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Additional Information

Wood characterization for energy application proceeding from pruning *Morus alba* L., *Platanus hispanica* Münchh. and *Sophora japonica* L. in urban areas

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Abstract

Pruning urban forests generates significant amounts of ligncellulosic biomass every year. The energy potential of this biomass is unclear. The aim of this research was direct analysis of the gross calorific value (GCV), elemental composition and moisture content of *Morus alba* L., *Platanus hispanica* Münchh. and *Sophora japonica* L. by means of laboratory equipment. This analysis allowed for further development of indirect GCV prediction models which are economically attractive and less time consuming to direct analysis. These models presented high coefficients of determination (R^2 0.66-0.96). It has been determined that the species with highest mean GCV is *Sophora japonica* L. (19615.68 kJ/kg- dry sample) whereas the one with the lowest is the *Morus alba* L. (18192.87 kJ/kg- dry sample). Elemental analysis showed highest carbon (48.22%), hydrogen (6.17%) and nitrogen (1.16%) content in *Sophora japonica* L. in dry samples. Sulfur was constant at the level 0.05% for all analyzed species. Also percentage of bark and wood density were determined. Mean percentage of bark was highest for *Platanus hispanica* Münchh. (13.05%) while wood density was highest for *Sophora japonica* L. (0.86 g cm^{-3}). This way the research has proven that the biomass produced by pruning urban forests appears to be an interesting source of renewable energy.

Keywords: Urban forest, urban biomass waste, GCV, elemental composition

1. Introduction

Numerous researchers have published mathematical models for predicting the calorific value of various biomass materials from the concentration of the main elements, such as percentage of carbon, hydrogen, nitrogen and others [1-3]. Models have been also derived from proximate analysis [4-6]. The indirect calculation of calorific value with this type of models is justified by the high cost of employing a calorimetric bomb [7-9]. The calorific value is constant for each material with defined elemental composition. The moles of each component in a sample are obtained by multiplying the sample weight by the weight percentage of each, divided by the atomic weight of each element being able to obtain its empirical formula $CHwOxNySz$, where w is the number of moles of hydrogen per mole of carbon; x is the number of moles of oxygen per mole of carbon; y is the number of moles of nitrogen per mole of carbon; z is the number of moles of sulfur per mole of carbon. In other words, the values of w, x, y and z are obtained by dividing the moles of each element contained in the sample by the moles of carbon. Based on these values a specific calorific value for dry material is given.

When measuring the calorific value of biomass, it has to be taken into account that it is a porous material with the ability of retaining water. Moreover, the moisture content of the material is likely to change its empirical formula and the gravimetric percentages of C, H, O and N. Therefore, standards for determining the calorific value for a particular material, such as UNE 164001:2005 EX [10], point to that it should be determined in the anhydrous state, in dry basis. In this state (without water), the calorific value of a material with defined composition would be constant and determination of indirect prediction models would not be applicable. Nevertheless, such models can be found very useful when the empirical composition varies in humidity, presence or absence of foliage, bark percentage or, when it comes to obtaining the calorific value of an indeterminate mixture of materials.

The development of mathematical models for indirect determination of the calorific value is useful in materials that may have variability in composition, and there is some uncertainty concerning the conditions of use, or the proportion in the mixture of materials. For that, economical and reliable methods are required. Such situation is commonly observed in the industrial field. For that, researchers as Jenkins et al. [11], Yin [6] and Callejón-Ferre et al. [7-8] provide models for specific types of mixtures.

Usually, the received biomass for combustion in industrial facilities is found with some moisture. Since forced drying processes excessively raise production costs, they are rarely used in the production of energy. Air drying rarely decreases moisture content below 20% in Mediterranean conditions [12-14]. Moreover, it is common that biomass power plants not only work with a well-defined type of material but also with variable mixtures of different types of biomass. For these reasons the composition of biomass used in industry has variability that directly influences the expected calorific value. The uncertainty of calorific value causes that its determination before the introduction of the materials in the boiler would be meaningful for understanding its energy performance. If the direct determination of the calorific value by means of a calorimetric bomb is more expensive than the determination of the composition, as demonstrated in this work, the development of indirect prediction models for calorific value from the percentage of the different elements is fully justified.

