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Title: Integral valorization of Leucaena diversifolia by hydrothermal and pulp processing

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Keywords: Leucaena diversifolia; Hydrothermal treatment; Autohydrolysis; Gross Heating Value; Ethanol-soda-anthraquinone delignification

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Abstract: Wood from the leguminous tree, Leucaena diversifolia, was subjected to hydrothermal treatment (autohydrolysis) at 160 to 180 ºC and 0 to 30 min. followed by ethanol-soda-anthraquinone delignification. The liquid phase contained 18.65 g of sugars per liter, and the solid phase had a gross heating value of 19.083 MJ/kg, but could also be uses as a source of cellulose pulp for the production of paper with tear, burst and tensile indexes of 2.4 Nm2/kg, 2.6 MPam2/kg and 40.7 KNm/kg respectively. Leucaena diversifolia lends itself readily to valorization for energy production, and also to integral, fractional exploitation by autohydrolysis and ethanol-soda-anthraquinone delignification, which can additionally bring environmental benefits to cropping zones.

Reviewers' comments:

Please make the following modifications to shorten the manuscript and to remove wording and typographical errors:

1. Modify title: Integral valorization of Leucaena diversifolia by hydrothermal and pulp processing.

The title has been changed.

2. The current abstract should be condensed:
Wood?? from the leguminous tree, Leucaena diversifolia, was subjected to hydrothermal treatment (autohydrolysis) at ...[what conditions?] followed by ethanol-soda-anthraquinone delignification. The liquid phase contained 18.65 g of sugars per liter, and the solid phase had a gross heating value of 19.083 MJ/kg, but could also be uses as a source of cellulose pulp for the production of paper with tear, burst and tensile indexes of ...., respectively. [Add concluding sentence as to the importance/utility of your study.]

The abstract has been modified and summarized

3. Shorten Introduction:
Leucaena diversifolia is a leguminous tree that can grow 6-20 m tall and is adapted toMediterranean conditions. The tree produces large around 70 tons/ha/year of biomass (ref?) and possesses a high re-sprouting ability. It fixes nitrogen in symbiosis with Rhizobium sp. And thus improves soil fertility and has been exploited for soil conservation and consolidation (Goel and Behl, 2002). Moreover, Leucaena produces hard and strong wood and high-quality forage. Lignocellulosic biomass such as that obtained from L. diversifolia can be converted to useful fractions through "biorefining" (Clark et al., 2011). One refining strategy involves treatments that hydrolyze some of the polysaccharides within the biomass. Hydrothermal treatment causes the total or partial dissolution of hemicellulses as the hydrolysis of acetyl groups gives rise to acetic acid which in turn catalyzes the hydrolysis of the polysaccharide (reference?) leading to the release of sugar oligomers, xylose and arabinose and other chemicals. These compounds can be used for a variety of applications in the chemical, pharmaceutical and food industries, and also as fermentation media for the production of substances such as ethanol fuel and xylitol (Rivas et al., 2002). The solid fraction from the hydrothermal process contains lignin and cellulose and can be employed as raw material for alcohol production, ruminant feed, raw material for pulp and paper making and for energy production. Removal of lignin from the solid fraction provides cellulose pulp for paper making. "Green" pulping methods involving no sulphur (e.g. the ethanol-soda-anthraquinone process) are now capable of providing pulp in a high yield, with low residual lignin, high brightness and good strength properties (Shatalov and Pereira, 2004). In the current study, a variety of Leucaena diversifolia that ...[what is the improvement?] was subjected to integral fractionation by autohydrolysis and by delignification. The liquor from the autohydrolysis treatment was evaluated as a source of oligomers and monosaccharides, and the solid phase was assessed as raw material for production of combustion energy and the manufacturing of cellulose pulp and paper.

The Introduction has been modified and summarized. Several references have been added.

4. 2.1. Source and analysis of biomass
Leucaena diversifolia biomass was obtained from trees grown for seven years on a plantation in Huelva (southwestern Spain). The plants were grown in a nursery in pots, inoculated with Rhizobium, and planted at 3 month of age in two plots (plants were placed at 1.8 x 0.6 m -10.800 plants/ha-) with a complete randomized block design with 4 replicates. No fertilizer was added to the plots which were made up of sandy loam with a pH of 6-8 and moderate to substantial depth. Leucaena diversifolia sample??? [what specifically? Trunks, branches, leaves, everything?] were milled to pass a 8-cm screen. The chips were reduced again {how?] to pieces 2 to 10 mm long, and fines were removed by sieving through a 0.6-mm mesh. Samples were air-dried, mixed and stored [how?] .....liquid chromatography (HPLC). Samples ["aliquots" apply to liquids only] with a particle size of < 0.5 mm were subjected to moisture, extractives determination (TAPPI T 264-cm-07) and to quantitative acid hydrolysis with 72% H2SO4 at 121 ºC and 2 atm for 60 min (TAPPI T 249 cm-09). The solid residue after hydrolysis was recovered by filtration through a 0.45 ?m filter and considered as Klason lignin. .....order to estimate (after corrections for stoichiometry and sugar decomposition) the cellulose (as glucan), hemicelluloses (as xylan), and acetyl group contents (Díaz et al., 2004). ....

Paragraphs have been changed and included the following phrases:
"*Leucaena diversifolia* wood samples (trunks and branches) were milled"
"The chips were reduced again in a mill laboratory"
"and stored in hermetic plastic bag."

5. 2.2. Biorefining process
Figure 1 shows the flow of processes carried out with the L. diversifolia samples. A hydrothermal treatment (autohydrolysis) was carried out in order to obtain a solid phase that was delignified with an ethanol-soda-anthraquinone process to obtain cellulose pulp and a liquid phase with hemicellulosics sugars.

The paragraph has been included.

6. 2.3.1. Operation conditions in hydrothermal treatment
Raw material and water were mixed at a liquid/solid ratio of 8 kg water per kg raw material on a dry basis (the moisture content of the material was considered to be water) and treated in a 2-L stainless steel reactor (Parr Instruments Company, Moline, IL). The reactor was fitted with four blade turbine impellers, heated by ..... An aliquot of the liquor was filtered through 0.45 ?m membranes and ..... A second aliquot (25 mL) was subjected to quantitative post-hydrolysis with 4 % H2SO4 at 121 ºC for 60 min before HPLC analysis. The calorific value of the autohydrolysis solid phase was determined in section 2.1.

Paragraphs have been changed.

7. 2.3.2. Experimental desing for hydrothermal treatment
.... This allowed relating the dependent (yield, soluble lignin, calorific value and glucose, xylose, arabinose, oligomers and acetyl group contents) and independent (temperature and time of process) variables of the autohydrolysis process with a minimum number of experiment. ..... Based on these previous studies with Leucaena diversifolia and others lignocellulosic materials, operation conditions were selected (Alfaro et al., 2010, Garrote et al., 2003, Alfaro et al.,

2009). The autohydrolysis temperature and autohydrolysis time were 160, 172 and 184ºC, and 0, 15 and 30 min (at operation temperature), respectively. The liquid/solid ratio was 8/1 in all experiments.....

Paragraphs have been changed.

8. 2.4. Ethanol-soda-anthraquinone pulping process
The operation conditions for pulping without prior autohydrolysis were: Chips with a length of 3-6 cm and a thickness of 1 cm, soda concentration in the cooking liquor 17% by weight, ethanol concentration 45% in volume, anthraquinone concentration 0.10% in weight, initial liquor/solid ratio of 8/1 (dry wt. basis), operation time 60 min and operation temperature 185ºC. For samples obtained after autohydrolysis, a soda concentration of 13% and a operation temperature of 170 ºC were used. Both pulps were obtained using a 8-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. Preheating was done for 25-30 min to reach the operation temperature. After completion of the treatment, the reactor was cooled, and the pulp was separated from the liquor and washed in a bag of 0.1 mm mesh. The pulp was defibered on a Sprout-Waldron refiner and passed again thought a strainer (0.4mm mesh) in order to isolate the uncooked material (<0.5%).

