Variations in Production and Oligomers Content Obtained Under Hydrothermal Treatment Among Five Fast-Growing Species

M.J. Díaz*[,1], R. Yañez[3], A. García Barneto[1], J.E. Martín Alfonso[1], M.J. Feria[1], R. Tapias[2] and M. Fernández[2]

[1]*Chemical Engineering Department, Facultad de Ciencias Experimentales, Campus El Carmen, Universidad de Huelva. 21071 Huelva Spain:* [2]*Agroforestry Science Department, Escuela Politécnica Superior, Universidad de Huelva, La Rábida, Palos de la Frontera (Huelva), Spain;* [3]*Chemical Engineering Department, Campus Ourense, Universidad de Vigo, Ourense Spain*

Abstract: In order to identify fast growing species utilizable for olygomer and monomer production, five fast growing species (*Paulownia fortunei, Chamaecytisus proliferus, Arundo donax, Leucaena.diversifolia and Sesbania grandiflora*) were tested. Concurrently, the biomass productivity of these species was also tested on a field scale. The biomass productivity of the selected species studied ranges from 0.36 to 21.30 t ha^{-1} (o.d.b.) under Mediterranean conditions for the year 1 sprouts. In addition, the hydrothermal treatment results show that the selected species could be employed as alternative raw material for the production of oligomers, leading to a high concentration of oligomers (9.4-23.4 g/L^{-1} at 190ºC).

Keywords: *Paulownia fortunei, chamaecytisus proliferus, arundo donax, leucaena diversifolia, sesbania grandiflora*, alternative pulp raw materials, hydrothermal treatment.

1. INTRODUCTION

There is a growing interest in the processes used to optimize lignocellulosic materials valorization. Because of this, the industry has an increased capacity to consume wood and non-wood chips, demanding not only forest wood stock, but also the prevision of the future industrial use of the wood that would be generated. The possible solutions involve a sustainable agricultural management that uses natural resources to enhance soil productivity without jeopardizing the land`s future potential. In this sense, the use of fast growing species could have a great advantage as these species provide remediation for the environmental problems associated with their industrial use. Moreover, the use of fast-growing species may offer some advantages in terms of soil restoration [1, 2] and the shorter time required to activate production in comparison with woody plants [3].

A possible efficient approach for lignocellulosic materials (LCM) processes is the "Biomass Refinery" philosophy [4]: the LCM is sequentially fractionated to obtain the main components (cellulose, hemicelluloses and lignin) in separated streams for an individualized profit of each. The first step in this fractionation can be autohydrolysis treatment, also known as hydrothermal treatment or hydrothermolysis. Autohydrolysis can solubilize oligomers almost quantitatively [5], dropping off the cellulose at solid phase and inducing little modifications in the lignin. The autohydrolysis chemical fundament is the hydrolysis reactions of the hemicelluloses in aqueous medium, so these reactions are catalyzed by protons. In the initial stages of reaction, the protons come form the auto-ionization of water. The liquid resulting phase is composed principally of oligomer by-products, xyloolygosaccharides (XO), monosaccharides, acetic acid, etc. The XO are the majority reaction products in the operation conditions usually gathered in the bibliography [6-8].

Moreover, the use of fast growing species for other uses, such as energy [9], alcohol production [10], pulp and papermaking [11], etc., has been extensively studied. However, few studies relate the production capacity of these species to their potential uses.

In this paper, we will evaluate different alternatives for the selected fast-growing species to quantify the variations of five different species a) on the yield obtained (total dry biomass and woody dry biomass), b) on the chemical composition changes of the raw material and c) on the chemical characteristics of the liquid obtained after an autohydrolysis treatment.

2. EXPERIMENTAL

2.1. Experimental Design for Field Experiments

Paulownia fortunei (Paulownia), *Chamaecytisus proliferus* (Tagasaste), *Arundo donax* (Arundo), *Leucaena.diversifolia* (Leucaena) *and Sesbania grandiflora* (Sesbania) were the species used in this work. The soil at the experimental site was sandy and loamy with a pH of 6-8, and having moderate to substantial depth. Field experiments

*Address correspondence to this author at the Chemical Engineering Department. Facultad de Ciencias Experimentales. Campus El Carmen. Universidad de Huelva 21071 Huelva Spain Tel: +34 959 21 99 90;
Fax: +34 959 21 99 83; E-mail: dblanco@uhu.es

