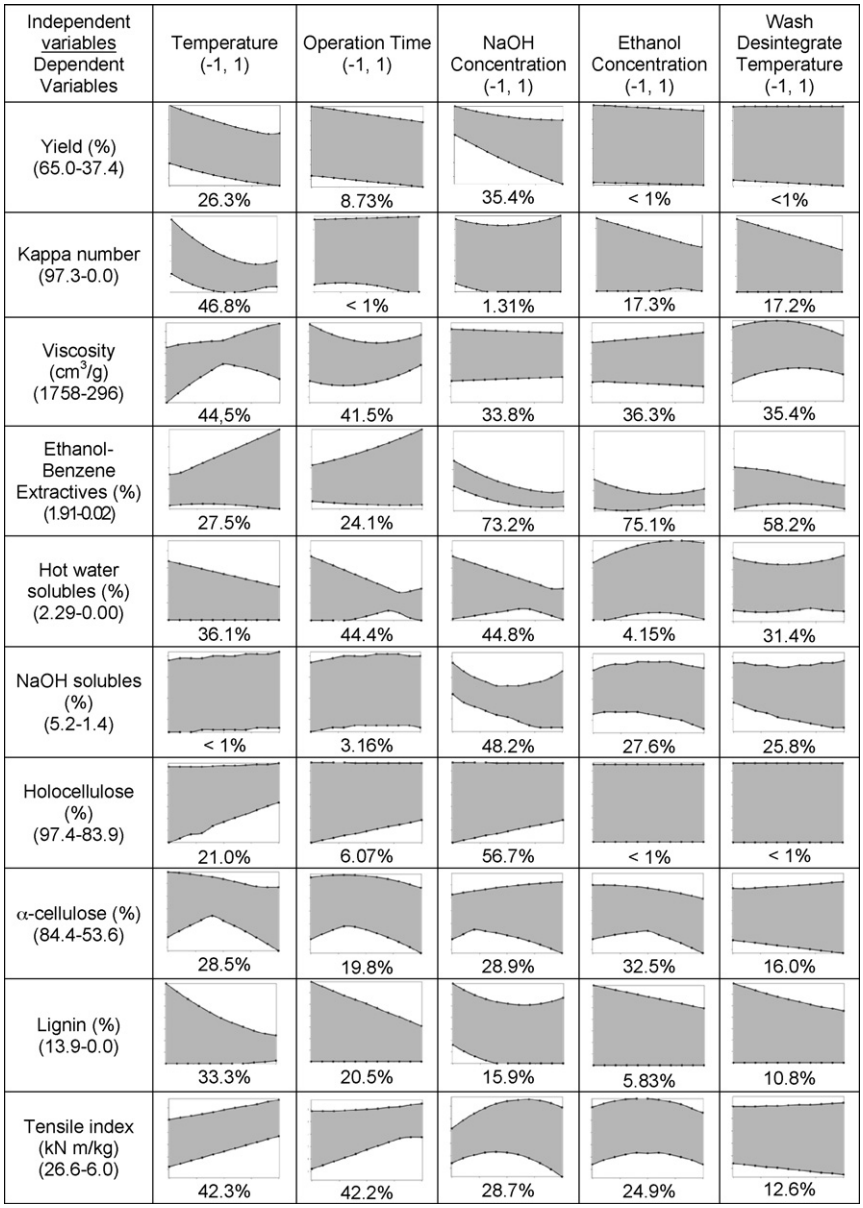

Fig. 1. Variation of dependent variables as a function of normalized independent variables.

effect being much less relevant than in the case of the remaining independent variable, although here we must highlight the positive effect over the kappa number of a greater wash-disintegration temperature. The response surface for the yield (no show) shows that greater yield is achieved at low independent variable levels with the influence of temperature being less pronounced at low alkali concentration levels. The remaining independent variables have a much lesser influence. The analysis is similar to the rest of the variables related to soluble contents. In the case of the 1%NaOH soluble contents and operating at low alkali concentration levels, it is also convenient to operate at low levels of ethanol concentration.

