CELLULOSE CHEMISTRY AND TECHNOLOGY

# BIOREFINING OF *LEUCAENA LEUCOCEPHALA*. ENERGY OPTIMIZATION OF BLACK LIQUOR AND POLYSACCHARIDE FRACTIONS

FRANCISCO LÓPEZ,[*] JAVIER M. FERIA,[*] JUAN CARLOS GARCÍA,[*]
M. TRINIDAD GARCÍA[*,**] and M. JESUS DÍAZ[*]

[*]*Chemical Engineering Department, Faculty of Experimental Sciences, Center for Research in Product Technology and Chemical Processes, Pro$^2$TecS, University of Huelva,*
*Av. 3 de Marzo s/n, 21071 Huelva, Spain*
[**]*Agrifood Campus of International Excellence, CeiA3, Huelva, Spain*
✉ *Corresponding author: Juan Carlos García Domínguez, juan.garcia@diq.uhu.es*

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A *Leucaena leucocephala* variety was pulped with the soda–anthraquinone process to obtain a liquid fraction for use as an energy source. To this end, the raw material was subjected to a two-stage fractionation process in order to optimize the black liquor and polysaccharide fractions for energy production. This aim was accomplished by using a hydrolysis treatment before pulping. Both the pretreatment and the pulping process were optimized with a view to obtaining the best possible pulp properties and renewable energy from the black liquor, and the results were compared with those obtained in the absence of prior hydrolysis.

Alkaline (soda–anthraquinone) cooking of the hydrolysis solid residue provided cellulose pulp and energy from black liquor at least as efficiently as without autohydrolysis and with the added advantage of using milder delignification conditions. Up to 46.6% of hemicellulose in the raw material was extracted as xylooligomers, xylose and furfural into the liquid phase.

***Keywords***: soda–anthraquinone process, energy, black liquor, autohydrolysis, *Leucaena leucocephala*, pulp

## INTRODUCTION

The growing concern about rising oil prices, and global warming and its consequences, has aroused widespread consensus on the need to reduce current dependence on fossil fuels.[1] Renewable energy sources have thus acquired increasing importance in responding to concerns over the environment and the security of energy supplies. Biomass is one such source and currently provides 7% of the amount of energy used worldwide. The use of residual biomass, such as that coming from forest residues, as biofuels has increased the demand for bioenergy and is bound to limit biomass availability in the not too distant future.

Currently available renewable energy resources include wood annual crops, and agricultural and forestry residues.[2] Lignocellulosic materials (LCMs) constitute a clean, inexpensive, massively available source of energy and chemicals in many world regions, the exploitation of which can help improve local economies; in addition, its sources are easy to cultivate and renewable, and possess a neutral carbon balance.[3]

Although the concepts of biorefining and energy optimization are not new, they have aroused especial interest lately with the advent of forest product biorefining, by which wood is hydrolysed before conventional pulping and papermaking in order to obtain a hydrolysate containing hemicellulose sugars of use as feedstock for biofuels, bioplastics and other products.[4] Similarly to oil refining,[5] biorefining can provide a wide range of products by appropriate fractionation. In fact, autohydrolysis yields a liquid phase rich in hemicellulose-derived sugars or oligomers without substantial dissolution of cellulose or lignin.[6] This allows chemicals and energy to be obtained in addition to pulp, and makes the process even more profitable.

The heating value of hemicellulose is roughly one half that of lignin (about 27.0 MJ/kg) and hence contributes little to the overall profitability of the process – which has an energy surplus. Therefore, separating hemicelluloses by biorefining prior to pulping may help increase industrial profitability in the pulp and papermaking sector in the future.[7] In fact, pulp mills may be the starting point for future integrated biomass refineries conceived as integrated facilities enabling the production of a wide spectrum of chemicals and biofuels from biomass.[5,8,9]

Under the biorefining concept, hemicelluloses (oligomers and monomers) can be extracted before pulping in order to obtain new biomaterials.[10–12] Previous studies found the mechanical properties of handsheets from pulp obtained with autohydrolysis/hot water extraction or steam explosion to be slightly worse than those for conventionally prepared paper.[13,14] This led us is to assess the potential of the solid phase remaining after autohydrolysis for obtaining paper by delignification. In previous work, we found delignification of eucalyptus[15], tagasaste[16] and paulownia wood[17–19] to be feasible under milder conditions if the raw material was previously hydrolysed; also, the properties of the resulting pulp were similar to those obtained in the absence of autohydrolysis and the residual black liquor had an even higher energy content.