Paragraphs have been changed.

9. 2.5. Beating process, formation and characterization of paper sheets
The resulting pulps were processed on a Valley beater, according to TAPPI T-200 sp-06, at different process times in order to obtain various drainage levels. The degree of refining was determined in a Shopper-Riegler refinometer (ºSR) according to TAPPI T- 227 om-09 Freeness of Pulp. Paper sheets were obtained using an ENJO-F-39.71 sheet former according to TAPPI T 205 sp-06.....The deviations for these parameters from their respective means were less than 5%.

Paragraphs have been changed.

10. 3.1. Chemical and energetic characteristics of raw material
Table 1 shows the chemical and energetic characteristics of Leucaena and other lignocellulosic materials. The Leuceana-derived material consisted of 32.2% cellulose (analyzed as glucan), (40.2% as ?-cellulose), 18.6% hemicelluloses, calculated as the sum of xylan, araban and acetyl groups, (32.6% based on holocelulose - ?-cellulose), and 21.5% Klason lignin (23.7% after quantitative acid hydrolysis). This composition is similar to that found by other authors for Leucaena diversifolia (refs) and other varieties of Leucaena (refs) and comparable to hardwoods, such as Eucalyptus globulus (refs). The hemicellulose content in Leucaena was similar to that of tagasaste (41.4%) (ref.) and herbaceus species (Alfaro et al., 2010, Garrote et al., 2003, Alfaro et al., 2009). The molar relatio of the monomers in L. diversifolia was calculated as xylose:acetyl groups:arabinose = 15.5:2.1:1. This composition is typical of acetylglucuronoxylans typically present in hardwoods (Pinto et al., 2005). The gross heating value (GHV) of L. diversifolia of 19.1 MJ/kg, is in between those for softwood (20.0 MJ/kg) and hardwood (18.8 MJ/kg) (ref?), similar to that of Ailantthus wood (19.0 MJ/kg) (ref?), somewhat higher than that of Eucalyptus globulus (Telmo et al., 2010), and much higher than those of wheat straw

(17.0 MJ/kg) or corn stover (17.8 MJ/kg) (Demirbas, 1997). The GHV for the solid residue remaining after Leucaena autohydrolysis is shown in Table 2 together with the contents of the autohydrolysis solid phase. The GHV for the solid phase ranged from 19.1 to 19.9 MJ/kg depending on the autohydrolysis conditions. Table 4 shows .... This further increases the intrinsic value of the compounds extracted into the liquor or reduces the energy cost associated with extraction by autohydrolysis.

Paragraphs have been changed and several references have been added.

11. 3.2. Products of hydrothermal treatment. Modeling and optimization.
Table 2 shows the normalized values of independent variables (temperature and operation time) and the Gross Heating Values, yield, Klason lignin and soluble lignin contents in the solid phase relative to the initial raw material, and also the glucan, xylan, araban contents and acetyl groups in the solid phase, relative to the initial respective polymer content in raw material. Table 3 [it seems Table 4 was mentioned before Table 3] shows the monomeric sugar and oligomer concentrations in the liquid phase in g/L and as percentage relative to respective polymer content in dry raw material. The results were modeled by using the multiple regression methodology described in section ..(Table 4). ..... temperature on yield was considerably smaller at short treatment times (yields of 90-96%) relative to long times (yields of 72-90%). .....The amount of soluble lignin was, in most cases, lower (2.1% in the raw material and 0.82-2.03% in the autohydrolysis solid fraction). This result suggests substantial dissolution of this fraction during autohydrolysis (Leschinnsky et al., 2009). ..... In a biorefinery process that includes paper production, the amount of sugars in solution should be as high as possible, but degradation of cellulose (as glucan) in the raw material should be avoided as far as possible in order to obtain pulp of acceptable properties (Alfaro et al., 2010). ..... In order to determine the values of the independent variables giving the optimum variable dependent results, the response surfaces for each dependent variable were plotted at maxima and minima levels of the independent variables (Figures 2 and 3). Figure 2 shows the three response surfaces for the glucan derivatives in both autohydrolysis phases. The influence of the variables was essentially linear despite .... Modeling the results for this hemicellulose fraction was also complicated. ....response surfaces of Figure 3. The hydrolysis of hemicellulosic xylan in the raw material was substantial over the operational range 0-1 for both operational variables. Based on the results presented in Table 2, xylan was .... [The following sentence is not clear: In principle, it is advisable to use medium or high temperatures and short or medium treatment times to extract xylose and xylooligomers similarly efficiently as with medium temperatures and long times, albeit with less efficient degradation of glucan (roughly 2 percent points more of glucan in the autohydrolysis solid phase based on the YGLS model of Table 4).] Autohydrolysis extracted araban to a similar extent as xylan derivatives, but time was more influential than temperature on its hydrolysis (see YARS equation in Table 4). .... 91.6 to 103.7% (data not shown). In regards to acetyl groups, the ..... As a rule, extraction of hemicellulosic derivatives from L. diversifolia was more efficient than that from other batches of the same plant grown for 3 years and subjected to non-isothermal treatments (Alfaro et al., 2009); however, it was less efficient than that from Chamaecytisus proliferus (Alfaro et al., 2010), another legume. The glucan fraction in Leucaena was less markedly .... Applying a similar thermal treatment to Paulownia fortunei, a tree species of similar composition as Leucaena ....

Paragraphs have been changed.
The phrase "In principle, it is advisable to use medium or high temperatures and short or medium treatment times to extract xylose and xylooligomers similarly efficiently as with medium temperatures and long times" has been changed by the sentence "In principle, it is advisable to use medium or high temperatures and short or medium treatment times to extract xylose and xylooligomers similarly as with medium temperatures and long times".
The phrase "albeit with less efficient degradation of glucan" has been changed by the sentence "Also there is less degradation of glucan".

12. 3.3. Characterization of paper sheets from solid phase post-autohydrolysis
Cellulose pulp was obtained from the autohydrolysis solid phase provided by a thermal treatment at 178 ?C for 0 min (non-isothermal conditions) [what does this mean? What was the temperature?], and the properties of paper prepared from this pulp were: Kappa number 40.4, viscosity 1119 g cm-3 and brightness 29.3 %. The conditions of the hydrothermal treatment preceding delignification were adjusted in such a way as to ensure a high content in cellulose (as glucan) in the solid phase and in potentially valorizable hemicellulosic sugars in the liquid phase. Based on the equations of Table 4, the resulting liquid phase should contain 2.4% xylose and 26.4% xylo-oligomers respect to the initial concentration of xylan in the raw material, whereas the solid phase should consist of 92.2% glucan. The yield of the solid phase would be 81%, its gross heating value 19.6 MJ/kg and the soluble lignin content in the solid phase 1.2% (i.e. 43% of all initial lignin would be dissolved by the autohydrolysis treatment). .....autohydrolysis solid phase. The Kappa number, viscosity, and brightness of this paper were 27, 1303 g cm-3, and 38.5%, respectively. .... the major strength-related properties of .....The data presented in Figure 4 allows the following conclusions: .....improved strength-related properties. Similar results were obtained in previous studies on another legume variety, Chamaecytisus proliferus, subjected ....markedly improved by the autohydrolysis treatment; however, there were also substantial ...

All paragraphs have been changed.

13. Table 1 is too confusing and should be separated into two Tables.

Table 1 has been divided into two tables 1a and 1b.

