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Corresponding Author: Mr Feria Infante Manuel Javier, Eng.

Corresponding Author's Institution: University of HUelva

First Author: Feria Infante Manuel Javier, Eng.

Order of Authors: Feria Infante Manuel Javier, Eng.; Lopez Francisco, Dr; Garcia Juan Carlos, Dr; Perez Antonio, Dr; Zamudio Minerva Ana Maria, Eng; Alfaro Ascension, Dr

Abstract: In this work, Leucaena leucocephala K366 was characterized chemical and energy terms, and assessed its potential as a lignocellulosic raw material and energetic and industrial crop specie, and its integral fractionation by autohydrolysis by evaluating its calorific value, holocellulose, glucan, xylan, araban, lignin and oligomers and monomers contents in autohydrolysis liquor and solid phase. Also, this paper will consider the influence of the temperature and time of autohydrolysis process from Leucaena leucocephala K366 to obtain a valuable liquor and a suitable solid phase to produce energy by combustion.
A valuable liquor was obtained from the autohydrolysis of Leucaena leucocephala K366 by simultaneously using operating temperatures and times in the medium-high ranges studied, namely: 172-184 ºC and 15-30 min. The optimum processing conditions provided an acceptable yield (16-26%), and high xylose and xylo-oligomer contents in the liquor (10.0 and 58.6%, respectively, of the amounts present in the starting raw material when operating at 184 ºC for 30 min). The araban fraction was extracted virtually completely —only 8.3% remained in the solid fraction—, and the acetyl group fraction was recovered in full. In addition, these conditions reduced the glucose content of the liquor to 2.9% of the amount present in the raw material while largely preserving the integrity of cellulose fibers.

Klason lignin was scarcely dissolved under the operating conditions of the auto¬hydrolysis process. This increased the calorific value of the solid phase by 9% (under the most drastic operating conditions) with respect to the starting raw material.

Suggested Reviewers: Rojas Orlando
North Carolina State University
ojrojas@ncsu.edu
Orlando is a famous researcher that to investigate adsorption behaviors at interfaces.

Gil Garrote
University of Vigo
gil@uvigo.es

Gil is working on the research chemical and biotechnological processing of plant biomass for the production of high added value products

Colodette Jorge Luiz
University Federal of Viçosa
colodett@ufv.br
Colodette is working on teaching and research in the chemistry of wood and pulp bleaching.

Opposed Reviewers:

Valorization of *Leucaena leucocephala* for energy and chemicals from autohydrolysis

Feria, M.J.[a,*], López, F.[a], García, J.C. [a], Pérez, A. [a], Zamudio, M.A.M. [a], Alfaro, A.[b]

[a] Chemical Engineering Department. Faculty of Experimental Sciences, Carmen Campus, University of Huelva, Av. 3 de Marzo S/N, 21071 Huelva, Spain.

[b] Agroforestry Department. Faculty of Experimental Sciences, Carmen Campus, University of Huelva, Av. 3 de Marzo S/N, 21071 Huelva, Spain.

*Corresponding author: Feria, Manuel Javier, Tel.: (+34) 959 21 99 88. FAX: (+34) 959 21 99 83. E-mail address: manuel.feria@.diq.uhu.es

Abstract

In this work, *Leucaena leucocephala* K366 was characterized chemical and energy terms, and assessed its potential as a lignocellulosic raw material and energetic and industrial crop specie, and its integral fractionation by autohydrolysis by evaluating its calorific value, holocellulose, glucan, xylan, araban, lignin and oligomers and monomers contents in autohydrolysis liquor and solid phase. Also, this paper will consider the influence of the temperature and time of autohydrolysis process from *Leucaena leucocephala* K366 to obtain a valuable liquor and a suitable solid phase to produce energy by combustion.

A valuable liquor was obtained from the autohydrolysis of *Leucaena leucocephala* K366 by simultaneously using operating temperatures and times in the medium–high ranges studied, namely: 172–184 °C and 15–30 min. The optimum processing conditions provided an acceptable yield (16-26%), and high xylose and xylo-oligomer contents in the liquor (10.0 and 58.6%, respectively, of the amounts present in the starting raw material when operating at 184 °C for 30 min). The araban fraction was extracted virtually completely –only 8.3% remained in the solid fraction–, and the acetyl group fraction was recovered in full. In addition, these conditions reduced the glucose content of the liquor to 2.9% of the amount present in the raw material while largely preserving the integrity of cellulose fibers.