Large quantity of residual biomass with potential energy and industrial end can be obtained from management operations of urban forests. The profitability of exploiting these resources is conditioned by the amount of existing biomass within urban community ecosystems, whose methods of quantification have been studied by Sajdak and Velazquez [15] and Velázquez et al. [16]. These researches point to the residual biomass which can be obtained by pruning of one tree. The obtained averages are 31.67 kg dry biomass/tree of *Morus Alba* L. located in street; 77.78 kg dry biomass/tree of *Morus Alba* L. located in the park; 23.98 kg/tree of *Platanus hispanica* Münchh; and 18.07 kg/tree of *Sophora japonica* L. Whole calculation of the residues in a city will depend on the inventory of each city. Therefore we cannot predict exactly. The aim of this research was focused on direct and indirect measurement of energy characteristics of lignocellulosic waste from urban tree pruning.

2. Materials and Methods

2.1. Vegetal Material

The species analyzed in this work were mulberry (*Morus alba* L.), *Platanus hispanica* Münchh. and *Sophora japonica* L., which are very popular ornamental trees in the Mediterranean areas. *Morus alba* L. known as white mulberry is a species of the family *Moraceae*, genus *Morus*; *Platanus hispanica* Münchh. (*Platanus acerifolia, Platanus hybrida*) is a tree in the family *Platanaceae*, genus *Platanus* and *Sophora japonica* L. also

known as *Styphnolobium japonicum* and Pagoda Tree is a species in the family *Fabaceae*, genus *Styphnolobium* [17]. All species are extensively cultivated ornamental, parkland and roadside trees in the temperate regions. They are widely observed in linear plantations in streets as well as isolated trees in gardens [18].

2.2. Fuel specification

The examined biomass takes origin from pruning operations of Mulberry, Hybrid plane and Pagoda tree. The specification of biomass was based on the norm UNE-EN 14961-1 [19]. According to this norm, the classification of the origin and sources of solid biofuel examined in this work are the following:

"1. Woody biomass
1.1.Woody biomass from forest, plantation and other virgin wood
1.1.7.Wood from gardens, parks, maintenance of roadsides, vineyards and orchards"

According to the specification of solid biofuels based on shape and properties, the analyzed material is classified as showed in Table 1.

Table 1. Specification of properties of wood logs.

Origin: According to paragraph 6.1 and Table 1 of UNE-EN 14961-1.	Woody biomass: *Morus alba* L. *Platanus hispanica* Münchh. *Sophora japonica* L.	
Commercial form	Logs, wood	
Dimensions		
Length (L) (maximum length of a single cut), cm	*Morus alba* L. *Platanus hispanica* Münchh. *Sophora japonica* L.	L 100+, (max. 380 cm) L 100, 100 cm ±5 cm L 100+, (max. 180 cm)
Diameter (D) (maximum diameter of a single cut), cm	*Morus alba* L. *Platanus hispanica* Münchh. *Sophora japonica* L.	D10, 2cm ≤D ≤10cm D10, 2cm ≤D ≤10cm D2-, D<2 cm
Humidity (M) (according to received mass)%	*Morus alba* *Platanus hispanica* Münchh. *Sophora japonica* L.	M45 M45 M45
Volume or weight, m^3 stacked or loose or kg as received	*Morus alba* L. *Platanus hispanica* Münchh. *Sophora japonica* L.	Mean dry weight 31.13kg street^{-1} tree; 77.78kg park tree^{-1} Mean dry weight 23.98kg tree^{-1} Mean dry weight 18.07kg tree^{-1}
Proportion by volume of stumps	*Morus alba* L. *Platanus hispanica* Münchh. *Sophora japonica* L.	Whole (unsplit) Whole (unsplit) Whole (unsplit)
Cut surface	*Morus alba* L. *Platanus hispanica* Münchh. *Sophora japonica* L.	Smooth and regular Smooth and regular Smooth and regular
Wet and rot	*Morus alba* L. *Platanus hispanica* Münchh. *Sophora japonica* L.	No No No