Holocellulose contents are greater at high alkali concentration, with this being the most influential independent variable (ethanol concentration and wash-disintegration temperature in equation 8 did not have a statistically significant coefficient over the ranges considered), although the temperature effect is more pronounced at lower alkali concentration levels. In this scenario, optimum levels of α-cellulose content may be reached. Fig. 3 shows that the greatest α-cellulose content may be obtained at high ethanol concentration and operation temperatures when alkali concentration is relatively low, below 16%.

Unlike previous work by Gillah [26,27] 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.

This would support the hypothesis that the *L. diversifolia* is suitable as a material for cellulose paste and paper 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 and with wash-disintegration temperatures between 40 °C and 50 °C. The optimum operation temperature would be high in the range taking into account the following: 185–190 °C. Applying these conditions to the models in Table 3, the following results would be obtained: yield, 46.5%, 1%NaOH solubles 3.04%, hot water solubles 0.63%, ethanol–benzene

Table 3
Equations yielded for each dependent variable.

Eq.	Equation	r^2	F
(1)	$YI = 50.00 - 4.57X_T - 2.31X_t - 5.72X_A - 0.70X_E - 0.46X_{WD} + 1.03X_TX_T + 1.33X_AX_A + 0.97X_TX_t - 1.31X_TX_A + 1.12X_TX_E - 0.57X_tX_A - 0.87X_AX_E - 0.52X_AX_{WD}$	0.99	124.6
(2)	$VI = 1329 + 217X_T - 179X_T^2 + 202X_t^2 - 184X_{WD}^2 - 120X_TX_A - 189X_TX_{WD} - 147X_tX_E + 83.6X_AX_E + 113X_EX_{WD}$	0.95	35.4
(3)	$KI = 14.22 - 17.20X_T - 7.64X_t - 10.44X_A - 2.06X_E + 18.17X_TX_T + 10.15X_AX_A + 8.77X_TX_t - 5.65X_TX_A + 3.28X_TX_E + 5.04X_TX_{WD} - 13.21X_tX_A - 2.81X_tX_E - 2.26X_tX_{WD} + 3.02X_AX_E + 3.17X_AX_{WD} + 13.65X_EX_{WD}$	0.99	115.9
(4)	$SS = 3.04 - 0.097X_t - 0.707X_A - 0.307X_E - 0.307X_{WD} - 0.234X_tX_t + 0.831X_AX_A - 0.324X_EX_E + 0.256X_{WD}X_{WD} + 0.206X_TX_t - 0.126X_TX_A + 0.094X_tX_A + 0.096X_tX_E - 0.199X_tX_{WD} - 0.451X_AX_E - 0.166X_AX_{WD}$	0.99	75.6
(5)	$EBE = 0.279 + 0.161X_T + 0.087X_t - 0.265X_A - 0.061X_E - 0.084X_{WD} + 0.072X_t^2 + 0.187X_A^2 + 0.182X_E^2 - 0.100X_{WD}^2 + 0.063X_TX_t - 0.153X_TX_A + 0.067X_TX_E - 0.127X_TX_{WD} - 0.132X_tX_A + 0.096X_tX_E - 0.048X_tX_{WD} + 0.037X_AX_E + 0.123X_AX_{WD} + 0.016X_EX_{WD}$	0.99	2601
(6)	$HW = 0.804 - 0.173X_T - 0.161X_t - 0.212X_A + 0.136X_E - 0.086X_{WD} - 0.273X_E^2 + 0.116X_{WD}^2 - 0.049X_TX_A - 0.037X_TX_E + 0.271X_TX_{WD} + 0.46X_tX_A - 0.054X_tX_E + 0.045X_tX_{WD} - 0.055X_AX_E - 0.112X_AX_{WD}$	0.99	263.4
(7)	$LI = 0.51 - 1.05X_T - 0.94X_t - 1.87X_A - 0.43X_E - 0.36X_{WD} + 1.39X_T^2 + 2.27X_A^2 + 0.40X_{WD}^2 + 1.52X_TX_t + 0.38X_TX_A + 0.61X_TX_E + 0.98X_TX_{WD} - 0.19X_tX_A + 0.80X_tX_E + 0.67X_tX_{WD} - 0.47X_AX_E - 0.35X_AX_{WD} + 0.64X_EX_{WD}$	0.99	433.2
(8)	$HO = 95.01 + 1.69X_T + 0.92X_t + 3.61X_A - 3.11X_AX_A - 0.70X_TX_t - 0.78X_TX_A$	0.95	65.5
(9)	$a\text{-}C = 78.69 - 0.81X_T - 0.91X_t + 0.56X_A - 2.68X_E + 1.17X_{WD} - 2.07X_TX_T - 2.82X_tX_t - 2.07X_AX_A - 1.73X_EX_E - 1.20X_TX_t - 4.04X_TX_A - 1.92X_TX_E - 1.72X_TX_{WD} - 0.65X_tX_A - 1.01X_tX_E - 2.46X_tX_{WD} - 1.20X_AX_E + 0.51X_AX_{WD}$	0.99	97.0
(10)	$TI = 17.34 + 1.83X_T + 1.46X_t + 0.75X_A - 2.79X_AX_A - 1.97X_EX_E - 0.66X_TX_t - 0.94X_tX_E + 0.94X_AX_E + 0.90X_AX_{WD}$	0.93	26.5