Leucaena crops provide large amounts of biomass and possess a high resprouting capacity (49.6 ± 10.67 ton/ha yr total dry weight,[5] harvested timber weight 86 kg total mass[17]). *Leucaena leucocephala* is a leguminous tree easily adapting to Mediterranean ecological conditions,[20,21] and having a high biomass productivity[22] and beneficial effects on degraded soil reclamation.[23] In this work, we used its K360 variety to obtain energy and chemicals. This species was previously used to obtain bioethanol by fermentation of sugars.[24] Also, *L. diversifolia* was pulped with soda–anthraquinone–ethanol, and the influence of the cooking variables on the properties of the resulting pulp and paper were examined.[25,26]

Under the broad concept of biorefining, research in the pulp and paper industry has been lately focused on ensuring sustainable development by using new technologies to improve pulping processes, optimize energy production and reduce chemical consumption. This objective is being fulfilled by using new technology and new raw materials such as non-wood plants instead of wood fibre.

In this work, a *L. leucocephala* variety was subjected to the soda–anthraquinone process to obtain pulp, which was characterized in chemical terms, and black liquor, which was assessed for energy potential. The process conditions were optimized to obtain the best possible pulp properties and the greatest energy recovery from the black liquor.

## EXPERIMENTAL

### Raw material

The *Leucaena leucocephala* K360 variety was obtained by *in vitro* replication. Plants were harvested after 7 years of growth in experimental energy crop plantations in Huelva (southwestern Spain), ground and milled into chips passing through an 8 cm screen. The chips were further reduced to pieces 2-10 mm long and no more than 2 mm thick in order to prevent alteration of their components, and fines were removed by sieving through a 0.6 mm mesh. All samples were air-dried and stored in a dark, dry place until use.

### Characterization of pulp and black liquor

Pulp was characterized in terms of moisture by drying to constant weight at 105 ºC (TAPPI T-264-cm-07, "Preparation of Wood for Chemical Analysis"), acetone extractives in accordance with TAPPI T 280 wd-06 ("Acetone Extractives of Wood and Pulp") and holocellulose.[27] Also, it was subjected to quantitative acid hydrolysis with 5 mL of 72% sulfuric acid at 30 C for 1 h, followed by addition of water up to 4% $H_2SO_4$ to effect post-hydrolysis at 121 ºC for 60 min in accordance with TAPPI T 249 cm-09. The resulting solid residue was recovered by filtration and taken to be Klason lignin (TAPPI T 222 om-06). Acid-soluble lignin was determined by using the standard method described in TAPPI T UM 250. Monosaccharides (glucose, xylose and arabinose) and acetic acid in the hydrolysates were quantified by high performance liquid chromatography (HPLC), using an Aminex HPX-87H ion-exchange column at 50 ºC, a mobile phase consisting of 0.005 M $H_2SO_4$ at a flow-rate of 0.6 mL/min and a refractive index detector.

The black liquor was characterized by determining the following properties: pH, residual alkali (titrated according to TAPPI T 625 wd-99, "Analysis of soda and sulfate black liquor") and % total dry matter (TAPPI T 650 om-09, "Solid content of black liquor"). In addition, the solid content of the black liquor for calorimetry was determined by using a CRYODOS 22960 freeze-dryer and a Parr 6300 Automatic Isoperibol Calorimeter in accordance with standards "CEN/TS 14918:2005 (E) Solid biofuels–Method for the determination of calorific value" and UNE 164001 EX .

### Autohydrolysis of *L. leucocephala* wood to obtain pulp

Wood chips, water, soda and anthraquinone were mixed in the required proportions and reacted in a 10 L stainless steel reactor from MK-Systems, Inc., using a recirculation ratio of 8 g water/g oven-dry wood (odw). The reactor was simultaneously heated and actuated to ensure efficient mixing and uniform swelling of Leucaena chips. The suspension was heated to 178 °C for 22.5 min by following the standard temperature profile[18] and then chilled to 25 ºC.

The pulping conditions were as follows: temperature of 161, 169 or 177 ºC; operating time of 60, 90 or 120 min; and soda concentration of 17, 21 or 25% plus 0.1% anthraquinone in a liquid/solid ratio of 8 g water/g raw material (odw). The reactor was operated as described above. Following cooking, the pulp was separated from the liquor and disintegrated without breaking fibers in a high concentration pulper machine for 20 min. Figure 1 depicts the operational scheme of the procedures for *L. leucocephala* wood autohydrolysis and subsequent pulping.

