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Chemical And Energetic Characterization, And Integrated Exploitation, Of Species With A High Biomass Production Potential By Fractionation Of Their Components

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ABSTRACT

In this work, we determined the properties of cellulose pulp and paper from six different lignocellulosic materials [*Eucalyptus globulus*, *Arundo donax*, *Leucaena diversifolia*, *Paulownia fortunei*, sunflower stalks and *Chamaecytisus proliferus* (tagasaste)], as well as the calorific value and chemical composition of their autohydrolysis liquor, with a view to assessing their potential for the obtainment of energy, sugars and other chemical products. An integral fractionation method based on autohydrolysis and organosolv delignification was used for this purpose. *Leucaena diversifolia*; *P. fortunei*; a Paulownia "trihybrid" consisting of *elongata, tormentosa* and *fortunei* varieties; sunflower stalks; and *C. proliferus* exhibited holocellulose, glucan, xylan and acetyl group contents similar to, or higher than, those of *E. globulus*, *A. donax* and various other lignocellulosic materials. The amounts of oligomers extracted from *C. proliferus*, *P. fortunei*, *L. diversifolia* and sunflower stalks at the highest temperatures studied exceeded those provided by eucalyptus. Sequential autohydroysis and organosolv delignification of *L. diversifolia* and *C. proliferus* provided cellulose pulp with an acceptable kappa number and paper sheets with good strength-related properties. *Paulownia fortunei* was the most interesting raw material among those tested; in fact, it provided ethanol pulp with a lignin content of 3.7 –15.3% and a kappa number of 40.5–74.1 after autohydrolysis at 190 ºC, and paper with a tensile index of 17.0–28.9 kN m/kg. These properties are similar to those of pulp and paper from eucalyptus wood. In addition, *P. fortunei* exhibited the highest calorific value among the studied materials (4683.8 cal/g).

Keywords: autohydrolysis, organosolv, leucaena, tagasaste, paulownia, sunflower stalks.

INTRODUCTION

The world is experiencing a growing shortage of raw materials that is especially severe in the energy sector and being worsened by the unfavorable environmental impact of a consumerist culture revolving around the exploitation of non-renewable resources. Ensuring sustainable development and material renewability entails finding and using new resources and chemical and consumer products where lignocellulosic biomass constitutes a “necessary” source of raw materials on account of its ubiquity, availability and low polluting power. In fact, lignocellulosic biomass has been widely acknowledged as the largest source of renewable energy available in the world to respond to the decline in fossil fuel sources [1-3]. Processing the whole material rather than only its sugar and amylaceous fractions to obtain ethanol by fermentation, its fibre fractions to produce cellulose pulp and some residual fractions or all for burning is the only way of exploiting the whole potential of such an abundant resource [4, 5].

Using biomass from forest or agrarian “crops” to extract energy or chemical products provides additional advantages such as a reduced use of fossil fuels, the release of no additional CO_2 into the atmosphere ‒in fact, any CO_2 generated is previously captured from it‒ and the ability to convert crops into net carbon sinks by increasing the amount of carbon accumulating in the soil via organic matter, dead leaves, roots, *etc.* Also, using resprouting plants and harvesting their aerial portion only ‒thus leaving roots and shoots intact‒ reduces the need for machine tillage ‒and hence energy usage‒ for as long as the plants retain their regrowing ability.

The virtually sole alternative to integral exploitation of lignocellulosic biomass in a single —usually thermal— process is its fractionation, which, however, is made difficult by the inability to separate its main components without degrading the chemical structure of some. One of the difficulties of using lignocellulosic components arises from the need to attack the compact lignin–hemicellulose matrix surrounding cellulose. This polysaccharide exists in amorphous and crystalline forms, the latter of which hinder penetration of chemicals and enzymes to hydrolyse cellulose. The complex structure, composition and network of chemical and physical bonds in lignocellulosic biomass preclude the use of separation techniques such as distillation, precipitation, crystallization and extraction for this purpose [6]. The extensive research conducted in this field has focused on a variety of highly specific issues and overlooked the need for a systematic, comprehensive compilation of available fractionation methods. In regard to such methods, Rijkens [7] discriminates between those based on delignification (*i.e.* the solubilization of lignin) and those relying on hydrolysis (*i.e.* the solubilization of polysaccharides). This was the origin of the “lignocellulosic material biorefinery” concept as the source of a wide range of products by analogy with the “oil refinery” concept. Although a number of refining schemes have been tested at the laboratory or pilot plant scale, none has to date been implemented on a commercial scale [8, 9].

Identifying the most suitable pretreatments or steps for the fractionation of lignocellulosic material is one of the most interesting targets for scientific research and development [10]. The integral fractionation of lignocellulosic biomass can be accomplished by hydrolysis (hemicellulose, cellulose) and delignification.

