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Chapter 12

Modeling the Calorific Value of Biomass from Fruit Trees Using Elemental Analysis Data

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Additional information is available at the end of the chapter

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Abstract

Pruning of fruit trees produces a great quantity of biomass each year that can be used for energy production. For this purpose, it is necessary to carry out an energy characterization of these pruned wastes, where the determination of heating value is significant. This value is usually measured by an adiabatic or isoperibolic calorimeter, which causes high economic costs and wastes time. The present study is focused on the development of indirect models for heating value prediction of biomass from orange trees *Citrus* × *sinensis* Osbeck, almond trees *Prunus dulcis* (Mill) D.A. Webb, and olive trees *Olea europaea* L. from an elemental analysis in order to reduce the time of determination as well as the economic costs. Residual biomass was classified and characterized according to CEN regulations such as received, without drying. Also, moisture content wet basis, bark ratio, density, heating value, and elemental composition (carbon, hydrogen, nitrogen, and sulfur) were measured. The influence of these variables on the heating value was analyzed. Finally, mathematical models were developed to predict this value for this studied species. These models showed coefficients of determination between 0.83 and 0.97, being suitable for industrial use.

Keywords: bioenergy, economical studies, wood residues, higher heating value

1. Introduction

A number of researchers have published mathematical models to predict the higher heating value of different biomass materials from the concentration of the main elements present, such

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as percentage of carbon, percentage of hydrogen, and percentage of nitrogen together with others [1–6]. On the other hand, other models have used proximate analysis [7–10] or structural analysis [9–11]. Indirect calculation of the higher heating value by means of these types of models is justified by the expensive cost of the use of calorimeters [3, 12]. The aim of this chapter is to compare the resources used in direct heat value determination with that used in indirect calculation from elemental analysis by means of prediction models in three common lignocellulosic materials coming from pruning Mediterranean fruit trees. In this work, predictive models of the heating value of biomass from pruning of *Citrus* × *sinensis* Osbeck (orange tree), *P. dulcis* (Mill.) D.A. Webb (almond tree) and *O. europaea* L. (olive tree) have been developed; the calorific value determined directly using the isoperibolic calorimeter was compared with that determined from the elemental composition of materials. The influence of the percentage of leaves, wood moisture content, bark percentage, and percentage content of C, H, N, and S was analyzed.

The heat value is an invariable parameter for a material with constant composition, defined by the empirical form $CH_wO_xN_yS_z$, 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, and z is the number of moles of sulfur per mole of carbon. The moles of each element are obtained by multiplication of the sample mass with its ratio and dividing by the atomic weight of each element. The values w, x, y, and z are obtained from the division of the moles of each element in the sample by the moles of carbon.

The capacity of retaining water in the biomass, caused by its porosity, must be considered in the measurement of the calorific value. The moisture content in the material changes its molecular formula, and therefore the gravimetric percentages of C, H, O, and N. For this reason, standards to determine the calorific value for a particular material, such as UNE 164001:2005 EX [13], require the material to be obtained in the anhydrous state, or with a known moisture content.

The problem in industrial applications is that the biomass materials received for the combustion in boilers show variation in their moisture content, they are sometimes mixed with leaves and even with other materials. Under these conditions, the heat properties are not constant. In order to measure the calorific value instantly, regression models are analyzed in this paper from the percentage contents of C, H, and N of the materials as received. Currently, there are devices capable of measuring these elements in 5 min [5, 6].

When there is variability in the composition, and uncertainty of the type of materials or proportion of the mixture thereof, the mathematical models for the indirect determination of the calorific value are only applicable in the scope where they were developed. This uncertainty is quite common in industry. Thus researchers, such as Francis and Lloyd [14], Ebeling and Jenkins [15], and Kathiravale et al. [16], have provided models for different types of mixtures. However, none of them showed an economical study to justify the use of the model. In this chapter, the development of models specific for the studied material is shown; in addition, an analysis was carried out to compare the cost of direct determination with an indirect mathematical model from elemental analysis.

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In industrial facilities, it is very difficult to find biomass received for combustion without some moisture. Because of processes increase production costs, they are rarely used in the production of energy wood. On the other hand, open air drying rarely decreases the moisture content below 20% [17, 18]. Moreover, it is normal that industrial boilers do not work with a well-defined type of material but with mixtures of different types of biomass. These reasons make the composition of the biomass used in industry variable that directly affects the expected calorific value. So, calorific determination before the introduction of the materials in the boiler is useful to understand the energy performance of the combustion. If this direct determination by the bomb calorimeter is more expensive than the indirect determination from their composition, developing predictive models is fully justified. This is studied in this work.

2. Materials and methods

2.1. Vegetal material

The species studied in this work were *Citrus* × *sinensis* Osbeck (orange tree), *P. dulcis* (Mill) D.A. Webb (almond tree), and *O. europaea* L. (olive tree). These three species are widely grown in the Mediterranean region; they represent 10% of the total cultivated area in Spain [19].

The studied orange variety was "Valencia Late". This is one of the latest varieties most cultivated in Spain. The harvesting begins from March, and it is usually pruned in summer after harvesting. Its main use is fresh consumption due to its high juice content. It also has high chances of industrialization [20].