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1. INTRODUCTION

With declining reserves and increasing price of fossil fuels, turns out to be untenable the social development model predominant in the EU due to the fact that it is based on the use of fossil fuels [1]. The way to a sustainable development and resource renewability includes the searching of new resources of products where lignocellulosic biomass are drawing attention as an economical and a renewable source of energy with others chemicals.In order to limit further climatic changes the global society was must to reduce the emissions of carbon dioxide substantially during this century. For achieve this porpuse the largest share of the reduction must take place in the energy systems where conventional use of fossil fuels may be replaced by an increasing use of renewable energy [2]. Nowadays in Spain, with the current legislation that gives priority to the production of “clean kilowatts”,

this use of the forest biomass have become these days an interesting strategy for many companies in Spain. The Renewable Energies Programme in Spain 2005-2010 of the Ministry of Industry, Tourism and commerce, stablish that in 2010 renewable energies must contribute 12% of energy consumption, 29.4% of electric energy generation and 5.75% of transport fuel consumption through bio-fuels [3].

The advantage of using food biomass for energy production is partly offset by competitivity problems [4]. We therefore propose to aim at obtaining high-quality competitive products and lead agriculture towards non-food uses [5,6]. This way, the choice of vegetable species of high biomass production is an issue (often called “energetic crops”), through research, selection and genetic improvement programs and the use of biomass for non-alimentary purposes (energy, cellulose pulp, paper, chemicals, boards, fabrics, etc.).

A variety of crops are currently used for energy production or industrial purposes. In addition to its traditional, dominant industrial pulping applications, lignocellulosic biomass crops can be used to obtain energy (e.g. poplar crops provide yields of up to 20 ton/ha [2]) and biogas (most grass crops are excellent, perennial sources of high yield energy with low energy inputs [7]) such as that produced from bioethanol obtained by processing wheat and maize with average yields of 8.7 ton/ha [8].

Leucaena gener is one of these crops with very high production of biomass and re-sprout capacity (more than 50 tons/ha/year, specially in annual crops, which are among the highest growing levels described in the bibliography [9,10]). Particulary, in this work, the variety K366 of *Leucaena leucocephala* was used as energetic crop and for other chemicals obtention. *Leucaena leucocephala* is a leguminous tree, arises from the easy adaptability to Mediterranean ecological conditions [11,12], high biomass productivity [13], beneficial effects in the restoration of degrade soils [14,15], and it has been described for various uses (production of bioethanol, conversion from the biomass crops to ethanol include sugar fermentation and lignocellulosic ethanol, i.e., fiber hydrolysis followed by fermentation [16], feed animal, to beef cattle producers in Queensland who grow leucaena pastures [17], paper production, pulping and papermaking of Leucaena by soda-anthraquinone-ethanol was studied using an experimental design in order to investigate the effects of cooking variables: temperature, time, soda concentration, ethanol concentration [18], etc.).

Another matter is the fact that in order to make integral use of vegetable species, its fractionation is necessary, but capable of providing a wide range of products in a similar way oil refineries do, following a scheme that could be summarised in the following sentence: “The biorefinery of tree: from pulp and paper to chemical products and energy” [1]. Currently, the identification of the best lignocellulose fractionation stages constitutes one of the most interesting fields for research and scientific development efforts [19] in a general framework of evaluation of the best lignocellulosic materials for their conversion and the contrast between biochemical and thermochemical platforms of conversion [20,21]. The autohydrolysis treatments is one of these possiblities. Using high temperature water, hydrolysis of acetyl group to acetic acid occurs. This acid acts as a catalyst, which produces the total or partial solubilization of hemicellulose [22]. The obtained solid fraction from authohydrolysis process, characterized by its high content of lignin and cellulose, could be employed as raw material

for alcohol production [23], ruminant feed [24], raw material for pulp and paper making [25] and also for energy production.

The objective of this study is to analyze the potential of utilizing a improved variety of *Leucaena leucocephala* as a energetic and industrial crop specie by evaluating its calorific value, holocellulose, glucan, xylan, araban, lignin and oligomers and monomers contents in liquid and solid phases postautohydrolysis. Also, this paper will consider the influence of the temperature and time of autohydrolysis process from *Leucaena leucocephala* K366 to obtain a valuable liquor and a suitable solid phase to produce energy by combustion.