Overall, the most important industrial processes for delignification are the soda/kraft and sulphite processes; however, delignification has also been accomplished —on a smaller scale or in purely academic work— via chemical processes involving organic solvents and high temperatures. The earliest such process was probably the ethanol pretreatment developed by General Electric in the 1970s to obtain biofuel [11]. The process also provided high-quality, unaltered lignin with various potential industrial uses [12]. Using ethanol as the technological core for refining lignocellulosic materials has led to the development of organosolv processes such as Lignol, which uses temperatures in the region of 200 ºC and a pressure of 2758 kPa to maximize extraction of lignin from wood chips and other sources of lignocellulosic biomass. Fractionation processes based on a delignification treatment usually focus on the subsequent hydrolysis or saccharification of the cellulose fraction in order to obtain fermentable media for producing ethanol [13-15].

Incorporating the hydrolysis of hemicelluloses into a more general process involving the integral fractionation of the raw material can be made easier by minimizing the use of chemical reagents other than those strictly needed for separation. This is specially so with autohydrolysis. At high temperatures, acetyl groups in lignocellulosic materials give acetic acid —in fact, lignocellulosic materials can give the acid at any temperature, but the dissociation equilibrium and overall process are slower at low levels—, which catalyses the dissolution of hemicelluloses. The resulting liquor essentially contains oligomers, acetic acid, furfural (or hydroxymethylfurfural) and some lignin [16].

In this work, we determined the heat power and chemical composition of cellulose pulp and paper from six different lignocellulosic materials [viz. *Eucalyptus globulus*, *Arundo donax*, *Leucaena diversifolia*, *Paulownia fortunei*, sunflower stalks and *Chamaecytisus proliferus* (tagasaste)], as well as the chemical composition of their autohydrolysis liquor, with a view to assessing their potential for obtaining energy, sugars and various other chemical products in addition to cellulose pulp and paper via an integral fractionation procedure based on autohydrolysis and organosolv delignification.

MATERIALS AND METHODS

Characterization of the raw materials

Samples of the six raw materials studied (*Eucalyptus globulus*, *C. proliferus*, *Paulownia fortunei*, *Arundo donax* L. and sunflower stalks) were milled to pass through a 8 mm screen; this particle size was found to result in no diffusional restrictions in preliminary tests. Samples were air-dried, homogenized in a single batch to avoid differences in composition among aliquots, and stored. Aliquots of the homogenized wood batch were subjected to moisture determination by drying at 105 ºC to constant weight and quantitative acid hydrolysis with 5 mL of 72 % sulphuric acid for 1 h, followed by post-hydrolysis with 4 % H_2SO_4 by adding water up to 148.67 g at 121 ºC for 60 min. Before HPLC analysis, the solid post-hydrolysis residue was recovered by filtration and labelled Klason lignin. Monosaccharides and acetic acid in the hydrolysates were determined by HPLC in order to calculate the sample contents in cellulose (glucan) and hemicelluloses (xylan, arabinan and acetyl groups), with provision for stoichiometric and sugar decomposition adjustments. Wood moisture was deemed water in the material balances. Thus, α-cellulose was glucan and holocellulose included glucan, xylan, arabinan and acetyl groups. 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·L^{-1}; flow rate, 0.6 mL·min^{-1}; column temperature, 50 °C; injected volume, 20 μL.

Superiors calorific values 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, using a Parr 6300 Automatic Isoperibol Calorimeter.

Hydrothermal treatment

Following mixing with water in the desired proportions, the raw materials were heated in a 2 L stainless steel Parr reactor fitted with double four-blade turbine impellers at non-isothermal temperatures from 165 to 200 ºC on external mantles for a preset time, and then cooled. The solid/liquid ratio was fixed at 1/8 kg oven-dry raw material/kg water for *A. donax*, *P. fortunei* and sunflower stalks, and at 1/6 —the lowest ratio ensuring homogenous mixing in practice— for eucalyptus and *C. proliferus*.

Once normal pressure was regained, the reactor was opened and samples of the resulting suspensions withdrawn. Solid residues were recovered by filtration and washed with distilled water, an aliquot of each being milled to a particle size less than 0.5 mm in order to determine cellulose (glucan), hemicelluloses (xylan, arabinan and acetyl groups) and lignin with the same methods as for the raw materials.

The resulting liquors were filtered through membranes of 0.45 μm pore size and used for the direct HPLC determination of monosaccharides (glucose, xylose and arabinose), furfural, 5-hydroxymethylfurfural (HMF), and acetic and formic acids. A second aliquot of liquid phase (25 mL) was subjected to quantitative post-hydrolysis with 4% sulphuric acid at 121 °C for 60 min prior HPLC analysis. The increase in concentration of monosaccharides and acetic acid resulting from the post-hydrolysis treatment was a measure of the concentrations of oligomers and bonded acetyl groups.