The almond variety studied was "Blaquerna". It is a self-fertile cultivar that is currently replacing other varieties of lower production. Almond pruning can be annual or biennial according to the development of the tree [21]. During the first 4 years, winter pruning is carried out focused on defining the architecture of the vegetation. From the fourth production year, pruning is performed to remove unproductive branches and to improve the fruit quality [22].

The studied olive tree variety was "Villalonga", which is the variety most widely used in Valencia, with a total cultivation area of 23,550 ha. Its main use is in the manufacture of oil and it is also used for fresh consumption [23].

To define these raw materials as biomass for biofuel, the standard UNE EN 14961-1:2011[24] was used. According to this standard, the analyzed samples in this work were classified by their origin and sources of solid biofuels: 1. Wood biomass → 1.1. Wood biomass from forest or plantation → 1.1.4. Residues from cuttings → 1.1.4.1. Fresh/green, hardwood (including leaves). Therefore, it would be "cutting hardwood waste" (1.1.4.1). Following the mentioned standard, the specifications of the properties of the studied biofuel are defined in **Table 1**.

Origin: Cutting hardwood waste (1.1.4.1)		Wood biomass (1.1) - *Citrus* × *sinensis* Osbeck - *Prunus dulcis* (Mill.) D.A. Webb - *Olea europaea* L.
Marketed form		Wood logs, firewood
Sizes (cm)		
Length (*L*) cm		
Citrus × *sinensis* Osbeck *L* 100 (max 100 cm ± 5 cm)	*Prunus dulcis* (Mill.) D.A. Webb *L* 100+ (max 153 cm)	*Olea europaea* L. *L* 100+ (max 182 cm)
Diameter (*D*) cm		
Citrus × *sinensis* Osbeck *D*10 (2 cm ≤ *D* ≤ 10 cm)	*Prunus dulcis* (Mill.) D.A. Webb *D*10 (2 cm ≤ *D* ≤ 10 cm)	*Olea europaea* L. *D*10 (2 cm ≤ *D* ≤ 10 cm)
Moisture content, M (% as it is received) CEN/TS 15149-1, CEN/TS 15149-2		
Citrus × *sinensis Osbeck* M 45 (≤45%)	*Prunus dulcis* (Mill.) D.A. Webb M 35 (≤35%)	*Olea europaea* L. M 40 (≤40%)
Volume or weight, m^3, kg, loose or piled as received		15–20 kg of each specied.
Volume ratio of split logs		Trunk without cuttings, whole branches
Cut surface[a]		Surface smooth and regular cut
Rust and rot		None of the samples has mold

[a] The use of chainsaw is considered to produce a smooth and regular surface.

Table 1. Specification of the properties of the energy wood pieces (EN 14961-1:2011) [22].

2.2. Sample preparation

The branches of each species, obtained from pruning, were divided into six size classes (0–1, 1–2, 2–3, 3–4, 4–5, and >5 cm). Five samples of each class were taken for analysis; therefore, it resulted in 30 samples per species. For sample preparation, the methods defined by the UNE-EN 14780:2012 [25] were followed. The main purpose of sample preparation was to reduce the size of the branches in test portions with the same initial composition, being representative of the original sample. Initial wet basis moisture content average in wood was about 42.24%. In **Figure 1**, the process of the preparation of the sample is shown. First step was to separate the leaves and wood of the 30 branches of each species arrived at the laboratory (**Figure 2a–c**). These leaves were crushed with hammer mill and stored in airtight jars with identification labels. On the other hand, the wood was milled until their sizes were lower than 3 mm. Special care was taken to avoid loss of fine particles and moisture during milling and other operations. Average wet basis moisture content in tested particles was 29.85%. The devices used for the sample preparation were as follows:

- Manual saw. In order to prevent the moisture loss at the border, cuttings of the central part was used for the analytical determinations. The pieces obtained using this device are shown in **Figure 2(d)**.

- Hammer mill crusher of stainless steel, equipped with a 3 mm screen.

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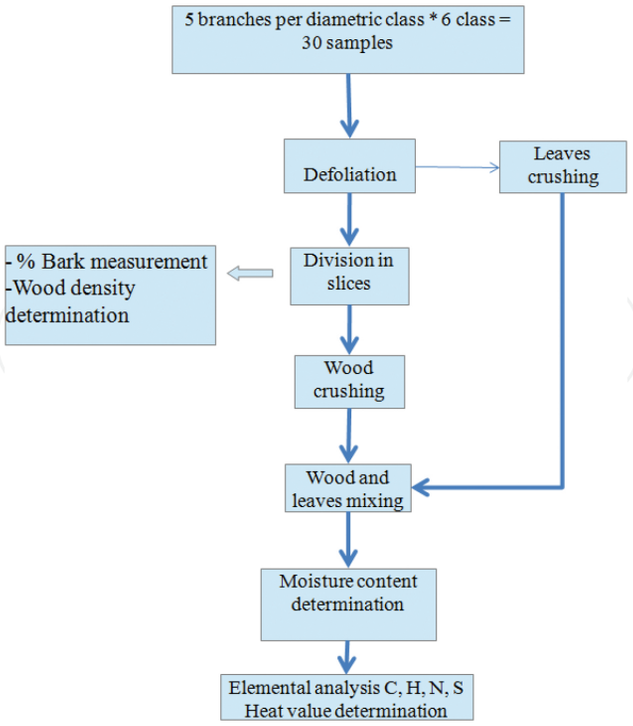


Figure 1. Sample preparation process.