2. MATERIALS AND METHODS

2.1. Raw material. Provision and characterization

A improved variety of *Leucaena leucocephala* (*Leucaena leucocephala* K366) has been used in this work. The studied material was a clone obtained by in vitro replication that was harvested after seven years of growth in plantations used to exploit biomass or experimental energy crops in Huelva (southwestern Spain). These plants were grown in a nursery, in 300 cm^3 pot holders; they were inured from bacterium Rhizobium and, when they were 3 months old, they were changed to the ground. Field experiments were carried out in two plots with a complete randomized block design with 4 replicates per provenance. Any fertilization was not added to plots. The soil at the experimental site was sandy loamy with a pH of 6–8 and having moderate to substantial depth.

Leucaena leucocephala samples were milled to pass a 8 cm screen. The chips were reduced again to pieces from 2 to 10 mm long in order to prevent alterations of their components and removed the fines by sieving through 0.6 mm mesh. 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 T 212 om-98), hot water solubles (TAPPI T 207 cm-93), ethanol-benzene extractives (TAPPI T 204 cm-97), α-cellulose (TAPPI T 203-om-93) and holocellulose [26] contents. All treatments in this study were in a completely randomized design with four replications (variation coefficient less than 3%. less than 1% for holocellulose and cellulose contents).

Aliquots from the homogenized wood (without extractable compounds) lot were subjected to moisture determination (drying at 105 ºC to constant weight) and to quantitative acid hydrolysis with 72% H_2SO_4 at 121 ºC for 60 min, following standard methods (TAPPI T 249-cm-85). The solid residue after hydrolysis was recovered by filtration and considered as Klason lignin (TAPPI T 222). Acid-soluble lignin was determined following standard method (TAPPI T 250-um-85). The monosaccharides (glucose, xylose and arabinose), 5-hydroxymethylfurfural (HMF), furfural, and acetic acid contained in the hydrolysates were determined by high performance liquid chromatography (HPLC), using a

column of exchange ionic Aminex HPX-87H to 30ºC, mobile phase, H_2SO_4 0.05 M; flow, 0.6 ml/min. Ashes were determined by calcinations (TAPPI T 244-om-93).

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

2.2. Autohydrolysis process and oligosaccharides determination

Raw material and water were mixed in the desired proportions and treated in a 2 L stainless steel reactor (Parr Instruments Company, Moline, IL) using a liquid/solid ratio of 8 kg water kg raw material^{-1}, on a dry basis (the moisture content of the material was considered to be water). Previous works demonstrated that the influence of the variation of the liquid/solid ratio is practically negligible [27]. 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 to be the beginning of the isothermal stage. The temperature of the process was automatically controlled via an internal cooling coil equipped with circuit-opening electrovalves which was used to cool the reactor after the highest 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. An aliquot of liquors was filtered through 0.45 μm membranes and used for direct HPLC determination of monosaccharides, furfural, 5- hydroxymethylfurfural and acetic acid. A second aliquot of liquors (25 ml) was subjected to posthydrolysis (with 4% sulfuric acid at 121 ºC and 2 atm during 20 min) before HPLC analysis. Operation conditions in HPLC are described in previous section for raw material. The increase in the concentrations of monosaccharides and acetic acid caused by posthydrolysis measured the concentrations of oligomers and acetyl groups bound to oligosaccharides [28].

For determination of solid fraction is used an aliquots ground to a particle size < 0.5 mm and subjected to moisture and extractives determination (TAPPI T 264-cm-97) and to quantitative acid hydrolysis with 72% H_2SO_4 at 121 ºC and 2 atm during 60 min, and then it was filtered through 0.45 μm and analyzed by HPLC; the solid residue after hydrolysis was recovered by filtration and considered as Klason lignin (TAPPI T 222). Acid-soluble lignin was determined following standard method (TAPPI T 250-um).

The calorific value of the autohydrolysis solid phase was determined as described above for the characterization of the raw material.