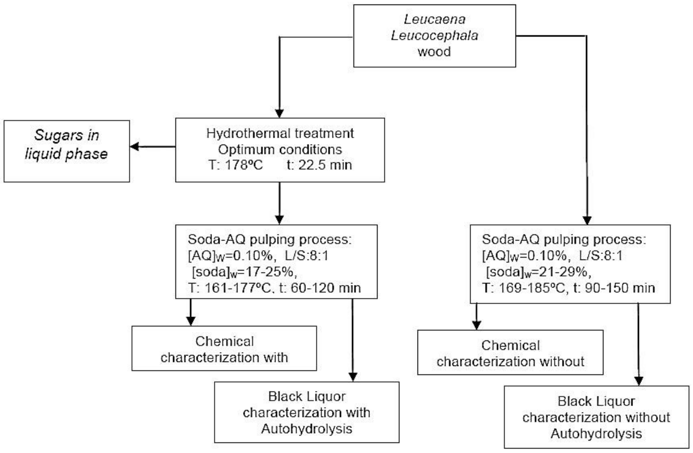

Figure 1: Scheme of experimental work. Abbreviations: $[\text{soda}]_w$: soda concentration by weight; $[\text{AQl}]_w$: concentration of anthraquinone by weight; T: process temperature (ºC); t: processing time (min); L/S: liquid/solid ratio

### Experimental design for the pulping process. Multiple regresion model

A $2^n$ central composite experimental factor design was used to relate the dependent variables of the pulping process (*viz.*, pulp yield, acetone extractives, holocellulose, glucose, Klason lignin, soluble lignin, heating value, pH, residual alkali, % solids and burst index) to the independent variables (*viz.*, temperature, time and soda concentration) with the minimum possible number of experiments. This allowed a second-order polynomial in the independent variables to be constructed and the statistical significance in the variables to be assessed. The independent variables were normalized by using the following equation.

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

where $X$, $\overline{X}$, $X_{\max}$ and $X_{\min}$ are the independent variable concerned and its mean, maximum and minimum value, respectively. The range of variation of each independent variable was determined experimentally (result not shown) or from reported values.[28,29]

The number of tests required was calculated to be $N = 2^n + 2 \cdot n + n_c$, $2^n$ 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 here, $N = 16$.

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

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

The independent variables used in the equations relating the two types of variables were those having a statistical significant coefficient (*viz.*, those not exceeding a significance level of 0.05 in Student´s *t*-test and having a 90% confidence interval excluding zero).

## RESULTS AND DISCUSSION

### Characteristics of raw material. Previous studies

The genus *Leucaena* was characterized chemically and assessed for cellulose pulp production in previous studies.[30–33] Also, the authors characterized some Leucaena varieties in previous work.[29,34–37] The materials were found to consist largely of cellulose (as glucan), with 37.2% (or 41.0% if determined in accordance with TAPPI T 203-om-93), followed by Klason lignin, with 24.1% – which is a higher content than that in *Eucalyptus globulus*[15] – and hemicelluloses (calculated as the combination of xylan, araban and acetyl groups), with 19.9%. This composition is comparable to those of other raw materials, such as *Eucalyptus globulus*. The dominant monomer in the hemicellulose fraction was xylose substituted with acetyl groups to a similar extent as other lignocellulosic materials, but less so with arabinose. This composition is typical of *O*-acetyl glucuronoxylans present in hardwood.[38] The content in acetone extractive compounds of the raw material was lower than that previously found in eucalyptus wood[35] and in other Leucaena-based materials (1.64-8.19%).[29–33] These compounds can adversely affect pulp production by forming pitch deposits.[39]

The holocellulose content of *L. leucocephala* K360 (70.6%) was similar (8.5% lower to 3.3% higher) to those in other Leucaena varieties, but by 5.5% higher than that for *E. globulus*. Klason lignin exceeded previously reported values for *L. leucocephala*.[30,33] By contrast, glucan, xylan, araban and acetyl group values were similar to those for other Leucaena varieties and eucalyptus wood.[33]

The gross heating value for *L. leucocephala* (18.9 MJ/kg) was slightly lower (2.0%) than that previously measured in *L. diversifolia*[40] and in other solid biofuels, such as willow chips and pine sawdust from one-year-old poplar – which never exceeded 20 MJ/kg[41] –, but higher than those of *Populus euramericana* and *E. globulus* (17.0-18.8 MJ/kg).[42]

## Autohydrolysis process

The operating conditions used in the autohydrolysis treatment preceding delignification were established in a previous work.[19] Such conditions ensured near-optimal extraction of hemicellulose derivatives with little degradation of cellulose polymers. The solid yield in autohydrolysis was of 77.7% and that in liquid phase of 22.3%. The composition of the liquid phase after autohydrolysis was 2.27% glucose, 6.38% xylose, 24.78% arabinose, 14.61% glucooligomers, 36.62% xylooligomers, 36.99% arabanoligomers, 1.96% furfural and 0.43% 5-OH methylfurfural. The composition and yield of the liquid phase are both consistent with those obtained by using the models of Feria *et al.*[19]– the differences were below 5% and 10%, respectively. In fact, based on such models, the yield of the liquid phase was 21.3% and its composition as follows: 2.42% glucose, 6.10% xylose, 23.48% arabinose, 14.51% glucooligomers, 38.28% xylooligomers and 38.74% arabanoligomers on a dry basis relative to the initial glucan, xylan and araban contents in the raw material – oligomer contents are given as monomer equivalents. Also, the concentrations of furfural and 5-OH methylfurfural were of 2.2% and 0.47%, respectively, of the initial xylan and glucan contents on a dry basis of the raw material.