2.3. Sample preparation

The analyzed Mulberry, Hybrid plane and *Sophora japonica* L. branches (without leaves) were divided into 4 classes, depending on their diameter. The diameter classes represent the base of the branch section, midway sections and the upper end section. Next, various wood samples within a diameter section were chipped with a hammermill and stored for laboratory tests. Within each species and diameter class, convection dried and open air dried samples were tested for calorific value and CHNS composition.

2.4. Determination of moisture content

The evaluation of drying process was done according to the norm UNE-EN 14774-2 [20]. The process took place in two types of conditions: open-air drying and oven drying. Open-air drying was carried out in laboratory environment with average temperature 21.32ºC and relative humidity 42.41%. A daily record of results took place until the stabilization of weight was obtained. During oven drying, samples were dried in a stove with controlled temperature $(105 \pm 2)^{o}$C. The drying time did not exceed 24h in order to avoid possible unnecessary loss of volatile substances.

2.5. Gross calorific value and elemental composition analysis

Gross calorific value (CGV) of wood samples of Mulberry, Hybrid plane and Pagoda Tree. were analyzed by means of a LECO AC500 Automatic Calorimeter, based on norm UNE-EN 14918 [21]. CHN determinations were carried out based on norm UNE-EN 15104 [22]. To measure the content of S (sulfur) a Tru-Spec Add-On Module was used [23-25]. The time and reactive cost for GCV determination was analyzed and compared with elemental analysis.

Gross calorific value (GCV) prediction models were developed from CHNS variables by means of Statgraphics 5.1 software. Among all tested equations (linear and quadratic), those with best results were selected. The correctness of the equations was tested by determining the coefficient of determination (R^2), standard deviation (sd) and mean absolute error (MAE). The multiple regression models for each species which gave highest R^2 have been validated.

For that, two independent data sets have been organized: one set (n=25) to generate the model and one set (n=5) for its validation. A t-test was used to compare the mean of real values and values calculated by a regression model. Additionally, the analysis of residual plots has been performed.

2.6. Determination of wood density

The employed methodology involved the determination of dry weight of samples by means of convection drying in temperature $(105\pm2)^{o}C$ until the stabilization of weight after 24 hours was obtained. The samples were immersed in a beaker with water. The obtained difference equivalent to the volume of displaced water, equals the volume of the sample submerged (Equation 1) [25]. The mean and standard deviation were calculated for the obtained densities.

$$D = \frac{Wd}{Vg}$$ (Equation 1)

Where
D= wood density (g cm^{-3})
Wd= oven-dried weight of wood (g)
Vg= green volume (cm^{3})

2.7. Determination of percentage of bark

To perform this study several branches of Mulberry, Hybrid plane and Pagoda Tree. were divided into 4 diameter classes. To determine the percentage of bark, the diameter over bark and the diameter under bark were measured with a digital caliper for all analyzed samples within a diameter class (Equation 2). The average percentage of bark was determined within each diameter class.

$$ba = \frac{dob^{2} - dub^{2}}{dob^{2}} \cdot 100\%$$ (Equation 2)

Where
ba = bark (%)
dob= diameter over bark (mm)
dub= diameter under bark (mm)

3. Results and discussion

Table 2 presents the values of elemental composition and gross calorific value of the studied biomass dried in stove and wet up to 10%.

Table 2. Characterization of examined biomass.