2.3. Experimental Design for the Autohydrolysis Conditions. Multiple Regresion Model

To be able to relate the dependent (yield, soluble lignin, calorific value and glucose, xylose, arabinose, oligomers, furfural, 5-hydroxymethylfurfural and acetyl groups contents) and independent (temperature and time of process) variables in autohydrolysis process with the minimum possible number of experiment, 2n 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 maximum and minimum values, respectively. The autohydrolysis temperature and autohydrolysis time used in the different experiments of the design were 160ºC, 172ºC and 184ºC; 0, 15 and 30 min (at operation temperature), respectively. The liquid/solid ratio is 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 (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. Raw material characteristics

The chemical characterization of the improved variety K366 of *Leucaena leucocephala* and other woods are shown in Table 1, where the *Eucaliptus Globulus* was used as reference. The majority fraction is cellulose (analyzed as glucan), at 37.2% (or 41.0 at TAPPI T 203-om-93), followed by the hemicelluloses (calculated as the sum of xylan, araban, acetyl groups) at 19.9% and Klason lignin at 24.1 % after of quantitative acid hydrolysis. This composition is similar to that found by other authors for *Leucaena leucocephala* and other varieties of Leucaena, comparable to hardwoods, such as *Eucalyptus globulus*, and other raw materials (table 1). With regard to hemicelluloses, the principal fraction affected by hydrothermal treatments, the molar relation between the different monomers, can be calculated.

Xylose: Acetyl groups: Arabinose = 17.1:1.8:1

In which, it is observed that the predominant monomer is xylose, with a high degree of substitution with acetyl groups (up to 9.5 xylose for each 1 monomer of acetyl groups) and to a lesser degree with substitutes such as arabinose. This composition is typical of acetylglucuronoxylans, which are typically present in hardwoods.

Table 2 shows selected calorific values reported by several authors. In short, softwood and related materials typically have values in the region of 20.0 MJ/kg and hardwood such as that from *Eucalyptus globulus* yields about 18.0 MJ/kg, whereas other deciduous plants (and their residues) give lower values. The gross calorific value for *Leucaena leucocephala* K366 is somewhat lower than those for softwood and pine, slightly higher than those for eucalyptus and hardwood (see Table 2), and much higher than those for residues of food plants and agricultural crops. This supports the use of the genus Leucaena as an energy crop, particularly on the grounds of the gross calorific value of its autohydrolysis solid fraction.

3.2. Autohydrolysis process. Modelling and optimization

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 previous experiences on *Leucaena diversifolia* and others lignocellulosic materials [29,30], the operations were carried out at temperatures and times of process indicated in the experimental design.

In Table 3 the variations with the temperature and time of the calorific values and different analyzed compounds (furfural and 5-hydroxymethylfurfural) of the liquor and solid phase yield and lignin contents, relative to the initial raw material, are shown. The results were modelled by using the above-described multiple regression methodology. The ensuing models are shown in Table 6.

In Table 4 the variations with the temperature and time of the different analyzed compound of the liquor relative to the content in each polymer fraction of the raw material (on dry basis) are shown. Also, in table 5 the variations of the different analyzed compound of the solid phase relative to the content in each polymer fraccion of the raw material are shown.

The discussion that follows is focused on the following assumption: the autohydrolysis of *Leucaena leucocephala* K366 provides an industrially useful liquor by virtue of its contents in xylose, xylo-oligomers and various other compounds. Also, its autohydrolysis solid phase can be used to obtain other chemicals or directly burnt for energy production.

The method error and analytical error were estimated by combining all fractions of autohydrolysis liquor and solid phase in Tables 3–5 with respect to the starting raw material in addition to the contents in ash, ethanol–benzene extractives and hot water soluble substances. The overall results ranged from 92.83 to 97.64%, so the cumulative errors were less than 4.6% with respect to the figure for the starting raw material and the same compounds: 97.26%.

The liquor yield (one hundred less solid phase yield) are between 6.0% and 26.0% and include: monomers, xylooligomers, minerals contents, proteins, degradation products (furfural and 5-hydroxymethylfurfural), glucooligomers, arabinooligomers, extractable compounds, solubilized lignin and non volatile solids.

The equation for solid yield (Y_{YI}) in Table 6 is a function of the linear terms for the variables, the time–temperature interaction and the quadratic term for the operation time. The former three revealed increased degradation and extraction of polysaccharides and other compounds as the operating temperature and time were increased. The positive sign of the quadratic term in the operation time should be ascribed to the increase in polysaccharide extraction being modulated by an increase in temperature and time. This confirms the hypothesis that the polysaccharide fraction is hydrolysed to lignocellulosic biomass at fairly high temperatures, but requires an also fairly long time to occur [41, 48]. In fact, the linear terms X_T and X_t were both statistically significant in all equations of Table 6, and so was the X_TX_t interaction in most.