## Characterization of pulp and black liquor after autohydrolysis

Table 1 shows the total yield and total contents in acetone extractives, holocellulose, Klason lignin, soluble lignin and glucan of the pulp as obtained with the proposed experimental design – the contents in xylan and araban were both negligible. Except for pulp yield, each result was the mean of at least 4 replications. Table 2 summarizes the properties of the black liquor from a pulping process preceded by autohydrolysis (*viz.*, pH, residual alkali, % solids and gross heating value). Each value was the average of three replications.

Substituting the values of the independent variables for each dependent variable into the polynomial expression used yielded the equations of Table 3. The differences between experimental and calculated values were less than 5% (holocellulose, Klason lignin, soluble lignin and glucan) or 8% (pulp yield and acetone extractives). Pulp yield was relatively high due to the effect of the process, including an autohydrolysis stage and a delignification stage. Klason lignin was unusually high at some experimental points as a consequence of the relative increase resulting from the prior extraction of hemicelluloses. In any case, the contents in Klason lignin were comparable to those obtained by applying an ASAM process, including prior autohydrolysis to aspen (difference of about 1%)[12] and much lower (9.7-19.4%) than those obtained by organosolv delignification with prior autohydrolysis of wheat straw[10] or soda–AQ cooking with prior autohydrolysis of paulownia (7-12%).[11] Soluble lignin contents were lower than those obtained by Huijgen *et al.*[10] from wheat straw and García *et al.*[11] from paulownia. Holocellulose contents were similar to those for paulownia reported by García *et al.*;[11] also, glucan contents were lower than those reported for aspen by Al-Dajani *et al.*[12] and wheat straw by Huijgen *et al.*[10] These authors used an identical biorefining scheme involving autohydrolysis and delignification. The pH, the contents in residual alkali and the proportions of solids in the black liquor were strongly dependent on the active alkali concentration used; also, the loss of gross heating value in the liquor with respect to the raw material was of only 5.1-20.4%.

Table 1
Normalized values of independent variables and chemical characterization of pulp obtained by using the proposed experimental design (% odb)

| $X_T$ | $X_t$ | $X_C$ | $Y$ (%) | Ac. extr. (%) | Holoc. (%) | K. lig. (%) | Sol. lig. (%) | Glucan (%) |
|---|---|---|---|---|---|---|---|---|
| 0 | 0 | 0 | 38.4 | 2.8 | 91.5 | 2.7 | 0.185 | 34.4 |
| 0 | 0 | 0 | 38.0 | 2.8 | 91.1 | 2.8 | 0.180 | 34.7 |
| –1 | –1 | –1 | 44.8 | 3.5 | 81.4 | 8.7 | 0.064 | 52.5 |
| –1 | –1 | +1 | 40.6 | 3.2 | 92.0 | 3.0 | 0.032 | 35.9 |
| –1 | 0 | 0 | 36.8 | 3.2 | 89.9 | 4.4 | 0.047 | 41.0 |
| –1 | +1 | –1 | 40.5 | 3.0 | 86.7 | 6.8 | 0.038 | 43.4 |
| –1 | +1 | +1 | 37.1 | 2.6 | 93.1 | 4.1 | 0.083 | 34.6 |
| 0 | –1 | 0 | 43.8 | 3.1 | 92.3 | 3.2 | 0.163 | 35.5 |
| 0 | 0 | –1 | 42.5 | 2.8 | 85.5 | 5.7 | 0.124 | 35.6 |
| 0 | 0 | +1 | 38.6 | 2.4 | 92.2 | 2.3 | 0.210 | 38.8 |
| 0 | +1 | 0 | 35.2 | 2.7 | 94.2 | 2.0 | 0.250 | 26.0 |
| +1 | –1 | –1 | 44.0 | 2.6 | 89.3 | 5.0 | 0.164 | 41.5 |
| +1 | –1 | +1 | 40.6 | 2.1 | 95.2 | 1.4 | 0.213 | 61.2 |
| +1 | 0 | 0 | 31.9 | 2.5 | 95.6 | 1.1 | 0.269 | 45.8 |
| +1 | +1 | –1 | 31.5 | 2.3 | 95.4 | 1.5 | 0.260 | 24.9 |
| +1 | +1 | +1 | 29.1 | 2.1 | 95.3 | 1.2 | 0.410 | 45.9 |

$X_C$ – alkali concentration, $X_T$ – operating temperature, $X_t$ – operating time, $Y$ – yield, Ac. extr. – acetone extractives, Holoc. – holocellulose, K. lig. – Klason lignin, Sol. lig. – soluble lignin