	Species	Drying process	Average	Standard deviation	Standard skewness	Standard kurtosis	Maximum	Minimum
GCV	Mulberry	W10	17127.62	157.02	-1.04	0.04	17301.26	16834.74
	Mulberry	Dry	18192.89	554.09	0.37	-0.60	19099.12	17396.23
	Hybrid plane	W10	17513.76	356.56	-0.01	-1.10	17972.79	17084.95
	Hybrid plane	Dry	18952.47	556.93	-0.08	-0.84	19707.48	18195.80
	Pagoda tree	W10	17970.49	198.41	1.16	-0.03	18317.13	17746.44
	Pagoda tree	Dry	19615.68	100.75	-1.20	1.66	19754.34	19418.78
C	Mulberry	W10	44.54	0.38	-0.15	-0.88	45.0	44.0
	Mulberry	Dry	48.22	0.67	-0.11	-0.37	49.3	47.2
	Hybrid plane	W10	44.1	0.58	0.41	-0.47	45.0	43.3
	Hybrid plane	Dry	48.48	0.64	0.41	-1.22	49.3	47.8
	Pagoda tree	W10	45.66	0.53	-0.10	1.15	46.6	44.7
	Pagoda tree	Dry	49.15	0.63	-0.23	-0.16	50.1	48.1
H	Mulberry	W10	6.36	0.07	0.48	-0.94	6.45	6.26
	Mulberry	Dry	5.92	0.03	-0.28	-0.73	5.97	5.87
	Hybrid plane	W10	5.83	0.08	0.89	0.72	5.99	5.73
	Hybrid plane	Dry	5.77	0.00	-0.51	-0.27	5.87	5.69
	Pagoda tree	W10	6.54	0.06	0.28	0.39	6.67	6.44
	Pagoda tree	Dry	6.17	0.10	-1.37	1.35	6.3	5.97
N	Mulberry	W10	0.60	0.14	0.64	-0.88	0.83	0.45
	Mulberry	Dry	0.86	0.13	-1.04	-0.60	1.01	0.62
	Hybrid plane	W10	0.67	0.12	0.15	-1.08	0.85	0.51
	Hybrid plane	Dry	0.78	0.13	-0.16	-1.02	0.94	0.61
	Pagoda tree	W10	0.90	0.21	1.69	0.78	1.34	0.72
	Pagoda tree	Dry	1.16	0.17	0.76	-0.64	1.42	0.98
S	Mulberry	W10	0.04	0.00	-1.67	1.54	0.05	0.04
	Mulberry	Dry	0.05	0.00	0.42	-0.57	0.05	0.04
	Hybrid plane	W10	0.05	0.00	-0.82	-0.74	0.05	0.04
	Hybrid plane	Dry	0.05	0.00	0.63	-0.11	0.06	0.04
	Pagoda tree	W10	0.05	0.00	-1.92	1.85	0.05	0.03
	Pagoda tree	Dry	0.05	0.00	-0.51	-0.45	0.05	0.04
% bark	Mulberry		9.49	3.83	1.20	-0.17	17.82	3.13
	Hybrid plane		13.05	4.80	1.74	0.92	25.43	6.57
	Pagoda tree		5.29	3.53	1.49	-0.18	13.46	0.14

W10: sample up to 10% moisture content in wet basis; GCV: gross calorific value (kJ kg^{-1}); C: carbon (%); H: hydrogen (%); N: nitrogen (%); S: sulfur (%).

As it can be observed, all variables show standard kurtosis and standard skewness between -2 and +2. This fact means that all of them follow a normal distribution, which is essential for the analysis. The average GCV of analyzed species ranges between 17-20 MJ kg^{-1} depending on the moisture content what gives similar results to those published by Gillon et al. [27] on residuals from landscape maintenance of broad-leaved species (18.80-21.10 MJ kg^{-1}) and by Yin [6] for biomass (14-23 MJ kg^{-1}). These results are also approximated to those found by

FAO [28] on net calorific value of road side green 14.1MJ kg^{-1} and Castells [29] for park residuals and wood slightly above 0.95 MJ kg^{-1}. The GCV found in this thesis are similar to those for agricultural residuals (15-17 MJ kg^{-1}) and to woody materials (18-19 MJ kg^{-1}) [9].