Figure 2. Images of sample preparation process.

Once the samples were crushed, leaves and wood were mixed in defined proportions in each group of size class. The different proportions analyzed were from 10% weight leaves/weight wood in the first sample, 20% weight leaves/weight wood in the first sample in the second, etc. up to 50% of mixture leaves/wood to the fifth sample. So, the effect of leaves on the calorific value was measured. This is very important in this study because pruned material used in boilers has always got a high percentage of leaves, and this influences the moisture content and composition. In many publications, the calorific value calculated referred to that of completely dry and bare material, but this condition is far from the actual applications. In this work, the analysis was focused on samples with variable elemental composition which is usually obtained due to variation in the percentage of leaf and bark content (caused by different size class) and the moisture content (obtained after outdoor drying). For this reason, neither the wood nor the leaf fractions were dried rigorously, but they only experience the natural loss of moisture content during the transport and storage prior to analysis.

2.3. Measurement process

Higher heating value, wet basis moisture content, and elemental composition (C, H, and N) of each sample were measured. For this, standards shown in **Table 2** were used.

Reference of standard	Standard
CEN/TS 14779	Solid biofuels—sampling—methods for preparing sampling plans and sampling certificates
CEN/TS 14780	Solid biofuels—methods for sample preparation
EN 14774-3	Solid biofuels—determination of moisture content—Stufe drying method part 3 moisture content analysis for overall sample analysis
EN 14918	Solid biofuels—determination of calorific value
CEN/TS 15104	Solid biofuels—determination of total carbon, hydrogen, and nitrogen—instrumental methods
CEN/TS 15290	Solid biofuels—determination of major elements
EN 14961-1	Solid biofuels—fuel specifications and classes—part 1: general requirements

Table 2. Methods used to sample and measure parameters.

The calorific value was measured by means of a LECO AC-500 isoperibolic calorimeter. Before analyzing the samples, the calorimeter was calibrated by the combustion of a reactive standard of a known calorific power (benzoic acid, 1 g). Subsequently, each sample was prepared with a mass between 0.1 and 1 g. This was introduced into a combustion vessel where a fuse wire caused ignition. Note that 10 ml of distilled water was added. Then, combustion vessel was sealed, and oxygen with a pressure of 3000 kPa was introduced inside the calorimeter . This container was placed in a bucket of water which was surrounded by an insulating layer to maintain a constant temperature. During analysis, the water temperature was measured by an electronic thermometer with an accuracy of 1/10,000 degree. In order to control energy exchange, the temperatures of the cuvette and the insulating layer were continuously monitored. With this, the device applies a correction to the result.The water temperature was monitored by a microprocessor in every 6 seconds. The difference between the water temper-

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ature before ignition and after ignition was processed through the calorimeter software, for obtaining the calorific value.

The weight percentage of carbon, hydrogen, and nitrogen was measured by means of a LECO TruSpec CHN analyzer. According to EN 14918, samples between 0.1 and 1 g were weighed. Then, they were wrapped in titanium sheets that is completely inorganic. These were placed in a feeding carrousel. The analysis cycle consists of three phases: purging, combustion, and analysis. In the purge phase, the sample is casted into the load compartment, which is sealed and atmospheric gases are removed. In the second phase, the sample is casted into a compartment at 950°C, and oxygen is injected for rapid and complete combustion. The gases pass through an afterburner at 850°C to oxidize and remove particles. The combustion gases are collected in the ballast (gas collection vessel). During the analysis phase, combustion gases are homogenized in the ballast. Subsequently, an aliquot of 3 cm^3 is purged with helium through infrared detectors of CO_2 and H_2O. Another gas loop aliquot is transported through hot copper to remove O_2 and transform the NO_X to N_2. Then, in order to remove CO_2 and H_2O, they are allowed to flow through the tubes containing Anhydrone Lecosorb. The N content is determined on a thermal conductivity cell. The results are shown as percent or kg/mg.

In order to calculate the cost of analysis all inputs were counted. Market prices of nine enterprises were checked. Consumables, labor maintenance, and amortization were considered. Cost of technical labor was estimated in 20 €/h. Residual value of the device was considered to be 10% of investment. Time of analysis was measured.

2.4. Percentage of bark

The percentage of bark in the branches was calculated after their classification according to six diameter classes: 0–1, 1–2, 2–3, 3–4, 5–6, and >6 cm:. The diameter influences the bark ratio [26]. For each diameter, class five samples were taken, so 30 samples in total were analyzed in each species. In each branch, diameter with bark and diameter without bark were measured using of a digital caliper with 0.01 mm accuracy, as shown in **Figure 3**. From these diameters, the percentage of bark was calculated by Eq. (1) [26], where *Bark* (%) is the percentage of bark; ϕ_{cc} is the diameter over bark; ϕ_{sc} is the diameter without bark:

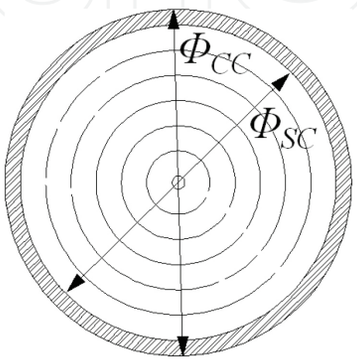


Figure 3. Measurements to calculate the percentage of bark.

$$\text{Bark } (\%) = \frac{\varphi_{cc}^2 - \varphi_{sc}^2}{\varphi_{cc}^2} \cdot 100 \quad (1)$$

2.5. Determination of wood density

Wood density is expressed as the mass of dry wood per unit volume. To calculate the density, first the samples were immersed in a beaker with water, calibrated to 250 mL. The volume was measured by the difference between the water level before and after immersing. Then the dry weight of the samples was determined; for this purpose, samples were placed in a drying oven at a constant temperature of 105 ± 2°C for 24 h. Mean and standard deviation for the densities are obtained by Eq. (2) [26]:

$$\rho_m = \frac{P_s}{V_v} \quad (2)$$

where ρ_m is the wood density (g·cm^{-3}), P_s is the dry weight of the sample (g), and V_v is the volume of the sample (cm^3).