Table 2
Normalized values of independent variables and properties of black liquor from *Leucaena leucocephala* pulping with prior autohydrolysis

| $X_T$ | $X_t$ | $X_C$ | pH | Residual alkali (g/L) | Solids (%) | GHV (MJ/kg) |
|---|---|---|---|---|---|---|
| 0 | 0 | 0 | 12.28 | 9.23 | 7.50 | 17.58 |
| 0 | 0 | 0 | 12.18 | 9.48 | 7.49 | 17.53 |
| –1 | –1 | –1 | 11.62 | 6.45 | 6.61 | 18.02 |
| –1 | –1 | +1 | 13.08 | 15.35 | 8.38 | 15.94 |
| –1 | 0 | 0 | 12.45 | 10.68 | 7.55 | 17.04 |
| –1 | +1 | –1 | 11.68 | 5.36 | 6.38 | 17.84 |
| –1 | +1 | +1 | 12.46 | 13.41 | 8.06 | 16.21 |
| 0 | –1 | 0 | 12.40 | 9.39 | 7.33 | 17.05 |
| 0 | 0 | –1 | 11.63 | 5.88 | 6.19 | 17.99 |
| 0 | 0 | +1 | 12.47 | 13.05 | 8.61 | 17.23 |
| 0 | +1 | 0 | 12.29 | 9.07 | 7.40 | 18.00 |
| +1 | –1 | –1 | 11.36 | 7.74 | 6.50 | 15.58 |
| +1 | –1 | +1 | 13.03 | 14.67 | 9.31 | 15.08 |
| +1 | 0 | 0 | 12.60 | 12.46 | 8.27 | 16.30 |
| +1 | +1 | –1 | 12.03 | 10.15 | 7.27 | 16.88 |
| +1 | +1 | +1 | 12.64 | 16.15 | 10.20 | 17.55 |

$X_C$ – alkali concentration, $X_T$ – operating temperature, $X_t$ – operating time

Table 3

Equations obtained for each dependent variable of the pulping process with and without autohydrolysis

| | | Equation | $R^2$ | Snedecor's *F* |
|---|---|---|---|---|
| With autohydrolysis | 1 | $Y_{YI} = 38.06 - 2.27 X_T - 4.04 X_t - 1.93 X_C - 3.63 X_TX_T + 1.52 X_tX_t + 2.57 X_CX_C - 2.03 X_TX_t$ | 0.989 | 98 |
| | 2 | $Y_{Acet} = 2.85 - 0.38 X_T - 0.19 X_t - 0.18 X_C + 0.32 X_TX_T - 0.20 X_CX_C + 0.11 X_TX_t$ | 0.974 | 76 |
| | 3 | $Y_{Holo} = 91.61 + 2.76 X_T + 1.45 X_t + 2.95 X_C + 0.95 X_TX_T + 1.45 X_tX_t - 2.92 X_CX_C - 1.39 X_TX_t - 1.28 X_tX_C$ | 0.992 | 111 |
| | 4 | $Y_{SL} = 0.185 + 0.106 X_T + 0.041 X_t + 0.03 X_C - 0.028 X_TX_T + 0.02 X_tX_t - 0.019 X_CX_C + 0.034 X_TX_t + 0.023 X_TX_C + 0.022 X_tX_C$ | 0.996 | 162 |
| | 5 | $Y_{KL} = 2.69 - 1.67 X_T - 0.57 X_t - 1.57 X_C + 1.27 X_CX_C - 0.36 X_TX_t + 0.56 X_TX_C + 0.79 X_tX_C$ | 0.998 | 695 |
| | 6 | $Y_{GL} = 34.48 + 1.19 X_T - 5.18 X_t + 1.85 X_C + 8.95 X_TX_T - 3.70 X_tX_t + 2.73 X_CX_C - 2.70 X_TX_t + 8.27 X_TX_C + 1.12 X_tX_C$ | 0.992 | 88 |
| | 7 | $Y_{pH} = 12.30 + 0.54 X_C + 0.21 X_TX_T - 0.26 X_CX_C + 0.11 X_TX_t - 0.22 X_tX_C$ | 0.971 | 68 |
| | 8 | $Y_{Alk} = 9.45 + 0.99 X_T + 3.71 X_C + 2.03 X_TX_T - 0.31 X_tX_t - 0.50 X_TX_C + 0.86 X_TX_t - 0.22 X_tX_C$ | 0.998 | 671 |
| | 9 | $Y_{sol} = 7.42 + 0.46 X_T + 0.12 X_t + 1.16 X_C + 0.43 X_TX_T + 0.28 X_TX_t + 0.29 X_TX_C$ | 0.996 | 337 |
| | 10 | $Y_{GH} = 17.56 - 0.37 X_T + 0.48 X_t - 0.43 X_C - 0.92 X_TX_T + 0.49 X_TX_C + 0.46 X_TX_t + 0.20 X_tX_C$ | 0.994 | 176 |
| Without autohydrolysis [27] | 11 | $Y_{YI} = 40.98 - 2.53 X_T - 1.99 X_t - 4.46 X_C + 2.94 X_CX_C - 2.49 X_TX_t + 0.89 X_tX_C$ | 0.981 | 76 |
| | 12 | $Y_{Acet} = 2.46 + 0.2 X_T - 0.19 X_t + 0.07 X_C + 0.32 X_TX_T + 0.27 X_tX_t - 0.23 X_CX_C + 0.19 X_TX_t - 0.14 X_TX_C$ | 0.980 | 43 |
| | 13 | $Y_{Holo} = 89.97 - 2.91 X_T - 3.17 X_t + 0.98 X_C - 2.10 X_TX_T - 2.80 X_tX_t - 1.19 X_TX_t$ | 0.991 | 169 |
| | 14 | $Y_{SL} = 1.02 + 0.37 X_TX_T - 0.33 X_tX_t - 0.18 X_CX_C + 0.05 X_TX_C - 0.05 X_TX_t$ | 0.967 | 59 |
| | 15 | $Y_{KL} = 1.91 - 0.614 X_T - 0.195 X_t - 0.451 X_C - 0.429 X_TX_T + 0.445 X_CX_C - 0.185 X_TX_c + 0.355 X_tX_C$ | 0.983 | 67 |
| | 16 | $Y_{GL} = 27.55 - 2.33 X_t - 1.39 X_C + 5.49 X_TX_T - 5.01 X_tX_t + 3.69 X_CX_C - 1.45 X_TX_C - 0.46 X_TX_t - 1.2 X_tX_C$ | 0.951 | 37 |
| | 17 | $Y_{pH} = 12.98 - 0.22 X_T - 0.13 X_t + 0.27 X_C - 0.23 X_CX_C + 0.14 X_TX_C - 0.11 X_TX_t - 0.06 X_tX_C$ | 0.985 | 77 |
| | 18 | $Y_{Alk} = 12.11 - 2.10 X_T - 0.48 X_t + 3.22 X_C + 0.57 X_TX_T - 1.03 X_CX_C - 0.45 X_TX_C$ | 0.993 | 205 |
| | 19 | $Y_{sol} = 8.97 + 0.57 X_T + 0.15 X_t + 0.83 X_C + 0.30 X_CX_C - 0.14 X_TX_t + 0.19 X_TX_C$ | 0.986 | 102 |
| | 20 | $Y_{GH} = 14.12 + 0.47 X_T + 0.11 X_t - 0.71 X_C - 1.08 X_TX_T + 0.32 X_CX_C + 0.32 X_tX_t + 0.13 X_TX_C$ | 0.993 | 160 |