In order to identify the values of the independent variables of the autohydrolysis process leading to the optimum values of yield and other dependent variables, and also to better envisage the cumulative error made in the determination of the different polysaccharide derivative fractions, the response surfaces for each dependent variable were constructed (Figs 1–6).

The response surface representing the variation of yield in the autohydrolysis solid phase (Fig. 1) confirms some of the above-described effects. Thus, the effect of the X_TX_t quadratic term was observed in the medium–low range of temperature and reflected the need for an appropriate combination of high temperatures and times in order to ensure efficient extraction into the liquor.

The autohydrolysis treatment raised the calorific value of the solid phase by up to 9% with respect to the starting raw material. This can be ascribed to the relative increase in the amount of lignin present in the solid phase as polysaccharides are extracted and to the increased calorific value of lignin relative to cellulose and hemicelluloses 49]. This further increase the intrinsic value of the compounds extracted into the liquor or reduces the energy cost associated with extraction by autohydrolysis.

Both the temperature and time linear terms, and the quadratic term, in the Y_{CV} equation of Table 6 are significant. This hinders accurate interpretation of the variation of the calorific value with the independent operation variables. However, the response surface for the equation (Fig. 2) clearly shows that the increase in calorific values occurs to a substantial extent above the central values in the operation ranges for the two independent variables, but much more markedly at their ends.

The content in Klason lignin of the autohydrolysis solid fraction reflected its nature as a non-soluble fraction of lignocellulosic biomass [50]. Thus, it ranged from 22.87 to 24.31% of the amount present in the starting raw material, so it changed by a mere 5.9% at most and had an average value of 23.64%. 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 T-222 (22.37%) and the HPLC protocol for the determination of sugars (24.13%).

This is not the case with the changes in soluble lignin. Thus, its content was much lower (1.61% in the raw material, Table 1, and 0.92–1.30% in the autohydrolysis solid fraction). This suggests substantial

dissolution of this fraction during the autohydrolysis process [51]. The linear terms in the Y_{SL} equation in Table 6 clearly reflect the influence, up to 3 times greater, of the operation time relative to the temperature. Also, the equation contains an $X_T X_t$ term which, as in the yield equation, modulates the increase resulting from the incorporation of the soluble lignin into the autohydrolysis liquor as the temperature and time are increased. The response surface for the amount of soluble lignin against the operating temperature and time (results not shown) revealed that the lignin content in the autohydrolysis solid phase increases much more rapidly in the medium–high temperature range, which suggests some resistance of soluble lignin to dissolution below such an operating range.

Table 3 additionally shows the contents in polysaccharide degradation products present in the autohydrolysis liquor as percentages of their respective amounts in the starting raw material. Furfural and 5-hydroxymethylfurfural come from the degradation of cellulose and hemicellulose. Polysaccharides were fairly moderately degraded (0.100–1.075% in combination) relative to previously reported values for the studied operating ranges [51-53]. Both compounds only increased appreciably above the medium temperature and time conditions. In fact, the term representing the interaction of both variables was the most significant in the Y_{FU} and Y_{HMF} equations of Table 6. The response surfaces for the two equations (results not shown) clearly exposed this effect.

The xylose and xylo-oligomer contents exhibited substantial variations (0.90–2.92% and 1.78–58.59%, respectively). Other authors have obtained oligomer extraction rates of up to 9.30% at temperatures of 180ºC [40]. The strongest dependence for xylose and xylo-oligomers was the linear dependence on the temperature and time. The interaction between both variables was also significant, which suggests a multiplying effect of the increase in temperature and time on the degradation of xylan, and the increase in xylose and xylo-oligomer concentrations in the autohydrolysis liquor. The foregoing is consistent with previous results of other authors for various materials [40]. Figure 3, which shows the four response surfaces for the contents in xylose and xylo-oligomers in the autohydrolysis liquor (Y_{XY}, Y_{XYOL}), and the xylan content of the autohydrolysis solid phase (Y_{XYS}), clearly confirms these results. The fourth surface represents the cumulative values for the previous three and allows one to envisage the analytical and method errors with respect to the initial xylan content in the starting raw material.