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were carried out in two plots, with a complete randomized block design with 4 replicates per species. In each block, 16 plants were planted in an area of 18 m^2; 9500 plants ha^{-1} for Leucaena, Tagasaste and Sesbania; 2500 plants ha^{-1} for Paulownia and 21000 plants ha^{-1} for Arundo. These relations draw attention to the interrelationships between plant density (and thus the extent to which space is occupied), average plant size (and thus, arguably, levels of recent disturbance), and the crop frequency distribution [12]. No fertilizer was added to the plots for Leucaenas, Tagasaste and Sesbania. Several nitrogen fixing species can convert substantial quantities of atmospheric nitrogen into a combined form [13]. Therefore, it is not necessary to supply N to crops, although it would be advisable to apply N during the plantation stage. However, high soil N levels, particularly as nitrates, are known to inhibit nodulation and the nitrogen-fixing process [14]. For Paulownia and Arundo one inorganic fertilizer (150 g $plant^{-1}$) was added.

Representative foliage and branch wood samples were collected (species-wise, quadruplicate) for moisture estimation and chemical analyses, in a random fashion. For yield estimation, four randomly selected plants per plot were cut at the base of the crown and immediately transferred to the laboratory in double-sealed polythene bags. After recording the fresh weights, they were dried to constant weights at 70°C, and ground to pass through a 2 mm sieve. Estimates of dry weight biomass were obtained from the fresh weights of the various plant types and their corresponding moisture contents. Dry/wet ratios were used to correct the field weight determinations and to obtain biomass on a per plant basis. The average biomass of component parts per plant was multiplied by the number of plants per plot and extrapolated to a hectare.

2.2. Characterization of the Raw Material

Four samples representing the selected species were collected. Total and wood dry weights were measured. The harvesting of samples started in January; at that time the specimens had an age of 1 year.

Wood trimming samples were milled to pass through an 8 mm screen, since no diffusional limitations were observed for this particle size in preliminary studies. Samples were air-dried, homogenized in a single lot to avoid differences in composition among aliquots, and then stored. The wood trimmings were used including the bark, which was very thin and difficult to strip off, and accounted for only 1-2% of the overall mass.

Aliquots of raw material or solid residue obtained from the hydrothermal treatment were milled to a particle size < 0.5 mm and subjected to moisture and determination of extractable compounds (TAPPI T-264-om-88) and to Quantitative Acid Hydrolysis with 72% H_2SO_4 following standard methods (T-249-em-85). The solid residue after hydrolysis was recovered by filtration and considered (corrected to its ash content) as Klason lignin. The monosaccharides (glucose, xylose and arabinose) and acetic acid contained in the hydrolysates were determined by HPLC, the features of which are mentioned below. Uronic acids were determined spectrophotometrically using galacturonic acid as a standard for quantification. Ashes were determined by calcination (T-244-om-93). Compositions of raw material are shown in Table **1**.

2.3. Hydrothermal Processing of the Lignocellulosic Samples

Raw material and water were mixed in the desired proportions and treated in a 600 cm^3 stainless steel reactor (Parr Instruments Company, Moline, Illinois, USA) using a liquid/solid ratio (LSR) of 8 kg water/kg raw material, on dry basis (the moisture content of material was considered as water). According to previous works, the influence of LSR is relatively low [5]. The reactor was fitted with four-blade turbine impellers, heated by an external fabric mantle and cooled by 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. Fig. (**1**) shows the heating profile of the reactor.

After treatment, solid residues were recovered by filtration, washed with water, air-dried and weighed for yield determination. An aliquot of the liquors was oven- dried to constant weight to determine the dry content (DC, g non volatile compounds/g liquid phase). A second aliquot was filtered through 0.45 mm membranes and used for direct

Table 1. Chemical Composition[a] of the One Year Selected Fast-Growing Species

	Holocellulose (%)	Klason Lignin (%)	Glucan (%)	Xylan (%)	Arabinan (%)	Acetyl groups (%)
[b]Paulownia.	59.93 (1.38)	27.22 (0.08)	34.18 (0.88)	18.31 (0.22)	1.13 (0.08)	3.31 (0.60)
[c]Tagasaste	70.32 (7.78)	19.80 (2.36)	38.91 (3.50)	19.96 (1.57)	0.63 (0.02)	4.39 (0.84)
[d]Arundo	67.23 (4.16)	23.02 (0.13)	35.15 (0.11)	18.24 (0.04)	0.84 (0.03)	3.84 (0.34)
[e]Leucaena	77.91 (2.50)	19.02 (2.51)	40.11 (2.40)	15.71 (1.62)	1.50 (0.10)	3.31 (0.28)
[F]Sesbania	74.89 (4.36)	27.51 (3.35)	50.83 (1.96)	15.35 (2.01)	1.28 (0.34)	3.23 (0.50)

[a]Percentages with respect to dray raw material (100 kg o.d.b.).
[b]*Paulownia fortunei*
[c]*Chamaecytisus proliferus*
[d]*Arundo donax*
[e]*Leucaena.diversifolia*
[f]*Sesbania grandiflora*
The values in brackets are standard deviation.