2.6. Prediction model of heat value

To obtain predictive models by regression up to three variables (C, H, and N) have been used. For evaluating the models, the coefficient of determination (R^2), root mean square of the errors (RMS), and mean absolute error (MAE) were obtained. The coefficient of determination, denoted by R^2, is a number that indicates the proportion of the variance in the dependent variable that is predictable from the independent variable. RMS represents the sample standard deviation of the differences between predicted values and observed values. The mean absolute error is an average of the absolute errors $|e_i| = |f_i - y_i|$, where f_i is the prediction and y_i is the true value. The model with the best fit had highest R^2, minimum MAE, and RMS.

For all equations, 30 data were used to develop the models, and another 15 independent data were used for validation. The statistical program used was Statgraphics Centurion XV©14, even for the calculation of the significance of the variables of the mathematical prediction models by the beta coefficients and Student's *t*-test. The data observed in the new experiments and predicted by the model were compared with paired-sample test based on the *t*-Distribution.

3. Results and discussion

Several tests were initially applied to check the normal distribution of the data, such as Shapiro-Wilk test [27, 28], Anderson-Darling test, and the Lilliefors test [29, 30]. In **Table 3**, statistical description of the studied variables is shown for each species. It is observed that the coefficient

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of skewness and kurtosis are between −2 and +2. This indicates that the observed samples are normally distributed.

Variable	Species	Average	Standard deviation	Coef. skewness	Coef. kurtosis	Max.	Min.
HHV (kJ/kg)	Almond	15840.63	234.752	−0.775	−0.435	17458.54	13744.85
	Orange	12653.35	230.03	−0.23	−1.044	14108.26	10781.85
	Olive	15234.97	243.7	−0.281	−0.717	16861.92	13354.64
C %	Almond	40.026	2.261	−0.382	−0.683	44.050	35.300
	Orange	31.192	2.414	−0.274	−1.158	34.800	26.650
	Olive	37.974	2.359	0.192	−0.706	41.800	33.600
H %	Almond	5.661	0.740	1.740	−0.239	7.410	4.875
	Orange	7.179	0.291	−0.284	−0.485	7.590	6.540
	Olive	6.911	0.275	−0.429	−1.061	7.285	6.390
N %	Almond	1.132	0.535	0.147	−1.415	1.935	0.349
	Orange	0.430	0.143	1.383	0.474	0.800	0.222
	Olive	0.549	0.178	−0.792	−0.871	0.812	0.219
S %	Almond	0.128	0.024	0.705	−0.055	0.182	0.088
	Orange	0.061	0.054	1.802	−0.898	0.166	0.006
	Olive	0.031	0.013	1.100	−0.031	0.063	0.015
Moisture content %	Almond	19.009	4.870	0.967	−0.392	30.314	12.291
	Orange	34.679	4.496	−0.457	−1.084	41.094	26.770
	Olive	31.085	7.659	−0.020	−0.637	46.070	18.490
Bark %	Almond	24.741	6.485	0.548	−1.070	36.282	13.830
	Orange	15.038	3.688	1.936	0.176	23.960	10.135
	Olive	16.469	4.297	1.586	1.235	28.260	10.500
Leaves %	Almond	30.231	14.434	0.235	−1.346	50	10
	Orange	30.417	14.590	−0.156	−1.325	50	10
	Olive	31.905	14.703	−0.483	−1.202	50	10

HHV, high heat value; C, carbon; H, hydrogen; N, nitrogen; S, sulfur.

Table 3. Statistical analysis of the studied variables in each species.

The calorific values are clearly influenced by the moisture content and the leaf content in the sample. The obtained calorific value for the three species was between 12 and 16 MJ/kg, which were relatively lower than values cited in the literature. This is because, in this work, we have studied samples of diverse diameters with different percentage of bark, without any drying process, and mixtures of wood and leaves in different proportions, so smaller high heat values (HHVs) were obtained. For example, González et al. [31] gave values of HHV for biomass from orange tree pruning as 16–18 MJ/kg. Yin [32] also analyzed mixtures of biomass and got HHV values 18 MJ/kg, but all these were measured on a dry condition basis.

To compare the calorific value of the three species studied, analysis of variance was performed. In **Figure 4**, LSD intervals are shown at 95% confidence level. It can be seen that the

HHV of almond and olive trees were similar, but that of orange was significantly lower, which may be due to the characteristics of wood, leaves, and bark with moisture.