14. Figure 1: Scheme of experimental work. Abbreviations: [soda] w: soda concentration by weight; [ethanol] v: concentration of ethanol by volume; [AQl] w: concentration of anthraquinone by weight; T: process temperature (ºC); t: processing time (min). L/S: liquid / solid ratio"

The abbreviations in Figure 1 have been modified.

15. Figure 2: Glucose and gluco-oligomers of the liquor and glucan of the solid as function of temperature and time of the autohydrolysis process

The title of Figure 2 has been changed.

16. Figure 3: Xylose and xylo-oligomers of the liquor and xylan of the solid as function of temperature and time of the autohydrolysis process

The title of Figure 3 has been changed.

17. Figure 4: Properties of the paper sheets vs. Shopper-Riegler degree.[Are the data points averages?]

The title of Figure 4 has been changed.

***Highlights**

Leucaena diversifolia lends itself readily to valorization for energy production, and also to integral, fractional exploitation by autohydrolysis and ethanol–soda–anthraquinone delignification, which can additionally bring environmental benefits to cropping zones.

The autohydrolysis solid phase can be used to obtain other chemicals, directly burnt for energy production or processed to obtain cellulose pulp. The liquid phase is rich in monomers and oligomers.

The autohydrolysis process facilitates refining of cellulose pulp allowing a significant improvement in resistance rates of the paper sheets.

Integral valorization of *Leucaena diversifolia* by hydrothermal and pulp processing

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Abstract

Wood from the leguminous tree, *Leucaena diversifolia*, was subjected to hydrothermal treatment (autohydrolysis) at 160 to 180 ºC and 0 to 30 min. followed by ethanol-soda-anthraquinone delignification. The liquid phase contained 18.65 g of sugars per liter, and the solid phase had a gross heating value of 19.083 MJ/kg, but could also be uses as a source of cellulose pulp for the production of paper with tear, burst and tensile indexes of 2.4 Nm2/kg, 2.6 MPam2/kg and 40.7 KNm/kg respectively. *Leucaena diversifolia* lends itself readily to valorization for energy production, and also to integral, fractional exploitation by autohydrolysis and ethanol–soda–anthraquinone delignification, which can additionally bring environmental benefits to cropping zones.

Keywords

Leucaena diversifolia, Hydrothermal treatment, Autohydrolysis, Gross Heating Value, Ethanol-soda-anthraquinone delignification

1. Introduction

Environmental prevention plans for industrial processes include provisions for efficient use of resources and raw materials to maximize yields while minimizing waste production and the consumption of energy –which should ideally come from renewable or non-fossil sources. Lignocellulosic biomass is a major renewable source of raw materials and energy integral exploitation of which can provide a number of environmental and economic advantages (Heinimö and Junginger, 2009).

Plant species used to extract energy from industrial crops should be ecologically integrated in a sound manner in order to avoid adverse impacts on the environment and competition between food crops. Using arable land to grow non-food crops can help reduce agricultural surpluses, develop rural economies, reduce aid-dependence and decrease the production of greenhouse gases (Gustavsson et al., 2007).

Leucaena diversifolia **is a leguminous tree that can grow 6-20 m tall and is adapted to Mediterranean conditions. The tree produces large around 40 tons/ha/year of biomass after three years of growth (Diaz et al., 2007) and 70 tons/ha/year after seven years of growth (this study) and possesses a high re-sprouting ability. It fixes nitrogen in symbiosis with Rhizobium sp. and thus improves soil fertility and has been exploited for soil conservation and consolidation (Goel and Behl, 2002). Moreover, Leucaena produces hard and strong wood and high-quality forage.**

Lignocellulosic biomass such as that obtained from *L. diversifolia* can be converted to useful fractions through "biorefining" (Clark et al., 2011). One refining strategy involves treatments that hydrolyze some of the polysaccharides within the biomass. Hydrothermal treatment causes the total or partial dissolution

of hemicellulses as the hydrolysis of acetyl groups gives rise to acetic acid which in turn catalyzes the hydrolysis of the polysaccharide (Garcia et al., 2011)) leading to the release of sugar oligomers, xylose and arabinose and other chemicals. These compounds can be used for a variety of applications in the chemical, pharmaceutical and food industries, and also as fermentation media for the production of substances such as ethanol fuel and xylitol (Rivas et al., 2002). The solid fraction from the hydrothermal process contains lignin and cellulose and can be employed as raw material for alcohol production, ruminant feed, raw material for pulp and paper making and for energy production.

Removal of lignin from the solid fraction provides cellulose pulp for paper making. "Green" pulping methods involving no sulphur (e.g. the ethanol-soda-anthraquinone process) are now capable of providing pulp in a high yield, with low residual lignin, high brightness and good strength properties (Shatalov and Pereira, 2004).

In the current study, a variety of *Leucaena diversifolia* (selected greenhouse) was subjected to integral fractionation by autohydrolysis and by delignification. The liquor from the autohydrolysis treatment was evaluated as a source of oligomers and monosaccharides, and the solid phase was assessed as raw material for production of combustion energy and the manufacturing of cellulose pulp and paper.

2. Materials and methods

2.1. Source and analysis of biomass

***Leucaena diversifolia* biomass was obtained from trees grown for seven years on a plantation in Huelva (southwestern Spain). The plants were grown in a**

nursery in pots, inoculated with Rhizobium, and planted at 3 month of age in two plots (plants were placed at 1.8 x 0.6 m -10.800 plants/ha-) with a complete randomized block design with 4 replicates. No fertilizer was added to the plots which were made up of sandy loam with a pH of 6-8 and moderate to substantial depth.

***Leucaena diversifolia* wood samples (trunks and branches) were milled to pass a 8-cm screen. The chips were reduced again in a mill laboratory to pieces 2 to 10 mm long, and fines were removed by sieving through a 0.6-mm mesh. Samples were air-dried, mixed and stored in hermetic plastic bag.**

The raw material was prepared in accordance with TAPPI T-257 and analyzed for the following parameters: 1% NaOH solubles (TAPPI T 212 om-07), hot water solubles (TAPPI T 207 cm-93), ethanol-benzene extractives (TAPPI T 204 cm-07), Klason lignin (TAPPI T-222 om-98), holocellulose (Wise et al., 1946), α-cellulose (TAPPI T 203 cm-09) and ash (TAPPI T-211) contents. All treatments in this study were in a completely randomized design with four replications (variation coefficient less than 3% and less than 1% for holocellulose and cellulose contents).

In addition, the cellulose and hemicellulose composition of the material, in the form of glucan, xylan, araban and acetyl groups, were determined by high performance liquid chromatography (HPLC). **Samples ("aliquots" apply to liquids only) with a particle size of < 0.5 mm were subjected to moisture, extractives determination (TAPPI T 264-cm-07) and to quantitative acid hydrolysis with 72% H_2SO_4 at 121 ºC and 2 atm for 60 min (TAPPI T 249 cm-09). The solid residue after hydrolysis was recovered by filtration through a 0.45 μm filter and considered as Klason lignin.** Acid soluble lignin was determined following standard method TAPPI T 250 wd-96.

The monosaccharides (glucose, xylose and arabinose) and acetic acid contained in hydrolysates were determined by HPLC in order to estimate **(after corrections for stoichiometry and sugar decomposition) the cellulose (as glucan), hemicelluloses (as xylan), and acetyl group contents (Díaz et al., 2004).** Chromatographic runs were done with an Agilent 1100 HPLC instrument equipped with an Aminex HPX-87H column packed with ion-exchange resin under the following conditions: mobile phase, sulphuric acid at 0.05 $mol \cdot L^{-1}$; flow rate, 0.6 $mL \cdot min^{-1}$; column temperature, 30°C; injected volume, 20 μL. Ashes were determined by calcination (TAPPI T 244-cm-99).