Similar comments can be made on the araban and acetyl group fractions except that both components were extracted in higher proportions than xylan. Thus, judging from the combined contents of arabinose and arabinoligosaccharides in the liquor, araban was extracted by more than 90% from the starting raw material under the strongest operating conditions. The numerical models for araban and acetyl groups in the liquor (Y_{AR} and Y_{AG}) were similar as regards statistically significant terms. Figures 4 and 5 depict their variation in graphical terms. The response surface for the accumulation of acetyl groups in the liquor and solid phase was not the result of a method or analytical error, but rather of their disappearance during the autohydrolysis process.

Glucan and its derivatives were extracted in relatively small amounts into the autohydrolysis liquor; also, they remained in the solid phase to a greater extent than did all other polysaccharides. These results are clearly confirmed by the response surfaces for the variables Y_{GL}, Y_{GLOL} and Y_{GLS} in Fig. 6.

Degradation in the form of glucose extraction was especially significant at high temperatures (the coefficient for X_T in the Y_{GL} equation of Table 6 was 24% greater than that for X_t, these two being the only significant terms in the equation). As can be seen from Fig. 6, the quadratic terms modulated the above-described primary effects.

The cumulative error for the combination of glucan in the autohydrolysis solid phase, gluco-oligomers in the liquor and glucose in the autohydrolysis liquor ranged from 94.05 to 98.84% of the proportion of glucan in the starting raw material (37.21%). The error is quite acceptable if one considers degradation of the polysaccharide and the intrinsic experimental error. The error for araban was between 92.96 and 98.99% of the 10.4% contained in the raw material. The combination of the contents in acetyl groups of the autohydrolysis liquor and solid phase ranged from 47.19 to 83.02%, which is consistent with the assumption of "partial consumption" of these groups in the autohydrolysis reaction. The greatest experimental error was that in the fraction of xylan derivatives, which ranged from 93.59 to 107.39% of the xylan content of the raw material (17.05%) and can be partly ascribed to the scarcely uniform contents in other polysaccharides containing the xylan molecule in addition to xylan itself.

4. CONCLUSIONS

A valuable liquor was obtained from the autohydrolysis of *Leucaena leucocephala* K366 by simultaneously using operating temperatures and times in the medium–high ranges studied, namely: 172–184 °C and 15–30 min. The optimum processing conditions provided an acceptable yield (16-26%), and high xylose and xylo-oligomer contents in the liquor (10.0 and 58.6%, respectively, of the amounts present in the starting raw material when operating at 184 °C for 30 min). The araban fraction was extracted virtually completely –only 8.3% remained in the solid fraction–, and the acetyl group fraction was recovered in full. In addition, these conditions reduced the glucose content of the liquor to 2.9% of the amount present in the raw material while largely preserving the integrity of cellulose fibers. Klason lignin was scarcely dissolved under the operating conditions of the autohydrolysis process. This increased the calorific value of the solid phase by 9% (under the most drastic operating conditions) with respect to the starting raw material.

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Tables

Table1: Chemical composition of Leucaena varieties and others lignocellulosic raw materials

Table 2: Gross calorific value of varieties of lignocellulosic raw materials

Table 3: Values of Independent Variables, solid yield, calorific value, composition of the solid fractions (Klason and soluble lignin) and composition of the liquid fraction (furfural and 5-OH methyl furfural) obtained in the autohydrolysis process using the proposed experimental design (relative to the initial raw material –dry mass-).

Table 4: Values of Independent Variables and composition of the liquid fractions obtained in the autohydrolysis process using the proposed experimental design (relative to the content in each polymer fraction of the raw material –dry mass-. Oligomer contents are give as monomer equivalents)

Table 5: Values of Independent Variables and composition of the solid fractions obtained in the autohydrolysis Process Using the Proposed Experimental Design (relative to the content in each polymer fraction of the raw material –dry mass-)

Table 6: Equations yielded for each dependent variable.