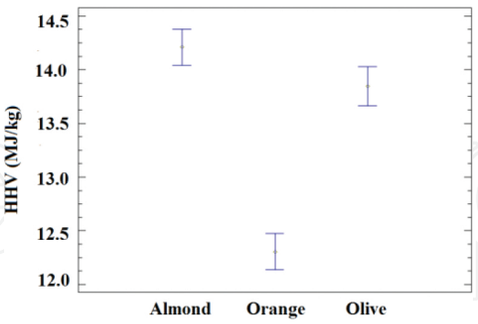


Figure 4. Intervals LSD for the calorific value of the species studied at 95% level of confidence.

Prunus dulcis	**C**	**H**	**N**	**S**	**% leaves**	**% bark**	**% moisture content**	**HHV (kJ/kg)**
C		−0.576*	0.1515	−0.3196	0.2535	−0.0076	−0.9844*	0.9739*
H	−0.576*		0.1712	0.397*	−0.0914	−0.1514	0.6393*	−0.5449*
N	0.1515	0.1712		0.4904*	0.8992*	−0.2699	−0.2055	0.2928
S	−0.3196	0.397*	0.4904*		0.3773	−0.3122	0.2873	−0.2427
% leaves	0.2535	−0.0914	0.8992*	0.3773		−0.09	−0.301	−0.3658
% bark	−0.0076	−0.1514	−0.2699	−0.3122	−0.09		0.0612	−0.0737
% moisture	−0.9844*	0.6393*	−0.2055	0.2873	−0.301	0.0612		−0.9786*
HVV (kJ/kg)	0.9739*	−0.5449*	0.2928	−0.2427	0.3658	−0.0737	−0.9786*	
Citrus × sinensis	C	H	N	S	% leaves	% bark	% moisture content	HHV (kJ/kg)
C		−0.8699*	−0.1595	0.5819*	−0.4233*	−0.5698*	−0.9551*	0.916*
H	−0.8699*		−0.1615	−0.5637*	0.165	0.4785*	0.8811*	−0.8249*
N	−0.1595	−0.1615		0.2159	0.7504*	0.2578	−0.0793	−0.1708
S	0.5819*	−0.5637*	0.2159		−0.173	−0.3339	−0.6484*	0.6292*
% leaves	−0.4233*	0.165	0.7504*	−0.173		0.1614	0.2708	−0.3111
% bark	−0.5698*	0.4785*	0.2578	−0.3339	0.1614		0.4213*	−0.7104*
% moisture	−0.9551*	0.8811*	−0.0793	−0.6484*	0.2708	0.4213*		−0.8464*
HVV (kJ/kg)	0.916*	−0.8249*	−0.1708	0.6292*	−0.3111	−0.7104*	−0.8464*	
Olea europaea	C	H	N	S	% leaves	% bark	% moisture content	HHV (kJ/kg)
C		−0.2761	0.8297*	0.0164	0.7945*	0.3936	−0.9715*	0.9752*
H	−0.2761		0.1347	0.2282	0.0321	−0.3109	0.3303	−0.279
N	0.8297*	0.1347		0.0287	0.9104*	0.1444	−0.7907*	0.8261*
S	0.0164	0.2282	0.0287		0.0894	0.0508	0.0596	−0.0737
% leaves	0.7945*	0.0321	0.9104*	0.0894		0.0024	−0.727*	−0.7955*
% bark	0.3936	−0.3109	0.1444	0.0508	0.0024		−0.4414*	−0.421
% moisture	−0.9715*	0.3303	−0.7907*	0.0596	−0.727*	−0.4414*		−0.9411*
HVV (kJ/kg)	0.9752*	−0.279	0.8261*	−0.0737	0.7955*	0.421	−0.9411*	

C, carbon; H, hydrogen; N, nitrogen; S, sulfur; HHV, calorific value.
* Pairs of variables with *p*-values below 0.05 (95% of significance level).

Table 4. Correlation coefficients of Pearson between the studied variables per species.

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Table 4 shows the correlation between analyzed variables. Significant negative influence of the percentage of moisture in the calorific value (HHV) is observed, with −0.97 Pearson coefficient. On the other hand, it is noted that a higher percentage of C increases the HHV (+0.97). It is observed that the percentage of H is associated with the highest moisture content (+0.63) and obviously decreases the percentage of carbon in the sample and the calorific value (−0.54). It is observed that the percentages of sulfur, leaves, and bark do not have a clear influence on the calorific value of almonds but have a negative influence on the olive and orange trees.

Specie	Model	R^2 adj. (%)	RMS	MAE
Mixing three species	HHV = 717.79 + 380.85·C + 7.61% leaves−14.00% bark	97.352	278.77	195.74
	HHV = 863.61 + 383.93·C − 15.257% bark	96.976	297.90	218.00
	HHV =769.58 + 371.80·C + 8.02% leaves	97.147	289.35	201.07
	HHV = 928.66 + 374.30·C	96.733	309.62	223.64
Prunus dulcis	HHV = 7624.11 + 237.76·C + 228.75·N – 83.37%w	97.131	166.21	125.38
	HHV = −1024.04 + 412.99·C + 272.54·N	96.743	177.08	133.28
	HHV = −1106.84 + 422.77·C	94.630	227.38	173.87
Citrus × sinensis	HHV = 4323.54 + 301.46·C – 72.74% bark	88.127	331.30	250.40
	HHV = 1254.39 + 365.79·C	83.17	394.46	303.26
Olea europaea	HHV = −790.92 + 421.37·C	94.858	231.17	118.44

HHV, high heat value (kJ/kg); MAE, mean absolute error; C, carbon; N, nitrogen; %w, moisture content in wet basis.