All HPLC determinations were in a completely randomized design with three replications (variation coefficient less than 4%).

Gross Heating Values of raw material were determined at a constant volume in accordance with "CEN/TS 14918:2005 (E) Solid biofuels-Method for the determination of calorific value" and UNE 164001 EX standards by using a Parr 6300 Automatic Isoperibol Calorimeter.

2.2. Biorefining process

Figure 1 shows the flow of processes carried out with the *L. diversifolia* samples. A hydrothermal treatment (autohydrolysis) was carried out in order to obtain a solid phase that was delignified with an ethanol-soda-anthraquinone process to obtain cellulose pulp and a liquid phase with hemicellulosics sugars.

2.3. Hydrothermal treatment

2.3.1. Operation conditions in hydrothermal treatment

Raw material and water were mixed at a liquid/solid ratio of 8 kg water per kg raw material on a dry basis (the moisture content of the material was

considered to be water) and treated in a 2-L stainless steel reactor (Parr Instruments Company, Moline, IL). The reactor was fitted with four blade turbine impellers, heated by an external fabric mantle, and cooled by cool water circulating through an internal loop. The reaction media was stirred at 150 rpm and heated to reach the desired temperature. Time zero was considered the beginning of the isothermal stage. The temperature of the process was automatically controlled via an internal cooling coil which was used to cool the reactor after the temperature and operating time were reached.

At the end of treatment, the solid residue was recovered by filtration and washed with distilled water for gravimetric yield determination. A fraction was used for pulping and another fraction was air-dried and milled to a particle size <0.5 mm. Milled samples were assayed for lignin (Klason and soluble), glucan, hemicellulose (xylan and araban) and acetyl groups using the same methods as for raw material analysis.

An aliquot of the liquor was filtered through 0.45 μm membranes and used for direct HPLC determination of monosaccharides and acetic acid. **A second aliquot (25 mL) was subjected to quantitative post-hydrolysis with 4 % H_2SO_4 at 121 ºC for 60 min before HPLC analysis. The calorific value of the autohydrolysis solid phase was determined in section 2.1.**

2.3.2. Experimental desing for hydrothermal treatment

A 2^n central composite experimental design that enabled the construction of second-order polynomial in the independent variables and the identification of statistical significance in the variables was used. **This allowed relating the dependent (yield, soluble lignin, calorific value and glucose, xylose, arabinose, oligomers and acetyl**

group contents) and independent (temperature and time of process) variables of the autohydrolysis process with a minimum number of experiment.

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 maximum and minimum values, respectively.

Several experiences from isothermal autohydrolysis were carried out in order to study the effect the severity of the process on the xyloolygomer production and cellulose degradation. **Based on these previous studies with *Leucaena diversifolia* and others lignocellulosic materials, operation conditions were selected (Alfaro et al., 2010, Garrote et al., 2003, Alfaro et al., 2009). The autohydrolysis temperature and autohydrolysis time were 160, 172 and 184ºC, and 0, 15 and 30 min (at operation temperature), respectively. The liquid/solid ratio was 8/1 in all experiments.**

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 our conditions, N = 10.

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

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

The independent variables used in the equations relating to both types of variables were those having a statistical significant coefficient (**those not exceeding a**

significance level of 0.05 in the student ´s-test – t < 2 - and having a 95% confidence interval excluding zero)

2.4. Ethanol-soda-anthraquinone pulping process

The operation conditions for pulping without prior autohydrolysis were: Chips with a length of 3-6 cm and a thickness of 1 cm, soda concentration in the cooking liquor 17% by weight, ethanol concentration 45% in volume, anthraquinone concentration 0.10% in weight, initial liquor/solid ratio of 8/1 (dry wt. basis), operation time 60 min and operation temperature 185ºC. For samples obtained after autohydrolysis, a soda concentration of 13% and a operation temperature of 170 ºC were used. The values of rest of variables were the same. These values of process variables were selected according previous works from the authors (Alfaro et al., 2009). Anthraquinone enhances strength-related properties relative to soda–ethanol paper.

Both pulps were obtained using a 8-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. Preheating was done for 25-30 min to reach the operation temperature. After completion of the treatment, the reactor was cooled, and the pulp was separated from the liquor and washed in a bag of 0.1 mm mesh. The pulp was defibered on a Sprout-Waldron refiner and passed again thought a strainer (0.4mm mesh) in order to isolate the uncooked material (<0.5%).

2.5. Beating process, formation and characterization of paper sheets

The resulting pulps were processed on a Valley beater, according to TAPPI T-200 sp-06, at different process times in order to obtain various drainage levels. The degree of refining was determined in a Shopper-Riegler refinometer (ºSR) according to TAPPI T- 227 om-09 Freeness of Pulp. Paper sheets were obtained using an ENJO-F-39.71 sheet former according to TAPPI T 205 sp-06.

The resulting paper sheets were analysed for Tensile Index (TAPPI T-494 om-96), Burst Index (TAPPI T-403 om-97), Tear Index (TAPPI T-414 om-98) and Gurley porosity (TAPPI T-460 om-96) following conditioning in accordance with TAPPI T-220 sp-96. Each value in the experimental results is an average of 12 samples. **The deviations for these parameters from their respective means were less than 5%.**

3. Results and discussion

3.1. Chemical and energetic characteristics of raw material

Table 1 shows the chemical and energetic characteristics of Leucaena and other lignocellulosic materials. The Leuceana-derived material consisted of 32.2% cellulose (analyzed as glucan), (40.2% as α-cellulose), 18.6% hemicelluloses, calculated as the sum of xylan, araban and acetyl groups, (32.6% based on holocelulose - α-cellulose), and 21.5% Klason lignin (23.7% after quantitative acid hydrolysis). This composition is similar to that found by other authors for *Leucaena diversifolia* (Alfaro et al., 2009) and other varieties of Leucaena (Jimenez et al., 2007) and comparable to hardwoods, such as Eucalyptus globulus (Garrote

et al., 2003). The hemicellulose content in Leucaena was similar to that of tagasaste (41.4%) (Alfaro et al., 2010) and herbaceus species.

The molar relatio of the monomers in *L. diversifolia* was calculated as xylose:acetyl groups:arabinose = 15.5:2.1:1. This composition is typical of acetylglucuronoxylans typically present in hardwoods (Pinto et al., 2005).

The gross heating value (GHV) of *L. diversifolia* of 19.1 MJ/kg, is in between those for softwood (20.0 MJ/kg) and hardwood (18.8 MJ/kg) (Demirbas, 1997), similar to that of Ailantthus wood (19.0 MJ/kg) (Demirbas, 1997), somewhat higher than that of Eucalyptus globulus (Telmo et al., 2010), and much higher than those of wheat straw (17.0 MJ/kg) or corn stover (17.8 MJ/kg) (Demirbas, 1997).

The GHV for the solid residue remaining after Leucaena autohydrolysis is shown in Table 2 together with the contents of the autohydrolysis solid phase. The GHV for the solid phase ranged from 19.1 to 19.9 MJ/kg depending on the autohydrolysis conditions. Table 4 shows the equations modelling the dependent variables of the autohydrolysis process. The equation for Y_{CV} reflects the linear variation of GHV for the solid residue with the operational temperature and treatment time; as can be seen, the highest GHV was obtained with the most drastic hydrothermal conditions.

The autohydrolysis treatment raised the calorific value of the solid phase by up to 4% with respect to the starting raw material. This can be ascribed to the relative increase in the amount of lignin and cellulose present in the solid phase as polysaccharides are extracted and to the increased calorific value of lignin relative to cellulose and hemicelluloses. **This further increases the intrinsic value of the**

compounds extracted into the liquor or reduces the energy cost associated with extraction by autohydrolysis.