Table 1

Raw Material	References	Cellulose (%)	Hemicellu-lose (%)	Lignin (%)
Leucaena leucopehala K366	This work			
1% NaOH solubles ……..32.0 % Hot water solubles ……. 13.0 % Alcohol-benzene extractives…… 5.2 % Hot water solubles after organic extraction… 7.9 % Ash…… 1.3 % Klason lignin (TAPPI)…….... 22.4 % Holocellulose……... 70.6 % α-Cellulose……..41.0 % Glucan……..… 37.2 % Xylan……17.1 % Araban…… 1.0 % Acetyl groups……... 1.8 % Lignin (after 72% sulphuric hydrolysis)…24.1 % Soluble lignin…… 1.6 % Calorific value……18.945 MJ/kg				
Leucaena	[29,30]	43, 40.8	17, 15.0	25, 26.9
Leucaena leucocephala *L. Leucocephala* Honduras) *L. Leucocephala* (India)	[31-33]	39.4, 41.0, 41.2, 44.4	28.9, 26.0, 32.9, 31.5	18.4, 26.0, 19.4, 21.4
Leucaena diversifolia	[33,34]	38, 40.10	27.8, 37.8	24.8, 19.09
Leucaena colinsi	[33]	43.8	37.0	17.0
E. gumífera and saligna	[29]	38.0, 45.0	16.0, 15.0	37.0, 25.0
Sugarcane bagasse	[35]	40.2	24.3	22.3
Eucalyptus	[36-38]	43.0, 46.8, 53.4	13.2, n.d., n.d.	25.3, 22.9, nd.
Paulownia	[39-41]	48.3, 44.0, 34.2	20.5, 21.2, 22.7	22.1, 27.8, 27.2
Pine Cone	[42]	32.7	37.6	24.9

Table 2

Raw naterial	Gross calorific value

Pine Cone	27.35[42]
Wood bark, Gossweilerodendron balsamiferum, Chlorophora excels, Cedrus atlantica, Wheat straw	20.5 – 20.3[44,45]
Spruce wood, Pinus pinaster, Softwood, Pseudotsuga menziesii, Pinewood	20.1-19.6 [43-45]
Hazelnut shell, Hazelnut seedcoat, Beech wood, Fraxinus angustifolia, Hymenaea courbaril, Fagus sylvatica, Olive husk, Entandrophragma , cylindricum, Ailanthus wood	19.3 -19.0[44,45]
Populus euro-americana, Hardwood, Quercus robur, Castanea sativa, Acer pseudoplatanus, Prunus avium, Salix babilonica	18.8-18.2 [44,45]
Corn stover, Tobacco stalk, Eucalyptus globulus, Tobacco leaf, Tea waste, Waste material, Corncob, Flax straw, Soybean stalk	17.8-17.0 [43-46]
Timothy grass, Barley atraw	16.7 ˜15.7 [43]

Table 3

Normalized values of Temperature (X_T) and Operation Time (X_t)		**Yield, %**	**Calorific Value (J/g)**	**Klason Lignin, %**	**Soluble Lignin, %**	**Furfural, %**	**5-OH methil furfural, %**
-1	-1	0.94	19384	24.09	1.21	0.06	0.04
-1	0	0.89	19526	23.53	1.12	0.06	0.06
-1	1	0.87	19754	23.09	1.03	0.06	0.07
0	-1	0.93	19303	23.14	1.30	0.06	0.04
0	0	0.85	19585	23.68	1.12	0.17	0.07
0	0	0.84	19599	23.74	1.16	0.18	0.06
0	1	0.80	19914	23.66	1.03	0.32	0.12
1	-1	0.88	19530	22.87	1.18	0.08	0.05
1	0	0.78	20000	24.25	1.02	0.28	0.18
1	1	0.74	20638	24.31	0.92	0.705	0.37

Table 4

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	1.34/0.69	0.90/0.22	1.50/0.02	1.67/0.05	2.51/1.29	1.78/0.43	2.19/0.03
-1	0	1.80/0.92	1.39/0.33	8.23/0.12	4.62/0.14	6.53/3.33	6.07/1.45	14.42/0.21
-1	1	1.87/0.95	1.52/0.36	13.07/0.19	6.51/0.20	9.35/4.75	12.84/3.06	24.71/0.36
0	-1	1.66/0.85	0.95/0.23	5.13/0.08	2.76/0.09	4.79/2.45	6.19/1.49	12.53/0.18
0	0	1.93/0.98	3.26/0.77	14.14/0.21	15.10/0.47	10.28/5.21	22.24/5.29	25.93/0.38
0	0	2.12/1.07	3.38/0.80	15.46/0.22	15.12/0.47	10.99/5.57	21.93/5.21	24.46/0.35
0	1	2.28/1.15	4.71/1.11	24.89/0.36	24.99/0.77	13.79/6.95	36.41/8.60	39.00/0.56
1	-1	2.14/1.09	1.97/0.47	12.78/0.19	7.43/0.23	8.80/4.48	13.41/3.20	27.17/0.40
1	0	2.44/1.23	6.14/1.45	21.70/0.31	26.14/0.80	16.02/8.05	36.64/8.63	39.40/0.57
1	1	2.92/1.46	9.97/2.34	32.80/0.47	47.19/1.43	17.05/8.53	58.59/13.74	51.90/0.74