Table 5. Prediction models proposed for the indirect calculation of calorific value.

Calorific models from elemental analyses are proposed in **Table 5**. All models show a high R^2 and relatively low standard error (RMS) and mean absolute error (MAE). All models are considered valid for calculating the calorific value, as an alternative to the calorimeter, reducing the time and cost of analysis. The *p*-values for all explanatory variables were less than 0.05. It is observed that the difference between the simplest models, whose explanatory variable is only carbon, and the more complicated is very small. Therefore, we recommend using the simplest, common to all species Eq. (3). In the variance analysis of the regression models, the *p*-value was less than 0.01 for all variables. This means that there is a significant relationship between variables and the volume for a confidence level of 99%:

$$HHV = 28.66 + 374.30 \cdot C \tag{3}$$

Vargas-Moreno et al. [4] conducted a review of models to predict the calorific value for different biomass materials based on elemental analyses. Most of these models reviewed gave determination coefficients between 0.8 and 0.99. For this reason, the correlation coefficients obtained in this work, higher than 0.8, were considered very acceptable (**Table 4**). However, on the other hand, Acda [33] proposed models with higher R^2 for different materials, but their models were obtained for dry materials and without leaves, whereas the models obtained in this study were obtained from mixtures of wood and leaves, and different moisture content, as received. Therefore, they are more applicable in actual situations in industries, where the material cannot be usually dried completely and they have different leaf percentage.

Velázquez-Martí et al. [5] already applied this method to obtain prediction models to predict a high heat value on lignocellulosic waste materials from urban tree pruning. In these works, the determination coefficients obtained are similar to those of the present work, between 0.7 and 0.9. This means that the presence of moisture causes decrease in accuracy of the calorific value calculated by prediction models.

It is observed that a higher carbon content (C) provides bigger calorific values. This coincides with many other studies [2, 34]. It is also shown in **Table 4** with a Pearson correlation coefficient of 0.97 between HHV and C. Because of this, all proposed equations for predicting the gross calorific value (**Table 5**), whether univariate or multivariate, present the variable C.

The sulfur (S) is not high in all species studied (**Table 3**), so it would not be a problem in biomass combustion boilers caused by this element. As it can be seen, in olive and citrus wood the S and N contents are lower than the limits established by the standard EN 14691-part 4 [35], which fix the conditions for chips used as biofuels in %N < 1% and %S < 0.1%. Almond has not got values excessive high. This allows preparing mixtures with materials with low N and S contents.

This discrepancy may be due to the extractive substances of plant biomass (sugars, tannins, sterols, fatty acids, resin acids, oligomeric terpenics, hydrocarbons, etc.) that influence the gross calorific value. Their contents depend on the species, the part of the plant, season, and the growing stage, among other factors [36]. Another explanation could be the botanical family of the studied species [37].

Once calculated using the prediction models, we proceeded to the validation of these data by applying them to new samples, whose observations were compared with the predicted values.

3.1. Comparison cost between direct and indirect measurement of HHV

Measurements with the isoperibolic LECO AC-500 calorimeter showed that the time per analyzed sample was 15 min, which includes sample preparation. As consumables, 6 L of pure oxygen measured at standard conditions (25°C and 1 atm of pressure) and a fuse for ignition of the sample are used. **Table 6** shows the cost of reagents. Device depreciation and calibration cost are respectively shown in **Tables 7** and **8**. The total costs for different number of analyzed samples are shown in **Table 9**.

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Consumable	Price per consumable pack		Consumption per sample		Analysis cost (€/analysis)
Standard for calibration ref. 502-208-T Ac. Benzoic	160.0	€/100 tablets	5 tablets/calibration		1.60
Spike for combustion ref. 502-815 Mineral oil	175.7	€/118 mL	0.25	mL	
Fuse for ignition ref. 502-462	38.2	€/375 fuse wire	1	Ud	0.10
Rent gas tank O_2	94.4	€/year			0.019
Gas O_2					2.25
Maintenance	1200	€/year			0.24
Technical labor	20	€/h	20	min/sample	6.67
			100	min/calibration	

Table 6. Cost of the reagents for isoperibolic LECO AC500 calorimeter (12/03/2013).

Acquisition cost	**50,000**	**€**
Useful life	10	
Residual value 10%	5000	€
Depreciation cost	0.9	€/sample

Table 7. Depreciation cost per sample of LECO AC-500 calorimeter.

	n	**Time (min/analysis)**	**Total time (min)**	**Cost (€)**
Number of analysis	5	20	100	33.33
Standard for calibration ref. 502-208-T Ac. Benzoic	5			8.00
Fuse wire, ref. 502–462	5			0.51
Gas O_2				11.25
Rent gas tanks + maintenance				1.294
			Total	54.39

n, number of analysis.

Table 8. Calibration cost of LECO AC-500 calorimeter.