To compare the GCV of different species, the analysis of variance was carried out. The LSD intervals at 95% are shown in Figure 1. It is observed, that the GCV is significantly different among the studied species.
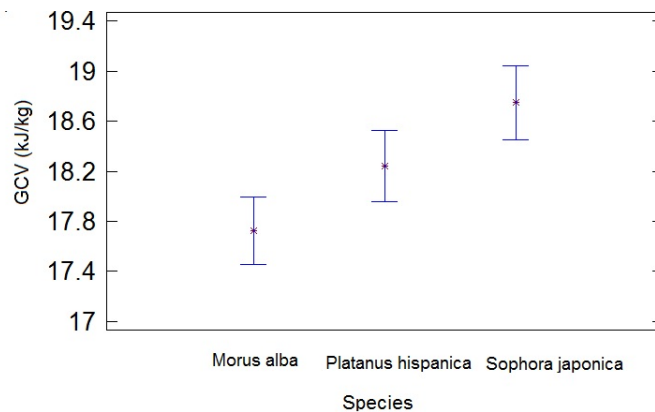

Figure 1. LSD intervals for GCV of species: Mulberry (*Morus alba L.*); Hybrid plane (*Platanus hispanica L.* Münchh*)*; Pagoda tree (*Sophora japonica* L.)

The concentration of C and H in the studied biomass was approximately 44-50% and 5.7-6.5% what has been found in the range of published data (C=42-71%, H= 3-11%) [30]. The N and S concentration in the examined residuals estimated at the level of 0.6-1.1% and 0.04-0.05% are low in comparison to those found in literature for biomass (N=0.1-12%, S=0.01-2.3%) [30-31]. This result is an advantage, as high concentration of N and S produces negative impact on the environment due to the emission of nitrogen oxides, sulfur dioxide and sulfur trioxide during combustion [31-33]. In the Table 2 can be seen that the stove-dried samples present higher mean concentration of carbon and calorific value while the %H generally decreases in dried environment. This is explained by the additional energy that must be used for H_2O evaporation in samples with moisture contents above 0%. Sulfur can be dependent from high concentration in soil and air environment. The results also indicate that Pagoda Tree is the species with highest values within most studied parameters (excluding %S).

The species with highest mean GCV was Pagoda tree (19615.68 kJ kg^{-1}-dry sample). The lowest mean GCV was observed with Mulberry (18192.87 kJ kg^{-1}-dry sample). Elemental analysis showed that carbon content varied from 48.22% in Pagoda tree to 49.15% in Mulberry, hydrogen content ranged from 5.77% in Hybrid plane to 6.17% in Pagoda tree nitrogen from 0.78% in Hybrid plane to 1.16% in Pagoda tree and sulfur was at the level 0.04-0.05 for all analyzed species. The results indicate that Pagoda Tree. is the species with highest values within most studied parameters.

The dependence of the studied variables is shown in Table 3. It can be observed that moisture content, percentage of C, and H have a high influence on the Gross Calorific Value (GCV) when those are considered separately what has been proved in other studies [7-8, 32-33]. What is more, it is important to point out that the high %H is related with the moisture content of the material, provided that the water has as formula H_2O. Therefore, the water content in the pores of the biomass modifies the weight of the material and the ratio of other elements in the sample composition.

Table 3. Pearson correlation coefficients of studied elemental composition.