Table 5

Normalized values of Temperature (X_T) and Operation Time (X_t)		Glucan, %	Xylan, %	Araban, %	Acetyl Groups, %
-1	-1	90.41	90.91	95.39	81.33
-1	0	85.73	87.52	75.35	74.44
-1	1	85.27	81.99	58.73	60.00
0	-1	90.73	88.64	78.65	71.11
0	0	85.14	74.97	54.79	47.85
0	0	85.04	74.85	55.46	48.33
0	1	82.53	60.92	32.06	26.07
1	-1	85.70	84.22	58.69	55.56
1	0	79.68	60.20	32.93	24.24
1	1	78.91	38.83	8.26	0.00

Table 6

Equation	R^2	F-Snedecor
$Y_{YI} = 84 - 5.00\ X_T - 5.67\ X_t + 2.00\ X_tX_t - 1.75\ X_TX_t$	0.986	90
$Y_{CV} = 19600.3 + 251.7\ X_T + 348.2\ X_t + 205.1\ X_TX_T + 184.5\ X_tX_t$	0.991	142
$Y_{SL} = 1.15 - 0.04\ X_T - 0.12\ X_t - 0.07\ X_TX_T$	0.962	51
$Y_{FU} = 0.197 + 0.147\ X_T + 0.147\ X_t + 0.156\ X_T\ X_t$	0970	64
$Y_{HMF} = 0.073 + 0.072\ X_T + 0.072\ X_t + 0.057\ X_TX_T + 0.074\ X_T\ X_t$	0.957	28
$Y_{GL} = 2.05 + 0.42\ X_T + 0.32\ X_t$	0.935	66
$Y_{XY} = 3.42 + 2.38\ X_T + 2.06\ X_t + 1.85\ X_T\ X_t$	0.976	124
$Y_{AR} = 14.97 + 8.56\ X_t + 7.41\ X_T + 2.11\ X_T\ X_t$	0.986	208
$Y_{AG} = 15.22 + 11.33\ X_T + 11.14\ X_t + 8.73\ X_T\ X_t$	0.995	614
$Y_{GLOL} = 10.95 + 4.01\ X_t + 3.91\ X_T - 1.57\ X_t\ X_t$	0.970	98
$Y_{XYOL} = 21.61 + 14.66\ X_T + 14.41\ X_t + 8.53\ X_T\ X_t$	0.998	1627
$Y_{AROL} = 26.17 + 12.86\ X_T + 12.29\ X_t$	0.994	726
$Y_{GLS} = 84.85 - 3.35\ X_T - 2.85\ X_t + 2.01\ X_tX_t - 1.91\ X_T\ X_T$	0.962	58
$Y_{XYS} = 74.31 - 13.67\ X_t - 12.86\ X_T - 9.12\ X_T\ X_t$	0.997	1222
$Y_{ARS} = 55.01 - 22.25\ X_t - 21.60\ X_T - 3.44\ X_TX_t$	0.998	1968
$Y_{AGS} = 48.89 - 22.66\ X_T - 20.32\ X_t - 8.56\ X_TX_t$	0.991	336

Where:

Y_{YI}, Y_{CV} and Y_{SL} denotes the solid yield, calorific value and soluble lignin contents in solid phase after autohydrolysis respect initial raw material (dry basis).

Y_{FU} and Y_{HMF} denotes furfural and 5-hidroxi methil furfural contents in liquid phase after aotuhydrolysis respect initial raw material (dry basis).

Y_{GL}, Y_{XY}, Y_{AR} and 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).

Y_{GLOL}, Y_{XYOL} and 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.

Y_{GLS}, Y_{XYS}, Y_{ARS} and 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.

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_{FU}, Y_{HMF}, Y_{GL}, Y_{GLOL}, Y_{GLS}).