Pulping and papermaking procedures

Cellulose pulp was obtained in the same reactor used for the hydrothermal pre-treatment. The operating conditions employed with each raw material are shown in Table 3.

Following cooking, each pulp was separated from its liquor and disintegrated, without damaging fibres, at 2500 rpm for 3 min, washed on a sieve of 0.16 mm mesh, defibered and passed through a Strainer filter (0.4 mm mesh) to isolate uncooked material.

Pulp was prepared for paper making in accordance with UNE 57-026 and sheets were obtained by using an ENJO F-39 former according to UNE 57-042-91.

Pulp samples were characterized by using the same procedures as for the raw materials (see "Characterization of the raw materials" above). Pulp determinations, however, included yield (TAPPI T-257), kappa number (TAPPI T-236 cm-85), viscosity (TAPPI T230 om-94, Capillary Viscometer Method) and tensile index (TAPPI 220 sp-96 and TAPPI 494 om-96).

RESULTS AND DISCUSSION

Tables 1 summarizes the reported chemical composition of various lignocellulosic materials previously used to obtain cellulose pulp, whether on a industrial scale or in research work, and Table 2 the composition of our six lignocellulosic materials, namely: *Eucalyptus globulus* –which is one of the plant species most widely used in Spain to obtain cellulose pulp–, *Leucaena diversifolia*, sunflower stalks, *Chamaecitysus proliferus* (tagasaste), *Paulownia fortunei* and *Arundo donax* –which is also widely used by the cellulose pulp and paper manufacturing industry. The table includes the results for a Paulownia hybrid including the species *elongata, tormentosa and fortunei*. Based on these preliminary results of biomass production (over 50 t ha^{-1} year^{-1}), and on the chemical properties of the materials, they appear to be highly effective choices for obtaining biomass fuel and cellulose pulp.

Leucaena and tagasaste are two legumes which facilitate recovery of degraded ground by fixing biological nitrogen. Also, symbiotic interactions between bacteria and plants provide the main source of nitrogen present in the biosphere. Woody legumes are known to prevent erosion, increase soil fertility and facilitate the establishment and growth of other plant species [17, 18]. Sunflower stalks constitute a useful agricultural residue for various purposes. Finally, Paulownia is a very interesting species on account of its high biomass production potential and suitability for the production of pulp and paper.

Table 3 shows the results of the autohydrolysis and organosolv delignification of the six lignocellulosic materials studied.

Because *E. globulus* is the most widely studied material in this context, its properties can be used as references for comparison with other materials. In fact, the operating conditions used were based on previous results of Garrote [19], who found oligosaccharide extraction from eucalyptus wood to peak at 10.3% at 196 ºC. The low glucose contents (only 0.5% relative to glucan in the raw material at 196 ºC) and high xylose contents (75.3% xylose + oligomers relative to xylan in the raw material at 196 ºC) in the autohydrolysis liquor suggest that the polymer retains most of its integrity even at high temperatures.

The holocellulose contents of *C. proliferus*, *L. diversifolia* and sunflower stalks exceeded those of eucalyptus by 20%, 14.1% and 10.9%, respectively, and were comparable to or higher than those of wheat straw [20], *Miscanthus* [21] and previously reported values for *Paulownia* [22, 23].

Paulownia fortunei exhibited a very low holocellulose content (14.9% lower than that of eucalyptus), which was not determined according to Wise et al. [24], but rather as the combination of glucan, xylan, araban and acetyl groups. Such a low value was inconsistent with the improved physical properties of paper sheets obtained following organosolv delignification of the hydrolysis solid residue; thus, their tensile index was quite similar to those for eucalyptus paper obtained under similar conditions. By contrast, the Paulownia trihybrid exhibited a substantially higher content which was similar to those reported by other authors [22, 23]. On the other hand, the glucan content of eucalyptus wood was higher than that of other tested materials; thus, it was 20.3–38.5% higher than those of sunflower stalks and *C. proliferus.* The lignin content of eucalyptus was also similar to or higher than those of the other raw materials. By exception, the Paulownia trihybrid exhibited chemical make-up properties similar to those of eucalyptus in all respects.

The hemicellulose (holocellulose–glucan) contents of all raw materials, which ranged from 41.4% for *C. proliferus* to 22.7% for *P. fortunei*, were higher than those for eucalyptus (20.5%). Also, *A. donax* excepted, this resulted in more efficient oligomer extraction in the liquid autohydrolysis step (Table 3).