	Moisture content	C	H	N	S	GCV
Mulberry						
Moisture content		-0.9672*	0.9789*	-0.7399*	-0.4512	-0.7750*
C	-0.9672*		-0.9248*	0.8505*	0.4747	0.6495*
H	0.9789*	-0.9248*		-0.6855*	-0.4823	-0.8530*
N	-0.7399*	0.8505*	-0.6855*		0.6278*	0.4730
S	-0.4512	0.4747	-0.4823	0.6278*		0.5724
GCV	-0.7750*	0.6495*	-0.8530*	0.4730	0.5724	
Hybrid plane						
Moisture content		-0.9619*	0.4550	-0.3955	-0.3119	-0.8210*
C	-0.9619*		-0.2451	0.5867*	0.3198	-0.9221*
H	0.4550	-0.2451		0.3346	-0.3913	-0.0822
N	-0.3955	0.5867*	0.3346		-0.0111	0.7832*
S	-0.3119	0.3198	-0.3913	-0.0111		0.2210
GCV	-0.8210*	0.9221*	-0.0822	0.7832*	0.2210	
Pagoda Tree						
Moisture content		-0.9823*	0.9714*	-0.6481	-0.5947	-0.9825*
C	-0.9823*		-0.9427*	0.7122*	0.5295	0.9834*
H	0.9714*	-0.9427*		-0.4907	-0.5908	-0.9327*
N	-0.6481	0.7122*	-0.4907		0.0520	0.7522*
S	-0.5947	0.5295	-0.5908	0.0520		0.4682
GCV	-0.9825*	0.9834*	-0.9327*	0.7522*	0.4682	

*pares of variables with P-values lover then 0.05; GCV: gross calorific value (kJ kg^{-1}); C: carbon (%); H: hydrogen (%); N: nitrogen (%); S: sulfur (%)

For indirect GCV calculation, prediction models from ratios of C, H, N, and S were developed. These models have high importance in the industry because the GCV of material is used in boilers and is usually unknown due to the influences of moisture content as demonstrated (Tables 2 and 3). The GCV determination with adiabatic calorimeter AC-500 takes 20 min sample^{-1}, and moisture content measurement takes 24 h using the norm UNE. The reagent used to calibrate the adiabatic calorimeter is the benzoic acid, which is dosed 5 g for 30 analyses, and 0.0117 Nm^3 oxygen. Each analysis uses a wire to ignite the sample and generate 586.14 watts of electricity. The estimated cost is 7.87 Euros per sample.

According to experience with leco CHN Truspec analyzer, the average time of the elemental analysis is 5.2 min sample^{-1} at 1172.28 watts. It uses 0.025 Nm^3 of helium, and 0.01 Nm^3 of oxygen. Spent reagents used for this are 300 g of anhydrone (Magnesium Perchlorate) and 60 g of lecosorb (Sodium Hydroxide) for every 800 samples of biomass; 140 g copper sticks, 10.5 g N-catalyst, and 6 g copper turnings in the reduction heater tube every six month. Other maintenance consumables are needed each 200 samples. The estimated reagent cost is 8.04 Euros per sample. Although the cost of direct assay reagents is slightly smaller than the elemental analysis, the last one is less time-consuming and therefore it is more favorable.

Therefore, the indirect measurement using regression equation from the ratios C, H, N and S leads to faster and consequently cheaper determinations (Table 4).

Table 4. Prediction models for indirect calculation of gross calorific value

Species	Function	R^2	sd	MAE
Mulberry	GCV = 3674.57 + 302.93·C	0.66	421.97	328.48
Hybrid plane	GCV= 4189.23 + 269.63 ·C + 2138.94·N	0.95*	201.20	158.40
Pagoda tree	GCV= -2080.66 + 439.47·C	0.96	174.26	132.758

GCV: gross calorific value (kJ kg^{-1}); C: carbon (%); N: nitrogen (%); MAE: mean absolute error; sd: standard deviation; R^2: coefficient of determination;*: R^2 adjusted.

All prediction models present high R^2 (0.66-0.96) and can be used to calculate the gross calorific value without the need of a calorimeter. This allows shortening the measurement process when necessary. The P-value in all explicative variables was lower than 0.05.

Figures 2, 3 and 4 show the variation of moisture content during the evaluation of the drying process carried out in both open-air drying and stove drying conditions. It is observed

that the minimum moisture content in open-air was obtained within 25-30 days and in stove drying conditions after 24 hours.
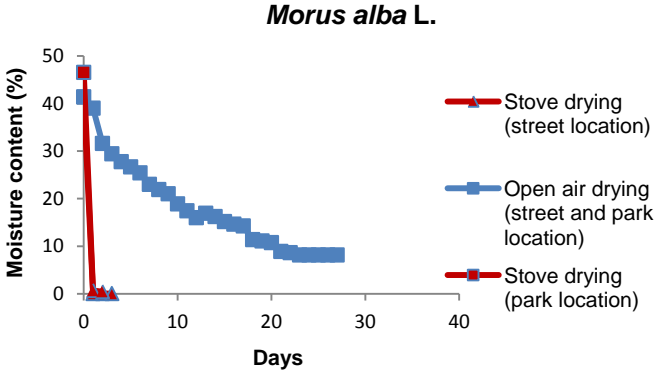
Morus alba L.