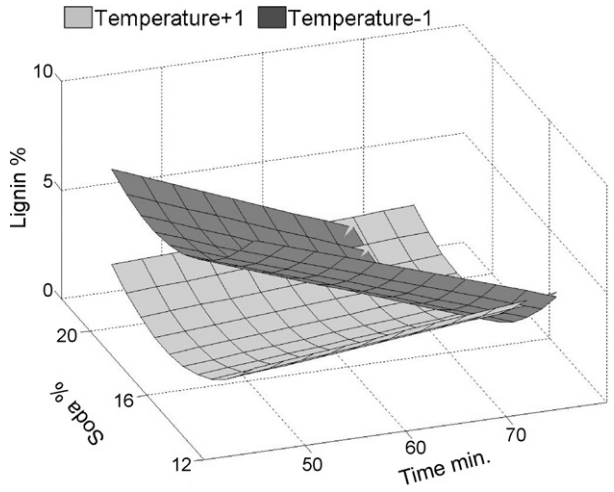

Fig. 2. Lignin variations as a function of 1% NaOH concentration and time operation at two temperature levels.

extractives 0.44%, holocellulose contents 96.7%, α-cellulose contents 75.8%, lignin contents 0.85%, kappa number 15.2, viscosity 1367 $cm^3\,g^{-1}$ and tensile index 19.2 kN m/kg, whose difference with regard to the experimental results in item +1 0 0 0 0 does not exceed 5% (Table 2), with the exception of the tensile index, with the difference being 6.5%.

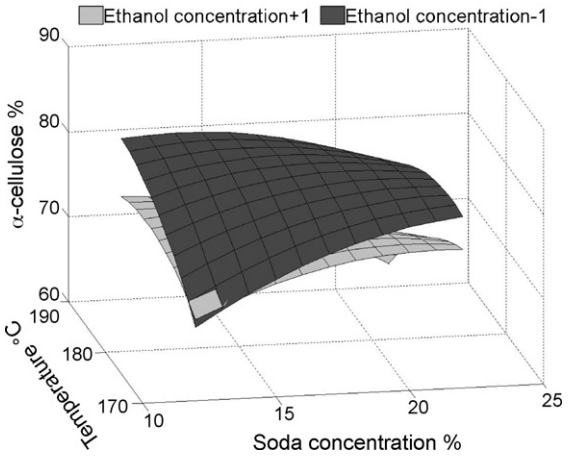

Fig. 3. α-cellulose variations as a function of 1% NaOH concentration and temperature operation at two ethanol concentrations levels.