The xylan contents of *Miscanthus* and kenaf (Ververis et al., 2004), *L. diversifolia*, Paulownia, *C. proliferus* and *A. donax* ranged from 15.7% to 19.9%, and were similar to each other and higher than those of eucalyptus (16.6 or 14.2%) [25]. Specially high was the xylan content of wheat straw (34.6%) [15], the highest value for the studied materials being that for sunflower stalks (23.9%). Other authors [26] had previously obtained similar glucan and lignin contents, but substantially lower xylan and araban contents, for *A. donax*.

Our results for *P. fortunei* differ markedly from those reported by Kalaycioglu et al. [22] and Jiménez et al. [23]. By exception, the glucan content reported by the latter authors, 37.4%, is similar to ours (34.8%). These differences can be ascribed in part to differences in climate, water availability, plant age and analytical methodology –the previous authors did not use HPLC. *Paulownia fortunei* exhibited the lowest holocellulose content and highest cellulose content among the studied materials. However, other authors [22, 23] previously reported higher holocellulose (78.8%) and lignin contents (22.1 and 22.4%) that are comparable to those of other materials and higher than those of eucalyptus. Finally, our xylan, araban and acetyl contents were similar to those previously found in other materials [20, 21, 25, 26, 27].

No significant differences in energetic potential between *E. globulus* and *L. diversifolia,* or between *E. globulus* and *C. proliferus*, were observed. The calorific value was especially high for *A. donax* and, above all, *P. fortunei.* On the other hand, sunflower stalks had significantly lower values.

In summary, sunflower stalks constitute the least useful crop —in fact it is an agricultural residue— among those studied on account of its low heat power and also low glucan content. On the other hand, *P.*

fortunei is the most promising of all judging by its high heat power and the high glucan content of its *fortunei-elongata-tormentosa* hybrid.

Hydrothermal treatments cause the dissolution of hemicellulosic polysaccharides present in the raw material. The process is facilitated by the acid conditions resulting from the release of acetyl groups from hemicelluloses [25]. The degradation of polysaccharides causes the release of their constituent monomers and oligomers; also, because the monomers are not completely stable in the cooking medium, they can yield furfural and hydroxymethylfurfural by dehydration of pentoses and hexoses, respectively [28]. These substances were all detected at very low concentrations (< 0.2 g/L), and only at the highest autohydrolysis temperatures (195–200 ºC).

Table 3 shows the concentrations of oligomers, sugars and various other substances in the liquors resulting from the hydrothermal treatments, as well as selected properties of the pulp and paper sheets obtained by organosolv delignification of the solid residues. The values shown are the proportions of extracted compounds, in g/L, relative to the content in each polymer fraction of the raw material (dry mass) in the liquid phase obtained from the autohydrolysis of the six lignocellulosic materials studied. The table also gives additional data for the less widely studied materials (viz. *L. diversifolia, C. Proliferus*, sunflower stalks and *P. fortunei*), but obtained at hydrolysis temperatures below and above those used with *E. globulus* and *A. donax* (175–200 ºC).

Overall, solubilization increased with increasing temperature of the hydrothermal treatment (especially in *C. proliferus*, where the amount of oligomers dissolved rose by a factor of 4 from 175 to 195 ºC). Xylose and acetic acid were also solubilized maximally at high temperatures (185–195 ºC). As noted earlier, the oligomer yield for *C. proliferus* exceeded that for eucalyptus at temperatures from 185 to 195 ºC. Arabinose was solubilized in very high proportions relative to its content in the raw material (*viz.* 95.2% at 195 ºC); however, its absolute concentration was very low owing to its low proportion in the raw material.

Solubilization of oligomers in sunflower stalks increased by 97% from 175 to 190 ºC and then decreased up to 200 ºC by effect of their thorough hydrolysis to simple sugars or other decomposition products. In fact, the content in acetic acid at 200 ºC (3.68 g/L, equivalent to 3.7% of dry mass of raw material) was much higher than that for any other material at any temperature. The concentration of formic acid reached levels up to 1 g/L, whereas those of furfural and 5-hydroxymethylfurfural never exceeded 0.1 g/L (results not shown). The oligomer yield of this raw material was higher than were those of eucalyptus, *A. donax*, *P. fortunei* and *C. proliferus*; in fact, it amounted to 21.5% dry mass of raw material and was the highest among all.

Solubilization of oligomers in *P. fortunei* rose 1.9 times from 180 to 200 ºC; by contrast, the increase from 190 to 200 ºC was less marked and accompanied by a decrease in the proportion of xylose extracted. *Leucaena diversifolia* exhibited a significant qualitative leap in oligomer extraction between 170 and 185 ºC, where it rose by a factor of 2.5. Exceeding these values caused the complete solubilization of the oligomer fraction, which suggests that this material affords optimal hemicellulose extraction at relatively low temperatures. On the other hand, oligomer extraction was especially inefficient with *A. donax*, even at high temperatures.