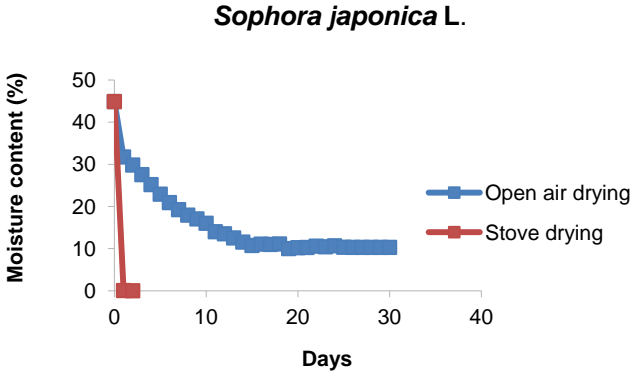Figure 2. Drying curve for Mulberry (*Morus alba* L.)

Sophora japonica L.

Figure 3. Drying curve for Pagoda tree (*Sophora japonica* L.)

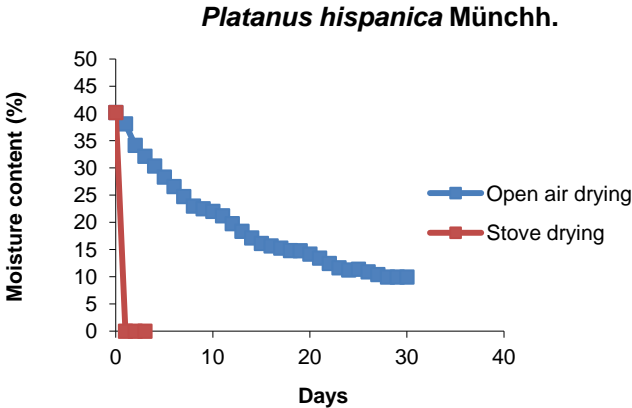**Platanus hispanica Münchh.**

Figure 4. Drying curve for Hybrid Plane (*Platanus hispanica* Münchh.)

Table 5 shows that the species with the highest mean density value is the *Sophora japonica* L..

Table 5. Density of analyzed species

Species	Mean (g cm^{-3})	sd
Mulberry	0.60	0.04
Hybrid plane	0.50	0.14
Pagoda tree	0.86	0.19

sd: standard deviation

According to published data on Mulberry yields a medium-weight hardwood with density 670-850 kg m^{-3} while Hybrid plane 625 kg m^{-3} [34]. Wood density varies depending on growth conditions and the measured part of the tree. The main stem is characterized by higher density than the branches what may explain the lower results obtained in this study.

4. Conclusions

The evaluation of drying process has been studied. The Mulberry, Hybrid plane and Pagoda tree. species had around 45% moisture content in wet basis. The highest density of all species was presented by Pagoda Tree (0.86g cm^{-3}).

C, H, N, S determination allows developing indirect methods to calculate the gross calorific value of the materials at different moisture content with fairly high precision. The applicability of these indirect methods is justified by its advantage over long time taking direct analyses by means of an adiabatic calorimeter.

On the other hand, the C, H, N, S determination also allows evaluating environmental benefits by the reduction of carbon dioxide emissions when these materials are used as a biofuel. From an environmental point of view, the increased recycling of recovered urban wood residual biomass can be seen as a positive evolution because it leads to incensement of the total volume of CO_2 stored as wood-based products, enlarging the life-cycle of the fixed carbon in the new recycled products.

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