3.2. Products of hydrothermal treatment. Modeling and optimization.

Table 2 shows the normalized values of independent variables (temperature and operation time) and the Gross Heating Values, yield, Klason lignin and soluble lignin contents in the solid phase relative to the initial raw material, and also the glucan, xylan, araban contents and acetyl groups in the solid phase, relative to the initial respective polymer content in raw material.

Table 3 shows the monomeric sugar and oligomer concentrations in the liquid phase in g/L and as percentage relative to respective polymer content in dry raw material. The results were modeled by using the multiple regression methodology described in section 2.3.2. (Table 4).

The solid phase yield obtained under such conditions was 25% lower than that provided by less drastic conditions. The yield exceeded 80% in 70% of the tests. The Y_{YI} model in Table 4 suggests a linear relationship of yield with both operational variables, to which it was inversely proportional. The statistically significant presence of the quadratic term X_tX_t and the interaction X_TX_t suggests that the influence of **temperature on yield was considerably smaller at short treatment times (yields of 90-96%) relative to long times (yields of 72-90%).** This confirms the hypothesis that the polysaccharide fraction is hydrolysed from lignocellulosic biomass at fairly high temperatures, but requires an also fairly long time to occur.

The content in Klason lignin of the autohydrolysis solid fraction reflected its

nature as a non-soluble fraction of lignocellulosic biomass. Thus, it ranged from 22.6 to 25.1% of the amount present in the starting raw material, so it changed by a mere 10.2% at most and had an average value of 23.3%. The errors inherent in the methods used to determine lignin preclude more precise conclusions; therefore, insoluble lignin can be assumed not to be degraded or solubilized in substantial amounts within the studied operating ranges. Its average value is close to the lignin content in the raw material as determined in accordance with TAPPI standard (21.5%) and the HPLC protocol for the determination of sugars (23.7%).

The amount of soluble lignin was, in most cases, lower (2.1% in the raw material and 0.82-2.03% in the autohydrolysis solid fraction). This result suggests substantial dissolution of this fraction during autohydrolysis (Leschinnsky et al., 2009). The treatment time was the more influential factor, and its influence and that of temperature, essentially linear –with a slight contribution of the quadratic term X_tX_t.

Glucan was the individual polysaccharide affected to the smallest extent by the autohydrolysis treatment, 90.1% to 98.1% of its content remaining in the autohydrolysis solid phase. **In a biorefinery process that includes paper production, the amount of sugars in solution should be as high as possible, but degradation of cellulose (as glucan) in the raw material should be avoided as far as possible in order to obtain pulp of acceptable properties (Alfaro et al., 2010).** Based on the foregoing, the glucose and glucooligomer contents in the autohydrolysis liquid phase were relatively low (0.3–1.7% and 2.2–8.4%, respectively).

The glucose content in the autohydrolysis liquid phase (Y_{GL} equation in Table 4) was only influenced by linear terms of the operational variables. Clearly, glucan dissolution as glucose in the liquid phase increased with increasing temperature and

treatment time. The glucooligomer content of the autohydrolysis liquid phase and the glucan content of the solid phase were clearly dependent on the quadratic terms $X_T X_T$ and $X_t X_t$, both of which were statistically significant. Although their coefficients were much lower than those for the linear terms, the presence of these two terms made interpreting the models more complicated.

In order to determine the values of the independent variables giving the optimum variable dependent results, the response surfaces for each dependent variable were plotted at maxima and minima levels of the independent variables (Figures 2 and 3). Figure 2 shows the three response surfaces for the glucan derivatives in both autohydrolysis phases. The influence of the variables was essentially linear despite the presence of significant quadratic terms. The mass balance for the glucan derivatives was subject to a negligible error (the experimental proportions ranged from 99.5 to 100.7%).

The xylose and xylooligomer contents exhibited substantial variations (0.2–8.8% and 1.1–51.9%, respectively - percentage relative to the content in xylan fraction of the raw material). These results are consistent with the variation of the xylan content of the autohydrolysis solid phase. In fact, the mass balance for xylan derivatives was less precise than that for glucan derivatives (total xylan contents ranged from 99 to 106%). **Modeling the results for this hemicellulose fraction was also complicated**. Thus, the Y_{Xy}, Y_{XYOL} and Y_{XYS} models in Table 4 contain statistically significant quadratic or interaction terms and are difficult to interpret in a semi-quantitative manner without the **response surfaces of Figure 3. The hydrolysis of hemicellulosic xylan in the raw material was substantial over the operational range 0-1 for both operational variables. Based on the results presented in Table 2, xylan was** hydrolysed to an approximately 20% greater extent (20.76% according to the Y_{XYS} model of Table 4).

Xylan hydrolysis increased markedly in the upper ranges of the independent operational variables (particularly with the treatment time, as can be inferred from the coefficients of the linear terms in the Y_{XYS} model of Table 4 and from Figure 3). **In principle, it is advisable to use medium or high temperatures and short or medium treatment times to extract xylose and xylooligomers similarly as with medium temperatures and long times. Also there is less degradation of glucan (roughly 2 percent points more of glucan in the autohydrolysis solid phase based on the Y_{GLS} model of Table 4).**

Autohydrolysis extracted araban to a similar extent as xylan derivatives, but time was more influential than temperature on its hydrolysis (see Y_{ARS} equation in Table 4). Although more than 90% of all araban initially present in the raw material was extracted under the most drastic conditions, the hemicellulose fraction obtained was less useful than that of xylan as it contained hardly 1% of the initial mass of raw material. The cumulative experimental error in the determination of araban in the liquid and solid phases was similar to that for xylan derivatives, with proportions from **91.6 to 103.7% (data not shown).**

In regards acetyl groups, the hydrothermal treatment caused the dissolution of hemicellulosic polysaccharides. The effect was strengthened by the release of acetyl groups from hemicelluloses increasing the acidity of the medium (Önnerud and Gellersted, 2003). All acetyl groups were dissolved under the most drastic treatment conditions used.

As a rule, extraction of hemicellulosic derivatives from *L. diversifolia* was more efficient than that from other batches of the same plant grown for 3 years and subjected to non-isothermal treatments (Alfaro et al., 2009); however, it was less efficient than that from Chamaecytisus proliferus (Alfaro et al., 2010), another

legume. The glucan fraction in Leucaena was less markedly degraded than that in Chamaecytisus, which in theory made the solid phase from the former more suitable for producing cellulose pulp with a biorefining scheme.

A comparison of the components extracted from the hemicellulose fraction of other plants such as sunflower stalks hydrothermally treated at 165–180 °C revealed that, although the stalks contained a similar amount of glycan and more xylan (23.9%) than Leucaena (15.5%), the resulting liquid phases contained similar amounts of glucose and xylose, and somewhat smaller amounts of oligosaccharides in Leucaena (16.8 g/L vs 21.0 g/L in sunflower stalks) (Caparrós et al., 2008). **Applying a similar thermal treatment to Paulownia fortunei, a tree species of similar composition as Leucaena** (34.2% glucan and 18.3% xylan) yielded less glucose (0.84 vs 1.12 g/L) but more xylose (2.05 vs 1.22 g/L) and oligomers (16.84 vs 8.08 g/L). Using similar conditions with eucalyptus provided greater amounts of dissolved sugars (Romani et al., 2011).