Only 3.1% of cellulose present in the raw material was solubilized under the most drastic heating conditions used in the autohydrolysis of *C. proliferus* (195 ºC). This suggests that the process is quite selective, and also that the cellulose is scarcely degraded, so it can be useful for other purposes such as obtaining cellulose pulp. The autohydrolysis conditions are not so strong as to dissolve cellulose since its crystal structure makes it difficult to hydrolyse relative to hemicelluloses [28]. This is an advantage inasmuch as it allows scarcely degraded cellulose to be obtained as a valorizable product [29, 30]. Similar results were obtained with the other materials and temperatures. Thus, cellulose degradation never exceeded 2.8%, 3.2% and 2.5% relative to glucan in sunflower stalks, *A. donax* and *P. fortunei*, respectively; these values, however, are still higher that those for *E. globulus* wood, which never exceeded 0.5%. *Leucaena diversifolia* set the standard again, with glucose extraction levels over 5% even at the lowest temperatures.

The amounts of oligomers extracted from all raw materials —*A. donax* excepted— in the highest temperature range exceeded those for eucalyptus. Those obtained from *C. proliferus* at temperatures below 185 ºC (1.9–9.4 g/L), *P. fortunei* and *L. diversifolia* below 190 ºC (2.6–14.7 g/L and 4.2–18.7 g/L respectively), and sunflower stalks below 180 ºC (7.6–16.8 g/L) were all greater than those for eucalyptus wood (8.7 g/L at 180 ºC).

Arundo donax provided the highest proportions of extracted oligomers and xylose, in addition to relatively high proportions of glucose and acetic acid, in the hydrolysis liquor. Therefore, it was the least suitable material for exploitation by autohydrolysis.

Overall, both sunflower stalks and *P. fortunei* can be efficiently hydrolysed at 180 and 190 ºC with minimal degradation of the solid phase and maximal extraction of xylan. At temperatures in the region of 200 ºC, Heitz et al. [31], and Garrote et al. [32], observed substantial depolymerization of cellulose and a reduction in the amount of cellulose fibres by effect of autohydrolysis. *Leucaena diversifolia and C. proliferus* required higher temperatures and were less efficiently extracted for xylose.

In summary, *A. donax* is the least suitable raw material among those studied on account of its poor polymer extraction. *Chamaecytisus proliferus* and *E. globulus* required similar temperatures for extraction of a similar amount of polymers. *Paulownia fortunei*, *L. diversifolia* and sunflower stalks provided amounts of extracted oligomers similar to those of *E. globulus* but at 10–15 ºC lower temperatures.

Examination of the properties of cellulose pulp and paper sheets obtained from the autohydrolysis solid residues revealed eucalyptus to provide better pulp that the other studied materials, which were harvested after short growth cycles (1–2 years only). The exception, again, was *A. donax*, which, under certain pulping conditions, and given its low autohydrolysis yield, reached pulp yields around 80%.

The best kappa numbers were obtained with *L. diversifolia* (12.5%), albeit at the expense of excessively degraded fibre and strength-related properties (viz. a tensile index of 3.72 kN m/kg and a viscosity of 303 mL/g). Among other effects, this reduced the tensile index by 65.5% relative to paper sheets obtained directly from the raw material in the absence of hydrothermal pretreatment. One should bear in mind that this cellulose pulp exhibited an acceptable kappa number relative to kraft pulp from *L. leucocephala* harvested after 10 years' growth (KN = 28, average tensile strength with a 200 H-factor and 20% effective alkali content) [33, 34]. Also, the tree production period was significantly shorter in this study, so it would be advisable to use milder organosolv delignification and autohydrolysis conditions. Such conditions could allow cellulose pulp with acceptable properties and 80% extractable oligomers with respect to the polymer content of each dry raw material to be obtained from autohydrolysis solid residues.

This was partly apparent for cellulose pulp from *C. proliferus,* a legume similar to *L. diversifolia*. Thus, lowering the autohydrolysis temperature (from 195 to 165 ºC) was found to result in improved strength-related properties (857 vs 755 mg/L viscosity and 5.9 vs 3.0 kN m/kg tensile index) and in increased yield (from 53.0% to 60.2%), with little effect on kappa number. Obviously, raising the proportion of extracted oligomers would require using a temperature around 185 ºC and milder conditions during the organosolv delignification step.

Cellulose pulp from sunflower stalks exhibited high lignin contents, and quite low viscosity and tensile index levels. This was so despite the relatively low autohydrolysis temperature used (180 ºC), which had resulted in substantial oligomer and xylose recovery. *Arundo donax* also exhibited substantial lignin contents in pulp and, although the strength-related properties (tensile index) of its paper were somewhat better, oligomer extraction was also poor. Therefore, neither material is recommended for obtaining oligosaccharides and cellulose pulp by sequential fractionation (autohydrolysis) and organosolv delignification.