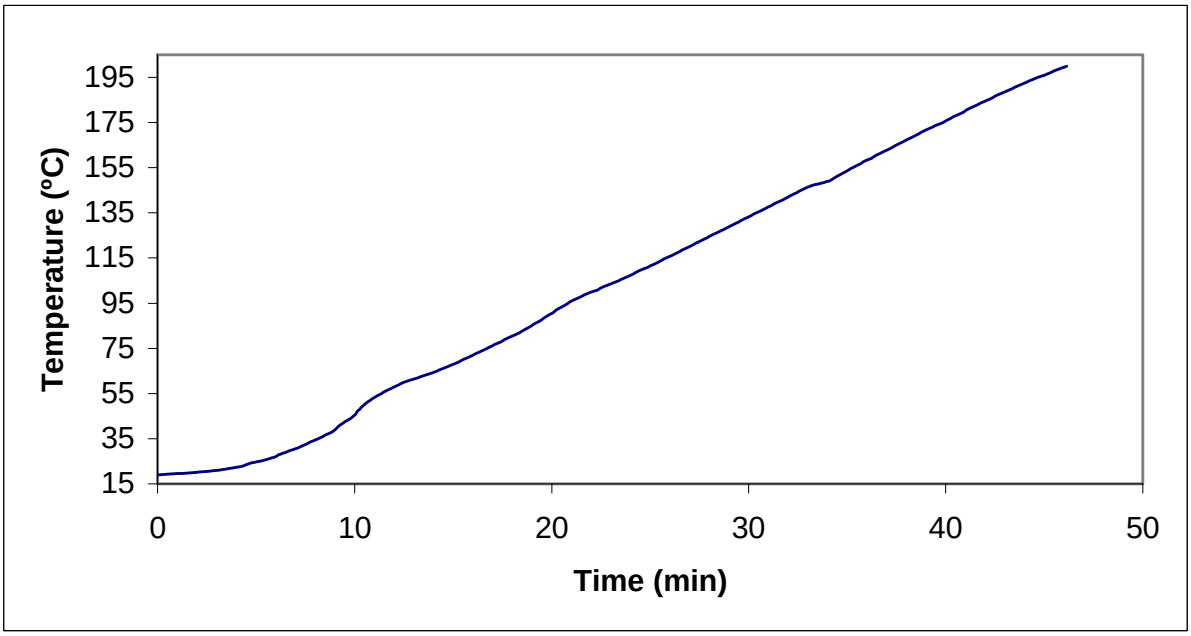

Fig. (1). Temperature profile in reactor during the heating process.

HPLC determination of monosaccharides, hydroxymethylfurfural (HMF) and acetic acid. A third aliquot was subjected to quantitative post-hydrolysis with 4% H_2SO_4 at 121ºC for 45 min, before 0.45 mm membrane filtration and HPLC analysis. The increase in monosaccharide and acetic acid concentration caused by post-hydrolysis provided a measure of the olygomer concentration. HPLC analyses were performed using a BioRad Aminex HPX-87H column at 30º C, eluted with 0.01 M H_2SO_4 at a flow rate of 0.6 mL·min^{-1}, using a Refractive Index detector to quantify glucose, xylose, arabinose, acetic acid, HMF and furfural.

3. RESULTS AND DISCUSSION

3.1. Chemical Characteristics of Raw Materials

Table **1** displays the chemical characterizations for the first year of the varieties selected as raw materials. Moreover, Table **2** shows the chemical characterization of the other raw materials (hardwoods, softwoods and alternative raw materials).

In the studied species, the major fractions were cellulose and lignin, followed by hemicellulosic components.

In Table **1**, higher values for Sesbania and lower values for Paulownia in holocellulose content with respect to other species are observed. The holocellulose contents found in the selected species are similar to those found for other similar raw materials (Table **2**). Under the studied conditions, olygomer content is positively correlated with the holocellulose content, therefore a greater yield could be supposed for Leucaena (77.9%), Sesbania (74.8%) and Tagasaste (70.2%).

As can be seen, Leucaena yielded a lower Klason lignin, similar to that found in Tagasaste. These values could suggest that these varieties may require low pulping of hydrothermal time and chemical charge compared to those of other raw materials. On the contrary, Sesbania and Paulownia lignin contents are higher than those found for other materials (Table **2**).