3.3. Characterization of paper sheets from solid phase post-autohydrolysis

In addition to determining and modelling the gross heating value for the autohydrolysis solid phase, we used this material to obtain cellulose pulp and paper with a view to assessing its potential valorization by biorefining. **Cellulose pulp was obtained from the autohydrolysis solid phase (carried out at 178 ºC for 0 min. non-isothermal conditions) and the properties of paper prepared from this pulp were: Kappa number 40.4, viscosity 1119 g cm^{-3} and brightness 29.3 %. The conditions of the hydrothermal treatment preceding delignification were adjusted in such a way as to ensure a high content in cellulose (as glucan) in the solid phase and in potentially valorizable hemicellulosic sugars in the liquid phase. Based on the equations of**

Table 4, the resulting liquid phase should contain 2.4% xylose and 26.4% xylo-oligomers respect to the initial concentration of xylan in the raw material, whereas the solid phase should consist of 92.2% glucan. The yield of the solid phase would be 81%, its gross heating value 19.6 MJ/kg and the soluble lignin content in the solid phase 1.2% (i.e. 43% of all initial lignin would be dissolved by the autohydrolysis treatment).

In parallel, we obtained unhydrolysed cellulose pulp from *L. diversifolia* under the conditions described in Section 2.4 except that the temperature and soda concentration were 15 °C and 4 percent points higher than those used to obtain pulp from the **autohydrolysis solid phase. The Kappa number, viscosity, and brightness of this paper were 27, 1303 g cm^{-3}, and 38.5%, respectively.** We hypothesized that the autohydrolysis treatment would destroy the cellulose matrix, thereby facilitating delignification by biorefining and that using the same operational conditions as in the absence of a autohydrolysis treatment would result in excessive degradation of cellulose fibres (Alfaro et al., 2010).

Figure 4 shows the results of the characterization tests for **the major strength-related properties of** the resulting paper (tear index, burst index and tensile index), as well as the Gurley porosity of handsheets made by applying variable refining as measured by the Shopper–Riegler index. **The data presented in Figure 4 allows the following conclusions:**

(*a*) The autohydrolysis treatment preceding delignification slightly degraded the strength-related properties and Gurley porosity of the resulting paper.

(*b*) The treatment substantially facilitated refining of the pulp and increased its strength as a result. This suggests that ethanol–soda pulp from the autohydrolysed material

is amenable to refining and can provide paper with substantially **improved strength-related properties.**

Similar results were obtained in previous studies on another legume variety, *Chamaecytisus proliferus*, subjected to organosolv delignification with ethanol (Alfaro et al., 2010), which is less favoured on a industrial scale.

As can also be seen from Figure 4, the improvement in physical properties of the paper sheets was maximal at low Schopper Riegler degree values (up to 20 °SR), whether or not the raw material was subjected to autohydrolysis. The improvement was also substantial between 20 and 38 °SR, but further refining (45–50 °SR) led to worse results. Therefore, pulp from autohydrolysed material should never be refined beyond 40 °SR.

The tear index for paper from autohydrolysed pulp was 18.8% higher at 20–21 °SR en even more so (53.7%) at 35–38 °SR. This was the strength-related property most **markedly improved by the autohydrolysis treatment; however, there were also substantial** improvements in burst index (22.8–39.0%) and tensile index (10.6–35.7%).

The tensile index and burst index of paper from *L. diversifolia* pulp obtained by non-isothermal autohydrolysis of the raw material, followed by refining at 38 °C, was 1.8 and 3.5 times higher, respectively, than that for eucalyptus paper at 181 °C and ethanol delignification (Garrote et al., 2003). Similar results were obtained relative to the legume tagasaste, which exposed the beneficial effect of the thermal treatment and the use of ethanol as delignifying agent on pulp refining (Alfaro et al., 2010) .

The combined use of non-isothermal autohydrolysis and ethanol–soda-anthraquinone delignification to obtain handsheets with improved strength-related properties yielded optimum results under those conditions leading to maximal removal

of lignin fibres while preserving part of hemicellulose. In fact, the hemicellulose fraction plays a central role in fibre swelling and interfibre bonding (García Hortal, 2007). It is therefore advisable to preserve a relatively high proportion of xylan –which amounted to 72.43% with the optimum autohydrolysis conditions. The physical properties of paper can be improved by refining the pulp, which removes the primary wall of fibres and facilitates their hydration and swelling, thereby increasing their flexibility and bonding capacity. Refining tends to optimize bonds between fibres at the expense of a loss of individual strength to an extent dependent on the particular raw material and pulping method (Hietanen and Ebeling, 1990).

4. Conclusions

Leucaena diversifolia lends itself readily to valorization for energy production, and also to integral, fractional exploitation by autohydrolysis and ethanol–soda–anthraquinone delignification, which can additionally bring environmental benefits to cropping zones. The gross heating value for *Leucaena* is 19.083 MJ/kg. The autohydrolysis solid phase can be used to obtain other chemicals, directly burnt for energy production or processed to obtain cellulose pulp. In addition to providing a liquid phase containing valuable chemicals (18.65 g/L of sugars at 178 °C), the autohydrolysis facilitates refining of cellulose pulp, allows the tear and tensile index to be increased by 53.8 and 22.2%.

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Tables

Figures

Table 1a

Leucaena diversifolia	**Chemical and energetic characteristics**
TAPPI characterization	Quantitative acid hydrolysis and HPLC characterization
1% NaOH soluble.....14.9 % Hot water solubles..... 4.8 % Alcohol-benzene extractives ..... 3.9 % Lignin (after 72% sulphuric hydrolysis) .....23.7 % Hot water solubles (after organic extraction) .....3.9 % Holocellulose.....72.8 % α-cellulose .....40.2 %	Glucan .....32.2 % Xylan.....15.5 % Araban.....1.0 % Acetyl groups .....2.1 % Klason lignin .....21.5% Soluble lignin .....2.1 % Ash .....1.4 %
Calorific value 19.083 MJ/kg	

Table 1b

Raw Material	Cellulose (%)	Hemicellulose (%)	Lignin (%)	References
Arundo donax (reed)	34.8	29.7	23.0	Caparrós et al., 2007
Chamaecytisus proliferus (tagasaste)	38.9	41.4	19.8	Alfaro et al., 2010
Eucalyptus globulus	43.0, 46.8, 53.4	13.2, n.d., n.d.	25.3, 22.9, nd.	Garrote et al., 2003
Eucalyptus gumífera and *saligna*	38.0, 45.0	16.0, 15.0	37.0, 25.0	Mok and Antal, 1992
Helianthus annus	33.8	40.4	19.9	Caparrós et al., 2008
Leucaena	43, 40.8	17, 15.0	25, 26.9	Mok and Antal, 1992
Leucaena leucocephala (Honduras) *L. leucocephala* (India)	39.4, 41.0, 41.2, 44.4	28.9, 26.0, 32.9, 31.5	18.4, 26.0, 19.4, 21.4	Mok and Antal, 1992 Jiménez et al., 2007
Leucaena diversifolia	38, 40.10	27.8, 37.8	24.8, 19.09	Alfaro et al., 2009
Leucaena colinsi	43.8	37.0	17.0	Jiménez et al., 2007
Paulownia	48.3, 44.0, 34.2	20.5, 21.2, 22.7	22.1, 27.8, 27.2	Feria et al., 2011, **García et al., 2011**

Table 2

Normalized values of Temperature (X_T) and Operation Time (X_t)		Gross Heating Value (MJ/Kg)	Yield (%)	Klason Lignin (%)	Soluble Lignin (%)	Glucan (%)	Xylan (%)	Araban (%)	Acetyl Groups (%)
-1	-1	19.143	96	23.3	2.03	98.1	98.7	95.4	81.3
-1	0	19.316	91	23.4	1.63	95.0	94.7	75.4	74.4
-1	1	19.634	87	23.1	1.36	92.6	84.1	58.7	60.0
0	-1	19.342	95	25.1	1.86	95.7	97.5	78.7	71.1
0	0	19.532	84	23.3	1.29	92.7	80.5	54.8	47.9
0	0	19.489	84	23.7	1.31	92.9	79.9	55.5	48.3
0	1	19.723	78	23.1	1.00	90.1	62.5	32.1	26.1
1	-1	19.386	92	22.6	1.57	95.6	90.8	58.7	55.6
1	0	19.666	77	22.6	1.15	91.9	63.4	32.9	24.2
1	1	19.870	72	22.7	0.82	90.1	41.4	8.3	0.0