Based on the strength-related properties of the paper sheets, sunflower stalks constitute the least useful material among those studied. *Chamaecytisus proliferus* exhibited strong cellulose degradation —and a decreased tensile index as a result— at autohydrolysis temperatures above 175 ºC. The best kappa number was that for *L. diversifolia*, which could be a suitable raw material for obtaining pulp and paper at an autohydrolysis temperature below 180 ºC. However, *P. fortunei* was possibly the most promising material tested and even a potential rival for eucalyptus. In fact, the strength-related properties (tensile index) of its paper were similar to or even better than those of eucalyptus wood on the lower temperature end and its kappa number much better —lignin contents were very low and consistent with kappa number development. In addition, using a hydrolysis temperature of 190 ºC prior to organosolv delignification ensured extraction of 64.1% oligomers, which exceeds the figure for eucalyptus at 196 ºC. Also, glucose degradation was less marked —albeit higher than in eucalyptus (2.2% vs 0.5%)—, and xylose and acetyl group extraction similar or higher.

CONCLUSIONS

Leucaena diversifolia; *Paulownia fortunei* and its “trihybrid” consisting of *elongata, tormentosa* and *fortunei* varieties; sunflowers stalks; and *Chamaecytisus proliferus* were found to contain 56.9–80.3% holocellulose, 33.8–44.0% glucan, 15.7–23.9% xylan and 3.3–8.8% acetyl groups; these contents are similar to or higher than those of *Eucalyptus globulus*, *Arundo donax* and various other lignocellulosic biomass materials. By contrast, the lignin contents of the former species (19.8–27.8%) are similar to or lower than those of the latter.

The amounts of oligomers extracted from *C. proliferus* (1.9–9.4 g/L), *P. fortunei* (2.6– 4.7 g/L), *L. diversifolia* (4.2–18.7 g/L) and sunflower stalks (7.6–16.8 g/L) in the highest temperature range studied (180–190 ºC) are greater than those for eucalyptus (8.7 g/L at 181 ºC). Overall, both sunflower stalks and *P. fortunei* can be efficiently hydrolysed at 180 and 190 ºC with minimal degradation of the solid phase and maximal extraction of xylan. On the other hand, *L. diversifolia and C. proliferus* require higher temperatures and are less efficiently extracted for xylose. Finally, *A. donax* is the least suitable material for exploitation by autohydrolysis.

As shown in this work, one can effectively use *L. diversifolia and C. proliferus* to obtain cellulose pulp with a kappa number less than 20 and 31, respectively, and paper sheets with acceptable strength-related properties, by sequential organosolv delignification and autohydrolysis at relatively low temperatures (185 ºC). Under these conditions, the amounts of oligomers extracted exceed 80% and 45%, respectively, of the oligomer contents in the dry raw materials.

Paulownia fortunei is the most potentially useful raw material among those studied here, with a tensile index of 17.0–28.9 kN m/kg, a kappa number of 40.5–74.1 and a lignin content in ethanol pulp autohydrolysed at 190 °C of 3.7%–15.3%. In addition, it affords recovery of oligomers, xylose and acetyl groups by 64.1%, 7.0% and 22.5%, respectively, at 190 ° C; these proportions are similar to or even higher than those for eucalyptus. In addition, *P. fortunei* provides the highest calorific value among the raw materials studied (4683.8 cal/g).

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Table 1. Chemical composition of various lignocelluloses materials (bibliography references).

	Arundo Donax [1]	*Hibiscus cannabinus* [2]	*Populus* [3]	*Eucalyptus Globulus* [4]	**Wheat straw** [5]	*Paulownia Fortunei* [6]	*Minscanthus sinensis* [1]
Glucan, %	30.5	40	36.3	53.4	55.4	48.3; 37.4	39.5
Klason lignin %	15.8-22.0	13.4	19.3	-	-	22.1; 22.4	-
Holocellulose %	-	-	-	-	76.2	78.8; 71.0	69.4
Xilan %	8.1	19	22.7	14.2	34.6		19
Araban %	0.6	1.8	0.6	0.4	5.6		1.8

[1] [26]. [2] [21]. [3] [23]. [4] [25]. [5] [20]. [6] [22].