The glucan content of Sesbania is higher than those found for the selected raw materials (Table **1**). The rest of the selected materials show glucan values comparable to those obtained in the other materials. However, Sesbania and Leucaena show lower xylan values with respect to Paulownia, Tagasaste and Arundo. The α-cellulose contents found in the studied species are in the range of the normal values expected for other raw materials and lower than those found for wood-based materials.

The quantity of xylan in the studied species shows similar values (15-20%). The arabinan in Tagasaste shows lower values than those shown in the rest of the studied species. On the contrary, this species shows higher values in acetyl groups than the rest of the studied species.

The highest cellulose/oligomer ratio among the selected species was found for Sesbania (3.1). This ratio is very important due to the capital role that hemicelluloses play in papermaking [24]. Lower values were found for Paulownia (2.3), Tagasaste (2.2), Arundo (2.1) and Leucaena (2.1).

3.2. Biomass Production

All the species showed adequate soil and climatic adaptation to the zone (La Rábida, Huelva, southwestern Spain). Biomass accumulation for the studied species shows wide variations (Table **3**).

Within the various species, significant differences in the yield obtained were observed. These results suggest a better initial development for seedlings in Arundo and Leucaena with respect to the others. The above ground biomass yield on a per hectare basis was significantly higher for Arundo, while Paulownia showed the lowest biomass production. Among the others, Leucaena yielded the highest total dry biomass (7.45 t ha^{-1}). These differences were expected, due

Table 2. Chemical Characterization of Some Raw Material

Raw Material	Holoce-llulose (%)	Lignin (%)	α-Cellulose (%)	References
Wood materials				
Eucalyptus globulus	80.5	19.9	52.8	[15]
Eucalyptus globulus	79.5	21.2		[16]
Pinus pinaster	60.5	30.2	42.9	[17]
Pinus pinea	69.6	26.2	55.9	[15]
Non-wood materials				
Cannabis sativa L. (hemp).		21.8	37.3	[18]
Cynara cardunculus L.	63.4	19.6	38.0	[18]
Gossypium hirsutum L. (cotton)	72.9	21.4	42.3	[19]
Hibiscus cannabinus L.(kenaf)				[20]
Panicum virgatum L. (switchgrass)	78.5	18.1		[21]
Panicum virgatum L. (switchgrass)	81.0	19.5		[22]
Triticum sp. (wheat straw)	70.7	21.7	41.3	[22]
Olea europaea (olive trimmings)	69.1	17.6	41.0	[23]

Table 3. Biomass Yielded in the First Year from Fast-Growing Species

Species	WD[a] (t ha^{-1}).	TD[b] (t ha^{-1}).
Paulownia	3.88 (0.63)	4.61 (0.92)
Tagasaste	1.38 (0.36)	2.20 (0.60)
Arundo	21.30 (5.40)	30.40 (0.54)
Leucaena	4.83 (0.17)	7.45 (0.96)
Sesbania	3.32 (2.16)	4.86(3.37)

The values in brackets are standard deviation.
[a]WD: Wood dry basis biomass (t ha^{-1}).
[b]TD: Total dry basis biomass (t ha^{-1}).

to the dissimilarities in plant density, average plant size and the crop frequency distribution.

The present study did not include any assessment of root characteristics; however, clear differences in the structure of the root systems among the species have been reported by Dimps *et al.*, [25], Burleigh and Yamoah [26], Bell [27] and Dick *et al.* [28]. These authors reported that less radial symmetry in the root system is negatively correlated with initial growth.

Moreover, great differences between total dry biomass and wood dry biomass (branches and leaves wasted) among the species have been found. In this case also, the higher difference corresponds to Arundo (9.1 t ha^{-1}). Furthermore, significant differences were found for Leucaena (2.6 t ha^{-1}) and Sesbania (1.5 t ha^{-1}). The smallest differences (most wood) have been found for Paulownia (0.7 t ha^{-1}) and Tagasaste (0.8 t ha^{-1}).

3.3. Chemical Characteristics of Liquors from Hydrothermal Treatment

The operational conditions employed in this study (temperature (T) and reaction time (t)) are shown in Fig. (**1**). These processes are very influenced by temperature, caused by the rate of the involved reactions in the hydrothermal fractionation. The temperature was varied between 25 to 190ºC and the subsequent reaction time. Under the selected conditions, little extent of hydrolytic reactions is found and the cellulose degradation is not important [5]. The exposed conditions were selected so that the experimental data obtained includes both the sugar generation and the oligomer decomposition [29-31].

Table **4** shows the values found for the chemical characterization of the liquid product from the hydrothermal treatment.