Table 3

Normalized values of Temperature (X_T) and Operation Time (X_t)		Glucose (%/g/l)	Xylose (%/g/l)	Arabinose (%/g/l)	Acetyl Groups (%/g/l)	Gluco-oligomers (%/g/l)	Xylo-oligomers (%/g/l)	Araban-oligomers (%/g/l)
-1	-1	0.3/0.15	0.2/0.05	1.3/0.02	1.0/0.03	2.2/1.14	1.1/0.27	4.2/0.04
-1	0	0.8/0.41	0.4/0.09	6.2/0.10	5.0/0.15	4.8/2.45	5.0/1.19	18.8/0.18
-1	1	1.6/0.79	2.5/0.59	14.3/0.21	18.9/0.58	6.2/3.15	13.5/3.20	21.2/0.20
0	-1	0.6/0.31	0.2/0.05	6.0/0.09	2.0/0.06	3.7/1.91	2.3/0.56	9.5/0.09
0	0	1.2/0.59	1.7/0.40	12.8/0.19	13.3/0.41	6.7/3.37	21.7/5.15	27.7/0.26
0	0	1.1/0.53	1.6/0.38	13.3/0.19	12.8/0.4	6.8/3.46	24.4/5.80	29.1/0.28
0	1	1.5/0.77	5.0/1.18	18.2/0.26	35.0/1.07	8.4/4.21	38.7/9.12	35.1/0.33
1	-1	0.6/0.33	0.9/0.21	6.6/0.10	7.2/0.22	3.8/1.94	8.2/1.97	13.5/0.13
1	0	1.2/0.61	2.9/0.67	13.6/0.19	20.1/0.61	7.0/3.50	34.7/8.16	37.5/0.36
1	1	1.7/0.84	8.9/2.05	20.2/0.29	58.4/1.77	7.7/3.86	51.9/12.15	50.5/0.48

Table 4

Equation	R^2	F-Snedecor
Solid phase		
$\mathbf{Y_{YI}} = 84 - 5.50\ X_T - 7.67\ X_t + 2.67\ X_tX_t - 2.75\ X_TX_t$	0.98	82
$\mathbf{Y_{CV}} = 19510.1 + 138.2\ X_T + 226\ X_t$	0.98	140
$\mathbf{Y_{SL}} = 1.35 - 0.25\ X_T - 0.38\ X_t + 0.10\ X_tX_t$	0.99	137
$\mathbf{Y_{GLS}} = 92.60 - 1.35\ X_T - 2.77\ X_t + 0.98\ X_TX_T + 0.45\ X_t\ X_t$	0.99	233
$\mathbf{Y_{XYS}} = 79.24 - 13.67\ X_T - 16.02\ X_t - 9.28\ X_T\ X_t$	0.99	354
$\mathbf{Y_{ARS}} = 61.39 - 13.12\ X_T - 20.35\ X_t$	0.99	403
$\mathbf{Y_{AGS}} = 29.28 - 19.60\ X_T - 26.01\ X_t + 24.44\ X_TX_T - 9.47\ X_T\ X_t$	0.99	373
Liquid phase		
$\mathbf{Y_{GL}} = 1.05 + 0.148\ X_T + 0.538\ X_t$	0.97	116
$\mathbf{Y_{XY}} = 1.63 + 1.57\ X_T + 2.49\ X_t + 1.29\ X_t\ X_t + 1.40\ X_T\ X_t$	0.99	123
$\mathbf{Y_{AR}} = 28.28 + 9.55\ X_T + 13.26\ X_t - 5.96\ X_t\ X_t + 5.04\ X_T\ X_t$	0.99	1230
$\mathbf{Y_{AG}} = 12.79 + 10.16\ X_T + 17.03\ X_t + 7.63\ X_t\ X_t + 8.53\ X_T\ X_t$	0.99	107
$\mathbf{Y_{GLOL}} = 6.8 + 0.88\ X_T + 2.095\ X_t - 0.98\ X_T\ X_T - 0.809\ X_t\ X_t$	0.99	135
$\mathbf{Y_{XYOL}} = 20.14 + 12.55\ X_T + 15.41\ X_t + 7.84\ X_T\ X_t$	0.97	76
$\mathbf{Y_{AROL}} = 12.58 + 2.98\ X_T + 6.47\ X_t - 2.11\ X_T\ X_T$	0.99	289

Where:

Solid phase:

$\mathbf{Y_{YI}}$, $\mathbf{Y_{CV}}$ and $\mathbf{Y_{SL}}$ denotes the solid yield, Gross Heating Value and soluble lignin contents in solid phase after autohydrolysis respect initial raw material (dry basis).

$\mathbf{Y_{GLS}}$, $\mathbf{Y_{XYS}}$, $\mathbf{Y_{ARS}}$ and $\mathbf{Y_{AGS}}$ denotes glucan, araban, xylan and acetyl groups contents in solid phase after autohydrolysis respect initial glucan, xylan, araban and acetyl groups contents in raw material (dry basis).

X_T and X_t denotes normalized autohydrolysis temperature and time, respectively.

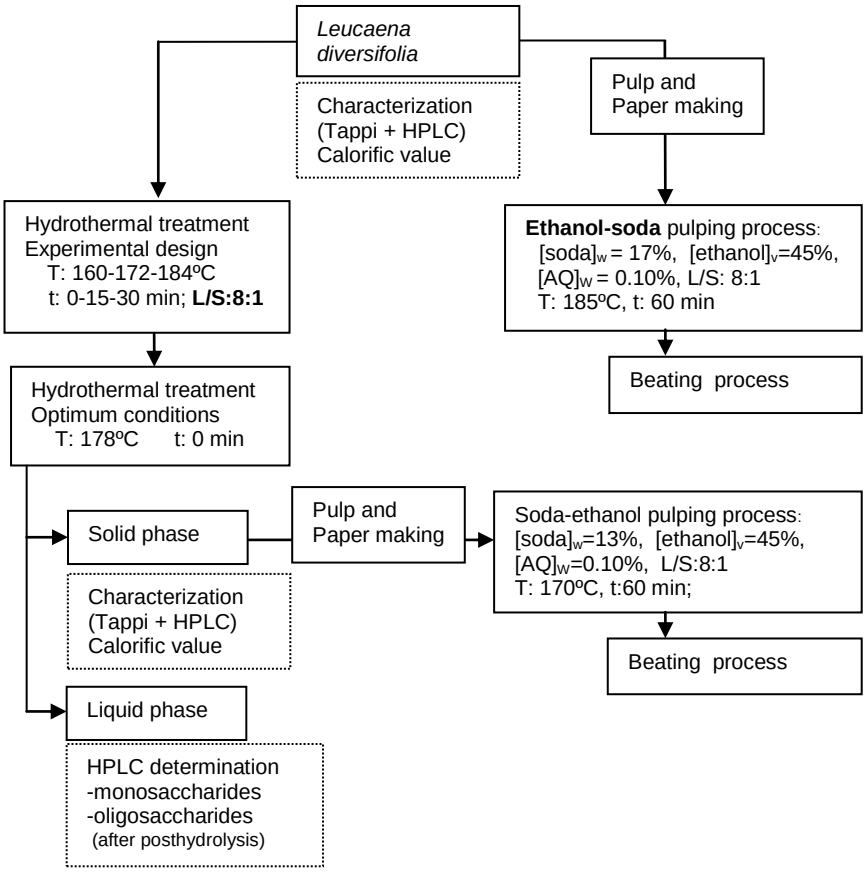
Liquid phase:

$\mathbf{Y_{GL}}$, $\mathbf{Y_{XY}}$, $\mathbf{Y_{AR}}$ and $\mathbf{Y_{AG}}$ denotes glucose, xylose, arabinose and acetic acid contents in liquid phase after autohydrolysis respect initial glucan, xylan, araban and acetyl groups contents in raw material (dry basis).