Sample number	Number of calibration	Technical labor time (h)	Technical labor cost (€)	Gasses (€)	Wire fuse (€)	Total cost (€)	Cost/sample (€/sample)
1	1	2.00	6.67	1.71	0.10	**64.03**	64.03
2	1	2.33	13.33	3.43	0.20	**73.67**	36.83
3	1	2.67	20.00	5.14	0.30	**83.31**	27.77
4	1	3.00	26.67	6.86	0.40	**92.95**	23.24
5	1	3.33	33.33	8.57	0.50	**102.59**	20.52
6	1	3.67	40.00	10.29	0.60	**112.23**	18.70
7	1	4.00	46.67	12.00	0.70	**121.87**	17.41
8	1	4.33	53.33	13.71	0.80	**131.51**	16.44
9	1	4.67	60.00	15.43	0.90	**141.15**	15.68
10	1	5.00	66.67	17.14	1.00	**150.78**	15.08
11	1	5.33	73.33	18.86	1.10	**160.42**	14.58
12	1	5.67	80.00	20.57	1.20	**170.06**	14.17
13	1	6.00	86.67	22.29	1.30	**179.70**	13.82
14	1	6.33	93.33	24.00	1.40	**189.34**	13.52
15	1	6.67	100.00	25.71	1.50	**198.98**	13.27
16	1	7.00	106.67	27.43	1.60	**208.62**	13.04
17	1	7.33	113.33	29.14	1.70	**218.26**	12.84
18	1	7.67	120.00	30.86	1.80	**227.90**	12.66
19	1	8.00	126.67	32.57	1.90	**237.54**	12.50
20	1	8.33	133.33	34.29	2.00	**247.18**	12.36
21	1	8.67	140.00	36.00	2.10	**256.82**	12.23
22	1	9.00	146.67	37.71	2.20	**266.46**	12.11
23	1	9.33	153.33	39.43	2.30	**276.10**	12.00
24	1	9.67	160.00	41.14	2.40	**285.74**	11.91
25	1	10.00	166.67	42.86	2.50	**295.38**	11.82

Table 9. Total costs for different number of samples analyzed by LECO AC-500 calorimeter.

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The time spent for elemental analysis using a TruSpec CHN analyzer is 5 min. The costs of the reagents, calibration, and amortization are respectively shown in **Tables 10–12**.

Consumable	Price per consumable pack		Consumption per sample		Analysis cost (€/analysis)
Standard for calibration EDTA ref. 502-092	44.8	€/50 g	0.2 × 8	g/calibration	0.18
Tin Foil for solid samples (Large Tin Foil ref. 502-397-400)	65.5	€/400 tin foil	1	Unit/sample	0.16
Rent tank O_2	94.4	€/year			0.019
Rent tank N_2	47.2	€/year			0.009
Rent tank He	47.2	€/year			0.009
Rent tank compressed air	47.2	€/year			0.009
Gas O_2	450.0	€/tank	1	Tank/200 analysis	2.25
Gas N_2	342.9	€/tank	1	Tank/200 analysis	1.71
Gas He	342.9	€/tank	1	Tank/200 analysis	1.71
Compressed air	126.2	€/year			0.03
Maintenance	1200	€/year			0.24
Technical labor	20	€/h	5	min/simple	3.33

Table 10. Cost of the reagents for elemental LECO TRUSPEC CHNS analyzer (12/03/2013) (supposing 5000 analysis per year).

		n	Time (min/analysis)	Total time (min)	Cost
Time of calibration calculation	Blanc test	15	5	75	
	Standard analysis	8	5	40	
				115	38.33 €
Standard for calibration	EDTA ref. 502-092	8			1.43 €
Tin foil for solid samples	Large Tin Foil ref. 502-397-400	8			1.31 €
Gases		8			18.00 €
Rent gas tanks + maintenance		8			2.30 €
				Total	61.37 €

n, number of analysis.

Table 11. Calibration cost of LECO Truspec CHNS analyzer.

Acquisition cost	**125,000**	**€**
Useful life	10	
Residual value 10%	12,500	€
Depreciation cost	2.25	€/sample

Table 12. Depreciation cost per simple of LECO Truspec CHNS analyzer.

In **Table 13**, the total costs of the elemental analysis with the analyzer LECO CHNS TruSpec are shown. When **Tables 9** and **13** are compared, it can be seen that the cost for determining the calorific value indirectly from elemental analysis is 23% cheaper than the direct measurement with AC500 LECO isoperibolic calorimeter for 25 samples. Moreover, time of determination is lower. The possibility to calculate the calorific value of a substance from its elemental composition reduces investment to a single computer, instead of two. This is very important in laboratories with limited resources of small and medium enterprises.

No. analysis	**Calibration**	**Calibration cost**	**Analysis time (h)**	**Technician labor**	**Gases**	**Tin foil**	**Total**	**Cost/sample (€/sample)**
1	1	61.37	2.00	1.67	2.25	0.16	**67.99**	67.99
2	1	61.37	2.08	3.33	4.50	0.33	**74.61**	37.30
3	1	61.37	2.17	5.00	6.75	0.49	**81.23**	27.08
4	1	61.37	2.25	6.67	9.00	0.66	**87.85**	21.96
5	1	61.37	2.33	8.33	11.25	0.82	**94.46**	18.89
6	1	61.37	2.42	10.00	13.50	0.98	**101.08**	16.85
7	1	61.37	2.50	11.67	15.75	1.15	**107.70**	15.39
8	1	61.37	2.58	13.33	18.00	1.31	**114.32**	14.29
9	1	61.37	2.67	15.00	20.25	1.47	**120.93**	13.44
10	1	61.37	2.75	16.67	22.50	1.64	**127.55**	12.76
11	1	61.37	2.83	18.33	24.75	1.80	**134.17**	12.20
12	1	61.37	2.92	20.00	27.00	1.97	**140.79**	11.73
13	1	61.37	3.00	21.67	29.25	2.13	**147.40**	11.34
14	1	61.37	3.08	23.33	31.50	2.29	**154.02**	11.00
15	1	61.37	3.17	25.00	33.75	2.46	**160.64**	10.71
16	1	61.37	3.25	26.67	36.00	2.62	**167.26**	10.45
17	1	61.37	3.33	28.33	38.25	2.78	**173.87**	10.23
18	1	61.37	3.42	30.00	40.50	2.95	**180.49**	10.03