Table 4. Product Distribution[a] of the Fast-Growing Species Under (190ºC, 1/8 Solid/Liquid Ratio) Non-Isothermal Autohydrolysis Treatment[b]

	Oligomers (g/L)	Glucose (g/L)	Xylose (g/L)	Arabinose (g/L)	Acetic acid (g/L)	HMF[b] (g/L)
Paulownia	9.45 (0.31)	0.72 (0.10)	1.13 (0.13)	0.41 (0.07)	0.52 (0.10)	0.11 (0.01)
Tagasaste	23.48 (1.94)	2.13 (0.42)	2.81 (0.31)	1.02 (0.22)	1.92 (0.21)	0.13 (0.02)
Arundo	17.24 (1.00)	0.81 (0.09)	0.64 (0.17)	0.21 (0.03)	1.33 (0.18)	0.12 (0.01)
Leucaena.	18.72 (1.13)	2.43 (0.31)	0.82 (0.16)	0.41 (0.13)	0.93 (0.11)	0.11 (0.03)
Sesbania	14.17 (1.26)	3.26 (0.63)	12.20 (0.90)	0.43 (0.16)	2.35 (0.37)	0.12 (0.02)

[a]Percentages with respect to dray raw material (100 kg o.d.b.).
[b]The values in brackets are standard deviation.

The behavior of the lignin fraction of wood can be assessed by the proportion of lignin remaining in the solid phase after the selected treatment (98%). Consequently, delignification was seen not to be an important effect of hydrothermal treatments.

The oligomers in the liquor obtained for Tagasaste and Sesbania reach higher values with respect to other varieties. This value represents 74.7% and 58.9% of the total of oligomers initially present in the raw material respectively. The high olygomer values obtained could be related to the high acetyl groups content in the raw material value. Under autohydrolysis treatment, the role of formation of hydronium ions, which catalyzes the oligomers depolymerization, from acetic acid is more important than for water autoionization. It is because the dissociation constant of acetic acid is higher than that of water [32]. In that form, the water autoionization role is limited to the initial reaction stages. The lowest value has been found for Leucaena (53.7%). Medium values have been found for Paulownia (36.7%), Arundo (53.7%) and Sesbania (58.8%). It is possible to emphasize that the Tagasaste reaches the highest value both in total oligomers and the maximum percentage extracted.

In the above-mentioned table, low glucose values among the species have been observed. This data is in agreement with the little cellulose degradation that occurs in treatments at temperatures below 230ºC [7]. However, a different behaviour, characterized by an increased susceptibility towards cellulose hydrolysis, has been determined for Sesbania, Leucaena and Tagasaste with respect to Arundo and Paulownia.

Among the oligomers (with the exception of glucose) xylose reaches higher concentrations; this is because the majority of the hemicellulosic fraction of the agricultural materials is xylan, a structure formed by xylose monomers with different ramification such as arabionse, acetyl groups or uronic acids [33]. In this form, the highest value has been found for Sesbania and few significant differences have been found for the rest of species.

In general, for the others parameters measured (arabinose and acetic acid), a similar relation to that obtained for xylose has been observed. This general trend has been previously described by Yañez *et al*., [34]. An exception could be made for Arabinose in Arundo, and lower concentrations than expected for this material have been found.

Furfural and hydroxymethyl furfural are sugar-dehydration products, therefore, the concentration of both products will increase in direct proportion to an increase in time and temperature.

Under these conditions, neither significant values (furfural) nor differences have been found for 5-hydromethyl furfural contents in the selected species.

4. CONCLUSIONS

The chemical characteristics of studied species (*Paulownia fortunei, Chamaecytisus proliferus, Arundo donax, Leucaena.diversifolia and Sesbania grandiflora*, report positively on its possible use as alternative source of oligomers.

Significant differences, both in total and wood dry biomass yield obtained**,** were observed within the different species. *Arundo donax* has obtained the highest value among all the evaluated varieties (30.4 t ha^{-1} in total dry biomass). On the contrary, the lowest total dry biomass has been found for *Paulownia fortunei*.

The study confirms the feasibility of the non-isothermal autohydrolysis treatment process for the selected species to yield sugar oligomers and hemicellulosic sugar**,** and low degradation product concentrations have been found.

Under this process, large amounts of oligomers in the liquor (with respect to initial raw material content) could be obtained for *Paulownia fortune* (36.7%), *Chamaecytisus proliferus* (74.7%), *Arundo donax* (53.7%), *Leucaena.-diversifolia* (49.5%) *and Sesbania grandiflora* (58.9%).

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