4. Conclusions

In accordance with biomass production (43.7 t ha^{-1} of total biomass in two 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* varieties in its second year of growth was the most suitable pulp and papermaking lignin cellulose material among the five *Leucaena* varieties studied.

The soda–ethanol–anthraquinone pulping could be and adequate process *L. diversifolia*. Suitable physical characteristics of paper sheets (tensile index) and acceptable chemical characteristics and yield pulping could be obtained by operating at high temperature (185–190 °C), and low or medium values for active alkali concentration (17%), pulping time (60 min) and ethanol concentration (45% v/v) and wash-disintegrate temperature (45 °C).

The pulp obtained at these conditions has suitable chemical (pulp) and physical (paper sheets) characteristics: yield (46.5%), 1%NaOH solubles (3.04%), hot water solubles (0.63%), ethanol–benzene extractives (0.44%), holocellulose contents (96.7%), α-cellulose contents (75.8%), lignin contents (0.85%), kappa number (15.2), viscosity (1367 $cm^3\,g^{-1}$) and tensile index (19.2) kN m/kg.

Acknowledgements

The authors acknowledge financial support from the CICYT-FEDER (Science and Technology Inter Ministerial Commission, Spanish Government–European Regional Development Fund), projects number CTQ2006-10329/PPQ and AGL2009-13113 and to the Ramón y Cajal and Juan de la Cierva programs (Spain's Ministry of Education and Science for additional funding).

References

[1] R.A. Sedjo, Biotech and planted trees: some economics and regularoty issues, AgBioForum 6 (3) (2003) 113–119.
[2] C. Ververis, K. Georghiou, N. Christodoulakis, P. Santas, R. Santas, Fiber dimensions, lignin and cellulose content of various plant materials and their suitability for paper production, Ind. Crops Prod. 19 (2004) 245–254.
[3] A. Shatalov, H. Pereira, Kinetics of organosolv delignification of fibre crop Arundo donax L., Ind. Crops Prod. 21 (2005) 203–210.