$Y_{YI}$ – solid yield (%), $Y_{Acet}$ – acetone extractives in pulp, $Y_{Holo}$ – holocellulose in pulp, $Y_{SL}$ – soluble lignin in pulp, $Y_{KL}$ – Klason lignin in pulp, $Y_{GL}$ – glucan in solid phase relative to raw material (dry basis), $Y_{pH}$ – pH of black liquor, $Y_{Alk}$ – residual alkali in black liquor, $Y_{sol}$ – solids in black liquor, $Y_{GH}$ – gross heating value of black liquor; $X_T$, $X_t$ 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

Identifying the independent variables with the strongest and weakest influence on the dependent variables in equations in Table 3 was made difficult by the former containing quadratic terms and other factors involving interactions between two independent variables. The results deserve some comment, however. Thus, temperature was the most influential factor on pulp yield and extractive contents, and also on the gross heating value of the liquor. On the other hand, the active alkali concentration was the most influential factor on holocellulose, Klason lignin and glucan contents, residual alkali and the solid content of the black liquor.

An increase in any of the three independent variables was invariably accompanied by a linear decrease in solid yield, which was significantly lower than those obtained by López *et al.*[37] for *L. diversifolia* in a similar soda–anthraquinone–ethanol process with no prior autohydrolysis (*viz.*, yields from 38.2% to 65.0%).

Our yields are more similar to those of other authors using delignification with prior autohydrolysis. For example, ASAM pulping of aspen provided yields of 51-53%;[12] organosolv cooking of wheat straw 50-59%;[10] soda–AQ cooking of stalks and kash 48-56%;[6] and soda–AQ cooking of paulownia 44-59%.[11]

A rough analysis of the quadratic and interaction terms suggested the need to use central values in the temperature range in order to increase yields and reduce the amounts of extractives or, alternatively, central values in the active alkali range to ensure increased holocellulose contents and decreased Klason lignin contents. The coefficients concerned modulated the effects of the linear terms.