$\mathbf{Y_{GLOL}}$, $\mathbf{Y_{XYOL}}$ and $\mathbf{Y_{AROL}}$, denotes gluco-oligomers, xylo-oligomers and araban-oligomers contents in liquid phase after autohydrolysis respect initial glucan, xylan and araban contents in raw material (dry basis) respectively. Oligomer contents are give as monomer equivalents.

The differences between the experimental values and those estimated by using the previous equations never exceeded 5% of the former (10% for Y_{YI}, Y_{SL}, Y_{GL}, Y_{GLOL}, Y_{GLS}).

Figure 1



Abbreviations: [soda] w: soda concentration by weight; [ethanol] v: concentration of ethanol by volume; [AQl] w: concentration of anthraquinone by weight; T: process temperature (ºC); t: processing time (min). L/S: liquid / solid ratio.

Figure 2

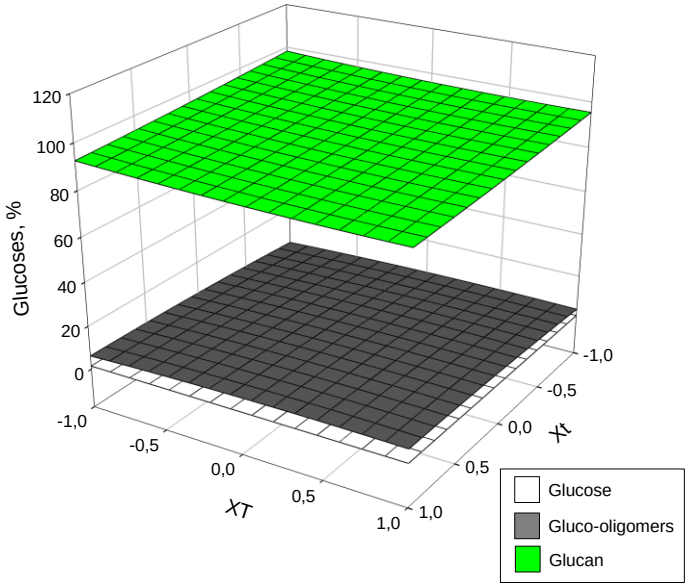

Glucoses, %
120
100
80
60
40
20
0
-1,0
-0,5
0,0
0,5
1,0
XT
XT
Glucose
Gluco-oligomers
Glucan

Figure 3

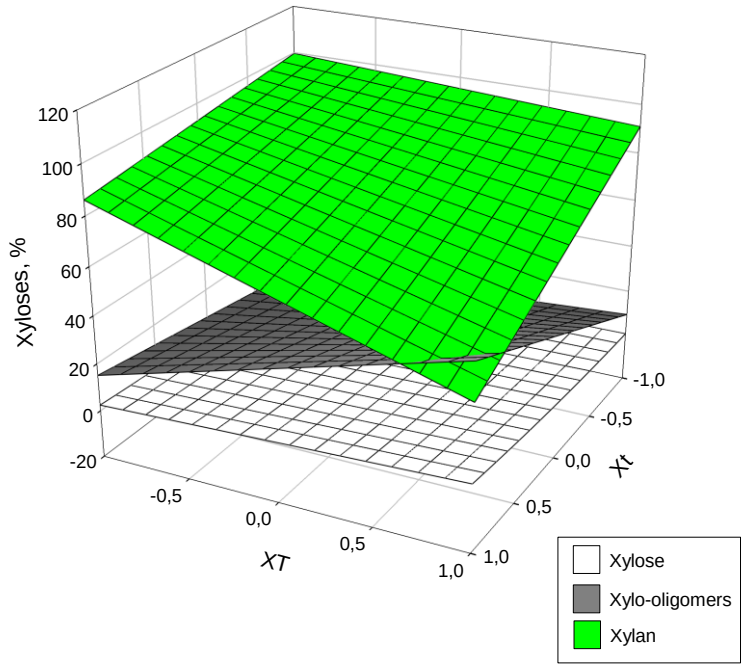
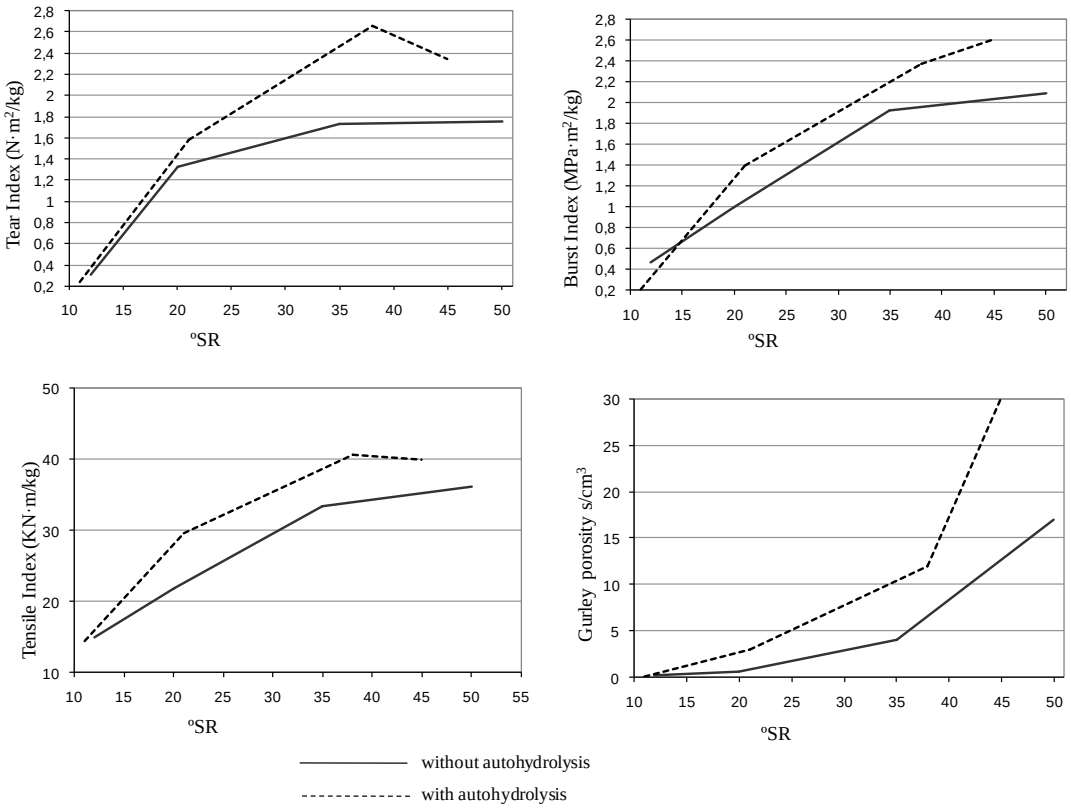

Xyloses, %
120
100
80
60
40
20
0
-20
-0,5
0,0
0,5
1,0
XT
-1,0
-0,5
0,0
0,5
1,0
Xt
Xylose
Xylo-oligomers
Xylan

Figure 4


Tear Index (N·m²/kg)
ºSR
Burst Index (MPa·m²/kg)
ºSR
Tensile Index (KN·m/kg)
ºSR
Gurley porosity s/cm³
ºSR
without autohydrolysis
with autohydrolysis