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No. analysis	Calibration	Calibration cost	Analysis time (h)	Technician labor	Gases	Tin foil	Total	Cost/sample (€/sample)
19	1	61.37	3.50	31.67	42.75	3.11	**187.11**	9.85
20	1	61.37	3.58	33.33	45.00	3.28	**193.73**	9.69
21	1	61.37	3.67	35.00	47.25	3.44	**200.34**	9.54
22	1	61.37	3.75	36.67	49.50	3.60	**206.96**	9.41
23	1	61.37	3.83	38.33	51.75	3.77	**213.58**	9.29
24	1	61.37	3.92	40.00	54.00	3.93	**220.20**	9.17
25	1	61.37	4.00	41.67	56.25	4.09	**226.81**	9.07
26	1	61.37	4.08	43.33	58.50	4.26	**233.43**	8.98
27	1	61.37	4.17	45.00	60.75	4.42	**240.05**	8.89
28	1	61.37	4.25	46.67	63.00	4.59	**246.67**	8.81
29	1	61.37	4.33	48.33	65.25	4.75	**253.29**	8.73
30	1	61.37	4.42	50.00	67.50	4.91	**259.90**	8.66
31	1	61.37	4.50	51.67	69.75	5.08	**266.52**	8.60
32	1	61.37	4.58	53.33	72.00	5.24	**273.14**	8.54
33	1	61.37	4.67	55.00	74.25	5.40	**279.76**	8.48
34	1	61.37	4.75	56.67	76.50	5.57	**286.37**	8.42
35	1	61.37	4.83	58.33	78.75	5.73	**292.99**	8.37
36	1	61.37	4.92	60.00	81.00	5.90	**299.61**	8.32
37	1	61.37	5.00	61.67	83.25	6.06	**306.23**	8.28
38	1	61.37	5.08	63.33	85.50	6.22	**312.84**	8.23
39	1	61.37	5.17	65.00	87.75	6.39	**319.46**	8.19
40	1	61.37	5.25	66.67	90.00	6.55	**326.08**	8.15
41	1	61.37	5.33	68.33	92.25	6.71	**332.70**	8.11
42	1	61.37	5.42	70.00	94.50	6.88	**339.31**	8.08
43	1	61.37	5.50	71.67	96.75	7.04	**345.93**	8.04
44	1	61.37	5.58	73.33	99.00	7.21	**352.55**	8.01
45	1	61.37	5.67	75.00	101.25	7.37	**359.17**	7.98
46	1	61.37	5.75	76.67	103.50	7.53	**365.78**	7.95
47	1	61.37	5.83	78.33	105.75	7.70	**372.40**	7.92
48	1	61.37	5.92	80.00	108.00	7.86	**379.02**	7.90
49	1	61.37	6.00	81.67	110.25	8.02	**385.64**	7.87
50	1	61.37	6.08	83.33	112.50	8.19	**392.26**	7.85

Table 13. Total cost of analysis by LECO Truspec CHNS analyzer.

4. Conclusions

The advantage of using indirect methods for determining the heat value based on regression models from the analysis of C, H, and N elements has been proven this paper. Time to determine the high heat value indirectly is 40% lower than the time taken using the calorimeter directly. The cost of indirect method is 23% cheaper. Along with the cost savings, reduced analysis time is associated with a lower environmental impact linked to the reagents used.

It is proved that a higher carbon content (C) provides bigger calorific values. However, hydrogen (H) has a negative influence, with a negative Pearson's coefficient. This is due to the fact that hydrogen is associated with the water content. As it is known, the moisture content decreases the high heat value of the biomass, therefore, hydrogen presents inverse proportionality with the heat obtained from combustion. The colinearity between the moisture content and the hydrogen ratio justifies that both were rarely considered in the same model to predict the heat value.

In this paper, models for determining the calorific value in samples of *Citrus* × *sinensis* Osbeck (orange tree), *P. dulcis* (Mill) D.A. Webb (almond tree), and *O. europaea* L. (olive tree) are proposed using an elemental analysis. The accuracy is high, obtaining coefficients of determination higher than 0.95, an average error of 223.64 kJ/kg, and a RMS of 309.62 kJ/kg.

According to the thermochemical characterization of plum wood, the residual biomass from pruning can be used as chips for bioenergy. These species did not have significant differences in C and H composition, between 30 and 40% C, between 5 and 7% H. However, small differences exist with respect to N and S. Olive and citrus wood have S and N contents lower than the limits established by the standard EN 14691-part 4 [32], which fix the conditions for chips used as biofuels in %N < 1% and %S < 0.1%. Almond has not got values excessive high but still it exceeds. This leads to the preparation of mixtures with materials with low N and S contents to decrease their content.

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