Black liquors constitute a useful fraction for obtaining energy by combustion. A large portion of wood (about 50%) is dissolved in the cooking liquor in a traditional Kraft pulp mill process. The black liquor thus obtained typically contains 12-15 wt% dry matter. Kraft black liquor contains four main groups of organic constituents, namely 30-45 wt% ligneous (polyaromatic) material, 25-35 wt% saccharinic acids (hydroxy acids), about 10 wt% formic and acetic acid, and 3-5 wt% extractives, in addition to about 1 wt% methanol and many inorganic elements, but mainly sodium (17-20 wt%) and sulphur (3-5 wt%). The composition of black liquor varies considerably depending on the particular wood type and cooking process used.[43] The properties of our black liquor exhibited a strong linear dependence on the active alkali concentration. This is consistent with the aforesaid increased extraction of solids – hemicelluloses, mainly – at increased active alkali concentration, and also with the associated increase in gross heating value – hemicelluloses possess a lower value than the cellulose fraction. The gross heating value of our black liquor was similar to those for cotton and olive residues, and higher than those for agricultural residues,[44] but not higher than those for wood materials (Table 2).

The pH of the black liquor was similar to the typical values for the traditional kraft process, where pH > 12 must be maintained in order to avoid precipitation of lignin. Our residual alkali contents were comparable to those obtained by Al-Dajani *et al.*[12] for aspen processed with ASAM following autohydrolysis (7.6-10%).

Solid extraction was less marked here than in a typical kraft process. Also, although total dry matter was measured in the black liquor from the reactor – and hence did not constitute the whole amount of solids extracted because the pulp washing liquid was not recovered –, it was similar to previously reported values of Wallberg *et al.*[43]

The surface responses from Figure 2 were plotted in order to better envisage the influence of the operational variables on the properties of the pulp and black liquor, and to compare the pulp and black liquor directly obtained from the raw material with those from the solid phase with prior autohydrolysis. Differences between two response surfaces represented the whole range of values for each dependent variable that was used at two extreme values (+1 and −1) for the most significant variable. Plotting the results for pulp obtained with and without autohydrolysis in the same figure revealed overlap between differences and allowed us to identify the particular operating conditions, affording the production of cellulose pulp and valorizable black liquor with a given value of some property from the raw material and the solid phase after autohydrolysis. Overall, soda–anthraquinone delignification of *L. leucocephala* allowed achieving similar pulp properties in the presence and absence of autohydrolysis.

However, there were wide overlapping ranges of the dependent variables, where the pulping conditions required for the solid phase from autohydrolysis were milder than those for the original material. The savings inherent in using a decreased temperature, time or alkali concentration were thus increased by the obtainment of highly valorizable liquor containing abundant sugars and oligomers. For example, the response surface for pulp yield (Fig. 2a) and that for acetone extractives (not shown) contained a wide range of identical values even when autohydrolysis was applied. The results for cellulose (Fig. 2c: holocellulose content) were also better with delignification plus autohydrolysis.

The best holocellulose contents were obtained by using high temperatures and medium active alkali concentrations. The operating time was an important variable in the processes involving delignification without autohydrolysis, but not in those including the latter treatment. Spatial overlap was less marked for Klason lignin (Fig.

2d); this was the result of reduced extraction of polysaccharides in the process including autohydrolysis, which increased the relative content of lignin. Using high temperatures in combination with long processing times and medium active alkali concentrations led to similar Klason lignin values, compared to using high active alkali concentrations.

The pH, the content in residual alkali (Fig. 2b) and the proportion of solids in the black liquor evolved very similarly. There was slight overlap and the process involving delignification without autohydrolysis proved more efficient.