Table 2. Chemical characterization of *Eucalyptus globulus*, *Paulownia Fortunei* and Paulownia "tri-hibrid" *Fortunei+Elongata+Tormentosa, Leucaena diversifolia*, *Arundo donax*, Sunflower stalks and *Chamaecytisus proliferus* (Tagasaste)

	Eucalyptus Globulus [2]	*Eucalyptus Globulus*	*Leucaena Diversifolia*	*Paulownia Fortunei*	Paulownia trihibrid	*Arundo donax*	Sunflower stalks	*Chamaecytisus proliferus*
Glucan, %	46.8	44.3	38.0	34.2	44.0	34.8	33.8	38.9
Klason lignin %	22.9	27.1	24.8	27.2	27.8	23.0	19.9	19.8
Holocellulose %	67.3(1)	66.7(1)	76.3	56.9(1)	65.2(1)	64.5	74.2	80.3
Xylan %	16.6	18.0	15.7	18.3	15.7	19.4	23.9	19.9
Araban %	0.54	1.10	1.50	1.13	1.10	1.50	0.37	0.65
Acetyl groups %	3.5	3.3	3.3	3.3	4.4	3.4	4.3	4.4
Superior calorific value (Constant volume) cal/g. Over dry basis		4491.4 (37.9)	4529.7 (7.9)	4683.8 (24.2)		4573.0 (9.1)	3822.6 (157.2)	4482.0 (29.6)
Superior calorific value (Constant volume) cal/g. (% Moisture)		4167.4 (35.4) (7.2%)	4210.0 (8.4) (7.0%)	4259.7 (21.8) (9.2%)		4166.6 (8.2) (8.9%)	3567.8 (146.8) (6.7%)	4278.0 (28.4) (4.0)

Percentages relative to the raw material (100 kg dry mass). Average value of four replicated.

[1] Holocellulose as: glucan + xylan + arabinan + acetyl groups

[2] [35].

Table 3.- Oligomers and monomer contents in the liguor in g/L and relative to the content in each polymer fraction of the raw material (dry mass) (oligomer contents are given as xylose equivalents). Chemical characteristics of cellulosic pulps and physical properties of paper sheets obtained by organosolv process (ethanol) from the solid residue of autohydrolysis. (note: "-" Indicates no significant levels with the level of indicated precision)

Eucalyptus Globulus [36]		
Autohydrolysis temperature[1]	181ºC	196ºC
Oligomers	8.7/52.4	14.3/62.0
Glucose	0.17/0.4	0.35/0.5
Xylose	1.01/6.1	3.07/13.3
Arabinose	-	-
Acetyl groups	0.21/6.0	0.56/11.5
ORGANOSOLV DELIGNIFICATION AFTER AUTOHYDROLYSIS AT 181ºC (15 experiments)		
Operation temperature between 145ºC and 175ºC, Operation time between 40 and 120 min and ethanol concentration betweeen 40 and 70%		
Yield %	56.2-76.1	
Tensile index N m/g	9.1-31.1	
Kappa number	53.5-100.7	

Arundo donax [37]							
Autohydrolysis temperature[1]	165ºC	170ºC	175ºC	180ºC	185ºC	190ºC	200ºC
Oligomers	-	-	-	0.8/3.2	3.0/12.3	3.2/13.1	7.2/29.5
Glucose	-	1.3/2.9	1.4/3.2	1.4/3.2	1.1/2.5	1.0/2.2	1.1/2.5
Xylose	0.2/0.9	0.5/3.4	1.0/4.0	1.2/4.7	0.6/3.7	0.8/3.2	0.9/3.6
Arabinose	0.1/3.3	0.1/3.3	0.1/4.0	0.1/6.7	0.2/9.3	0.2/12.0	0.3/14.0
Acetyl groups	0.4/8.8	0.9/20.0	0.9/20.9	1.0/24.4	1.6/36.8	2.2/51.2	2.9/67.9
ORGANOSOLV DELIGNIFICATION AFTER AUTOHYDROLYSIS AT 185ºC (35 experiments)							
Operation temperature between 160ºC and 200ºC, Operation time between 30 and 130 minutes and ethanol concentration between 20 and 60%							
Yield %	23.5-79.7						
Tensile index kN m/kg	2.6-12.4						
Kappa number	38.8-141.9						
Glucan %	46.2-76.8						
Xilan %	2.9-22.9						
Acetyl groups %	0.2-3.2						
Lignin %	8.7-25.8						

Leucaena Diversifolia [38]							
Autohydrolysis temperature[1]	165ºC	170ºC	175ºC	180ºC	185ºC	190ºC	195ºC
Oligomers	4.2/23.0	6.2/33.8	8.3/45.4	9.5/51.9	15.4/84.2	18.7/102.2	20.0/109.3
Glucose	2.4/5.1	2.5/5.3	2.4/5.1	2.5/5.3	2.4/5.1	2.4/5.1	2.4/5.1
Xylose	0.4/2.0	0.5/2.5	0.4/2.0	0.5/2.5	0.7/3.6	0.8/4.1	1.1/5.6
Arabinose	-	0.1/5.3	0.2/10.6	0.2/10.6	0.3/16.0	0.4/21.3	0.4/21.3
Acetyl groups	0.3/7.3	0.4/9.7	0.4/9.7	0.5/12.1	0.6/14.5	0.9/21.8	1.1/26.7