[4] S.D. Mansfield, H. Weineisen, Wood fiber quality and kraft pulping efficiencies of trembling aspen (*Populus tremuloides* Michx) clones, J. Wood Chem. Technol. (2007) 135–151.
[5] G.R. Rout, S. Samantaray, P. Das, Chromium nickel and zinc tolerance in *Leucaena leucocephala* (K8), Sivae Genet. 48 (1999) 3–4.
[6] Y. Ma, N.M. Dickinson, M.H. Wong, Interactions between earthworms, trees, soil nutrition and metal mobility in amended Pb/Zn mine tailings from Guangdong, China Soil Biol. Biochem. 35 (10) (2003) 1369–1379.
[7] M.J. Díaz, M.M. García, M.E. Eugenio, R. Tapias, M. Fernandez, F. López, Variations in fiber length and some pulp chemical properties of Leucaena varieties, Ind. Crops Prod. 26 (2007) 142–150.
[8] B. Vanlauwe, N. Sanginga, R. Merckx, Recovery of Leucaena and Dactyladenia residue 15N in alley cropping systems, Soil Sci. Am. J. 62 (1998) 454–460.
[9] N.K. Sharma, P.N. Singh, P.C. Tyagi, S.C. Mohan, Effect of Leucaena mulch on soil–water use and wheat yield, Agric. Water Manage. 35 (3) (1998) 191–200.
[10] B.A. Rijkens, Hydrolyses processes for lignocellulosic material, in: CECD Workshop Cellulose Programme, Braunschweig, Germany, 1984.
[11] M. Oliet, M.A. Gilarranz, J.C. Domínguez, M.V. Alonso, F. Rodríguez, Ethanol-based pulping from *Cynara cardunculus* L., J. Chem. Tech. Biotech. 80 (2005) 746–753.
[12] E. Muurinen, Organosolv pulping. A review and distillation study related to peroxyacid pulping, PhD Thesis. Department of Process Engineering, University of Oulu, Finland, 2000.
[13] P.W. Hart, B.N. Brogdon, J.S. Hsieh, Anthraquinone pulping of kudzu (Pueraria lobata), Tappi J. 76 (4) (1993) 162–166.
[14] Z. Li, J. Li, G.J. Kubes, Kinetics of delignification and cellulose degradation during kraft pulping with polysulphide and anthraquinone, J. Pulp Paper Sci. 28 (7) (2002) 234–239.
[15] P. Khristova, O. Kordsachia, R. Patt, S. Dafaalla, Alkaline pulping of some eucalyptus from Sudan, Bioresour. Technol. 97 (4) (2006) 535–544.
[16] S. Abrantes, M.E. Amaral, A.P. Costa, A.P. Duarte, *Cynara cardunculus* L. alkaline pulps: alternatives fibres for paper and paperboard production, Bioresour. Technol. 98 (2007) 2873–2878.
[17] L.E. Wise, M. Marphy, M. DïAdieco, Chlorite holocellulose, its fractionation and bearing on summative wood analysis and on studies on the hemicelluloses, Paper Trade J. 122 (2) (1946) 35–46.
[18] R.S. Malik, D. Dutt, C.H. Tyagi, A.K. Jindal, L.K. Lakharia, Morphological, anatomical and chemical characteristics of *Leucaena Leucocephala* and its impact on pulp and paper making properties, J. Sci. Ind. Res. 63 (2) (2004) 125–133.
[19] F. López, M.M. García, R. Yáñez, R. Tapias, M. Fernández, M.J. Díaz, Lecaena species valoration for biomass and paper production in one and two year harvest, Bioresour. Technol. 99 (2008) 4846–4853.
[20] D. Dutt, C.H. Tyagi, R.S. Malik, Studies on effect of growth factor on morphological, chemical and pulp and paper making characteristics and its impact on fluff generation, Indian J. Chem. Technol. 14 (6) (2007) 626–634.
[21] L. Loewendahl, O. Samuelson, Carbohydrate stabilization during soda pumping with addition of anthraquinone, Tappi J. 61 (2) (1978) 19–21.
[22] R.C. Francis, S. Shin, S. Omori, T.E. Amidon, T.J. Blain, Soda pulping of hardwoods catalyzed by anthraquinone and methyl substituted anthraquinones, J. Wood Chem. Technol. 26 (2) (2006) 141–152.
[23] L. Serrano, I. Egües, M. González Alriols, R. Llano-Ponte, J. Labidi, Miscanthus sinensis fractionation by different reagents, Chem. Eng. J. 156 (2010) 49–55.
[24] F. López, A. Alfaro, M.M. García, M.J. Díaz, A.M. Calero, J. Ariza, Pulp and paper from tagasaste (Chamaecytisus proliferus L.F. ssp palmensis), Chem. Eng. Res. Des. 82 (A8) (2004) 1029–1036.
[25] M.J. Díaz, A. Alfaro, M.M. García, M.E. Eugenio, J. Ariza, F. López, Ethanol pulping from tagasaste (Chamaecytisus proliferus L.F. ssp palmensis). A new promising source for cellulose pulp, Ind. Eng. Chem. Res. 43 (2004) 1875–1881.
[26] P.R. Gillah, R.C. Ishengoma, Kraft pulping of *Leucaena leucocephala* grown in Morogoro, Tanzania, Holz. Roh. Werkst. 51 (5) (1993) 353–356.
[27] P.R. Gillah, R.C. Ishengoma, Bleaching of kraft pulps from *Leucaena leucocephala* grown in Tanzania, Holz. Roh. Werkst. 53 (6) (1995) 389–391.