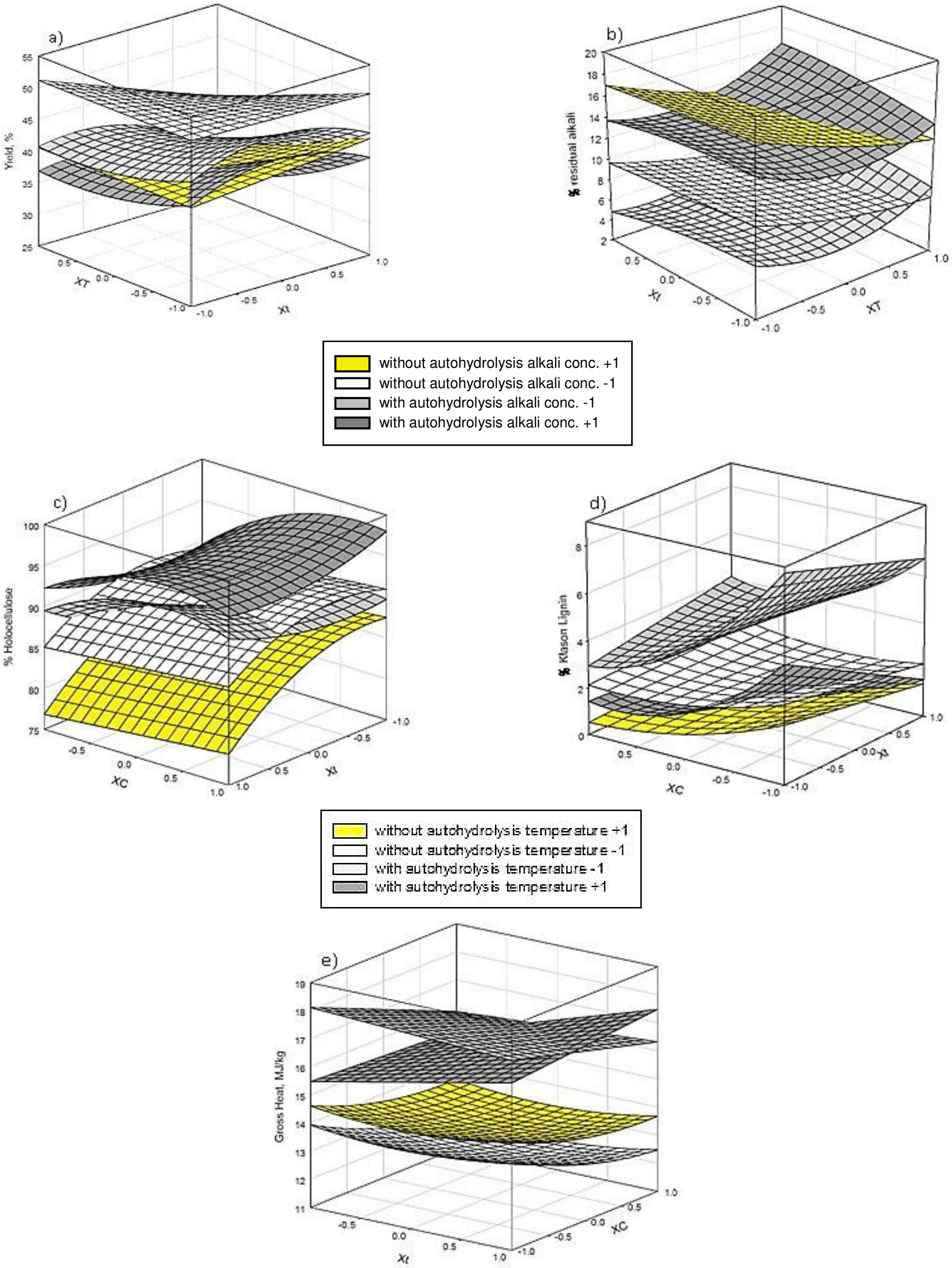

Figure 2: Variations of properties as a function of temperature (+1 and -1 response surfaces), alkali active concentration and time of process

For example, the response surface for the residual alkali concentration exhibited lower values of the variable with autohydrolysis – the surface responses for pH and solid content (not shown) were very similar – than without it.

Delignification with prior autohydrolysis provided black liquor with gross heating values (Fig. 2e) clearly exceeding those obtained in the conventional delignification process. Heating values peaked at increased levels of the three operational variables. However, near-optimal levels could be easily obtained by using values of the variables at the intersects of the response surfaces at a temperature level of +1 or –1 with an active alkali concentration around the central value (0) of its operating range in the experimental design (*e.g.*, +1 for temperature, +1 for operating time and 0 for active alkali concentration).

The properties of the cellulose pulp obtained with conventional delignification and prior autohydrolysis in the experimental design were as follows: pulp yield 34.0% *vs* 27.6%, acetone extractives 3.25% *vs* 2.41%, holocellulose 77.8% *vs* 96.8%, glucan 25.2% *vs* 33.0%, Klason lignin 0.49% *vs* 0.09%, soluble lignin 1.01% *vs* 0.36%, pH 12.5 *vs* 12.4, residual alkali 10.1 g/L *vs* 13.02 g/L, solids 9.55% *vs* 8.71% and gross heating value 13.94 *vs* 17.21 MJ/kg. The optimum operating conditions for the two processes were as follows: temperature 185 *vs* 177 ºC, operating time 150 *vs* 120 min and alkali active concentration 25% *vs* 21%. Therefore, the process involving an autohydrolysis stage, in addition to alkaline delignification, provides suitable pulp with the added advantages of giving a valorizable liquid phase that contains hemicellulose derivatives and a black liquor with an increased heating value. In addition, autohydrolysis affords milder delignification conditions.

## CONCLUSION

*Leucaena leucocephala* has proved a suitable raw material for biorefining in two stages: autohydrolysis and alkaline delignification. Autohydrolysis allows up to 46.6% of hemicelluloses in the raw material to be extracted as xylooligomers, xylose and furfural into the liquid phase. Alkaline cooking of the solid residue from this stage with NaOH–AQ allows the production of cellulose pulp and energy from the black liquor more efficiently than in the absence of prior autohydrolysis and with milder delignification conditions. In addition, autohydrolysis provides a hemicellulose-containing liquid phase with added value.

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