ORGANOSOLV DELIGNIFICATION AFTER AUTOHYDROLYSIS AT 195ºC

Operation temperature: 185ºC, Operation time: 60 min, NaOH concentration: 21%, Anthraquinone concentration: 0.05%, Solid/liquid rate: 1/8 and Ethanol concentration: 30%. Without hydrothermal pretreatment: Yield: 39.7%, Kappa number: 16.1, Viscosity: 486 mL/g and Tensile index: 10.77 kN m/kg,

Yield %	40.3
Tensile index kN m/kg	3.72
Kappa number	12.5
Viscosity (ml/g)	303

Paulownia Fortunei [39]

Autohydrolysis temperature[1]	160ºC	180ºC	190ºC	200ºC
Oligomers	2.6/11.4	9.8/42.9	14.7/64.1	18.6/81.1
Glucose	0.9/2.2	1.1/2.5	0.9/2.2	0.7/1.6
Xylose	1.1/4.6	1.2/5.4	1.6/7.0	1.9/8.3
Arabinose	0.2/14.9	0.5/33.3	0.6/42.5	0.6/41.8
Acetyl groups	0.3/7.0	0.5/12.1	0.9/22.5	1.2/29.7

ORGANOSOLV DELIGNIFICATION AFTER AUTOHYDROLYSIS AT 190ºC (15 EXPERIMENTS)

Operation temperature between 150ºC and 180ºC, Operation time between 30 and 90 min and ethanol concentration between 30 and 60%

Yield %	35.5-47.2
Tensile index kN m/kg	17.0-28.9
Kappa number	40.5-74.1
Glucan %	71.2-81.6
Xilan %	3.8-9.8
Acetyl groups%	0.7-2.2
Lignin %	3.7-15.3

Sunflower stalks [40]

Autohydrolysis temperature[1]	165ºC	170ºC	175ºC	180ºC	185ºC	190ºC	200ºC
Oligomers	7.6/31.8	9.0/37.8	10.9/45.6	16.8/70.3	19.4/81.2	21.5/90.0	18.6/77.9
Glucose	0.40/1.2	0.48/1.4	0.96/2.8	0.64/1.9	0.96/2.8	0.80/2.4	0.56/1.7
Xylose	1.04/4.2	1.28/5.4	1.36/5.7	1.60/6.7	1.52/6.4	2.08/8.7	1.68/7.0
Arabinose	0.00/0	0.08/21.6	0.16/43.2	0.24/64.9	0.40/100	0.48/100	0.48/100
Acetyl groups	0.32/7.4	0.40/9.3	0.80/18.6	0.88/20.5	1.92/44.7	1.92/44.7	3.68/85.6

ORGANOSOLV DELIGNIFICATION AFTER AUTOHYDROLYSIS AT 180ºC

Operation temperatures: 145 and 175ºC, Operation times: 40 and 120 min, Ethanol concentration: 50 and 70%.

Yield, %	52.0	36.3
Cellulose, %	56.0	69.1
Lignin, %	19.5	18.2
Viscosity, ml/g	353	551
Tensile index, kNm/kg	2.38	3.81

***Chamaecytisus proliferus* (tagasaste)** [38, 41]

Autohydrolysis temperature[1]	165ºC	175ºC	185ºC	195ºC
Oligomers	1.9/9.6	3.3/16.6	9.4/47.2	13.9/69.8
Glucose	0.9/2.3	1.1/2.8	1.1/2.8	1.2/3.1
Xylose	0.6/3.2	0.7/3.5	0.9/4.5	1.7/8.5
Arabinose	0.1/23.0	0.2/31.7	0.4/63.5	0.6/95.2
Acetyl groups	0.2/3.9	0.2/4.6	0.4/9.1	0.8/18.2

ORGANOSOLV DELIGNIFICATION AFTER AUTOHYDROLYSIS

Operation temperature: 175ºC, Operation time: 90 min, Ethanol concentration: 60%, Wash temperature: 70ºC, Desintegrate temperature: 45ºC. Without hydrothermal pretreatment: Yield 42.6%, Kappa number 66, Viscosity 1056 mL/g and Tensile index 7,8 kN m/kg

Autohydrolysis temperature	165ºC	175ºC	185ºC	195ºC
Yield, %	60.2	58.4	58.2	53.0
Kappa number	34.6	34.6	31.0	28.8
Viscosity, ml/g	857	762	770	755
Tensile index, kNm/kg	5.0	5.9	4.5	3.0

[1] Maximum temperature of non isothermal operation.