

Article

Residual Agroforestry Biomass–Thermochemical Properties

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Received: 26 September 2019; Accepted: 21 November 2019; Published: 25 November 2019



Abstract: Research Highlights: Biomass from Mediterranean agroforestry vegetation may be a potential source of renewable energy. However, due to the high heterogeneity of this type of resource, the study of its characteristics becomes necessary for its efficient use. Objectives: The aim of this study was to evaluate the thermal and chemical properties of 14 different kinds of agroforestry biomass groups: shrubs, forest, and agricultural wastes. Materials and Methods: The higher heating value (HHV), the elemental analysis (C, H, O, N, S), ashes, mineral elements (Na, K, Ca, Mg, and P), trace elements (Mn, Fe, Zn, Ni, Cu, Cr, and Cd) and halogen elements (F and Cl) were quantified and compared with CEN/TS 147775 and CENS/TS 14961 standards, looking forward to future use for energy purposes, namely through combustion processes, as an alternative to fossil fuels. Results: The shrubs present the highest values of higher heating value (20.5 MJ kg⁻¹), followed by the forest wastes (19.2 MJ kg⁻¹) and the lowest in the agricultural wastes (18.5 MJ kg⁻¹). Concerning the elemental analysis, the difference between groups C, H, and O are very small and not statistically significant, while for N, S and ashes values are higher in agricultural than shrubs and forestry wastes. The same tendency was found for the mineral nutrients. For the trace elements, the lowest content of Mn, Fe, and Zn is found in agricultural, Ni, and Cr content in the shrubs and Cu in the forest wastes. The halogen elements are present in greater amount in shrubs than agricultural and forest wastes. Conclusions: Although the high values of the halogen elements which may raise sintering problems and corrosive effect on metal parts in furnace and boiler, in general the shrubs biomass are those with better characteristics for energy uses, namely through combustion processes.

Keywords: energy; higher heating value; chemical analysis; wastes

1. Introduction

As Portugal is essentially agroforestry, 90% of the territory being occupied by forests, shrubs and agriculture [1], its potential for biomass production is highly substantial. However, due to this country dependence on fossil fuels, it is essential to leverage the economic potential of these resources, thereby reducing the severity of forest fires and increasing the country's economic performance.

The production of biomass for energy is considered to be an important step in developing sustainable communities and managing greenhouse gas emissions effectively.

In recent years, interest in thermochemical biomass conversion processes in fuels, chemicals, and other materials has increased due to the global problems associated with the intensive use of fossil fuels [2].

According to Evangelou et al. [3], biomass is currently the only renewable source of fixed carbon, and thus is the only source in the long term for the production of transport fuels.

There are numerous reasons for using this resource for energy production: firstly, biomass is the only renewable organic resource and is also one of the most abundant resources. Secondly, biomass fixes carbon dioxide in the atmosphere by photosynthesis [4]. However, handicaps of woody biomass, such as lower energy density and heating values, and high moisture content leading to degradation and self-heating, make the handling and transportation costlier and more complex [5].

Two fundamental aspects related to biomass use as fuel are: (1) to extend and improve the basic knowledge on composition and properties; and (2) to apply this knowledge for the most advanced and environmentally safe use [6].

Forest biomass originating from Mediterranean forest vegetation could be a potential source of renewable energy, but due to its diversity there is a need for better understanding and detailed examination of its main fuel characteristics. According to Cuping et al. [7], the research on chemical elemental characteristics of biomass fuels is beneficial for those to find suitable energy conversion technologies and for various energy conversion processes to use favorable biomass feedstock.

Agroforestry biomass has highly variable composition and properties, especially with respect to moisture, structural components and inorganic constituents. The major and minor elements in biomass, in decreasing order of abundance, are commonly C, O, H, N, Ca, K, Si, Mg, Al, S, Fe, P, Cl and Na, plus Mn, Ti and other trace elements [8].

The non-combustible content of biomass is referred to as ash, which are generated during biomass burning. High ash content leads to fouling problems, especially if the ash is high in metal halogens. Unfortunately, biomass fuels, especially agricultural crops/residues tend to have a high ash with high potassium content [9].

The ash content of biomass affects both the handling and processing costs of the overall biomass energy conversion [7], as well as it significantly reduces the energy efficiency obtained from a specific source of biomass. [10].

There are already many published works that agree that HHV is a key parameter for the evaluation of the energy content of the different types of biomass [11–14]. Also, there are a number of formulae proposed in the literature to estimate the higher heating value (HHV) of biomass fuels from the basic analysis data, namely, elementary chemical analyzes [12,13,15–26]. Moreover, according to the Directive 2000/76/EC [27] the thermal use of solid biofuels is influenced by the kind of solid biofuel used, its physical characteristics and its chemical composition. Thus, the calorific value of wood can be related to chemical composition [28]. In addition to its influence on the calorific value, the knowledge of the chemical elements present in biomass for energy purposes is extremely important insofar as part of them can be a serious consequence of the emission of toxic gases into the atmosphere. Thus, for efficient use of biomass conversion technologies, it is crucial to know the features of the different agroforestry biomass types, namely their thermochemical properties. In this way, the main objective of this study is the thermal and chemical characterization of residual of agroforestry biomass produced in Northern Portugal.

2. Materials and Methods

2.1. Plant Material

Fourteen types of agroforestry wastes distributed by three groups (agricultural, forest and shrubs) were collected in two distinct areas of northern Portugal: Ave river basin and Sabor river basin, whose biomass productivity per unit area/year are shown in Table 1. In each of these basins 6 samples were taken for each type of biomass, making a total of 84 samples by basin. However, as the varieties

of *Vitis vinifera* differ in two basins, for this type of biomass it was decided to sample 12 specimen per basin, to maintain an equal number of samples per type of biomass (12).

Table 1. Productivity of each agroforestry biomass group present in the two sampled areas (ton ha⁻¹ year⁻¹).

	Ave River Basin (139,000 ha)	Sabor River Basin (241,000 ha)
Agricultural wastes	0.24	1.07
Forest wastes	2.88	2.26
Shrubs	1.3	1.91

Source: Enes et al., 2017. Evaluation of residual forest biomass in the Ave and Sabor river basins. 8th National Forest Congress, Viana do Castelo, Portugal. Abstracts book. p. 148.

For the agricultural and forest wastes group were used sampling plots with 500 m² were used and for the shrubs 25 m².

In each group of biomass, the following species were analyzed: *Olea europaea* L.; *Prunus dulcis* Miller and *Vitis vinifera* L. (agricultural wastes); *Eucalyptus globulus* Labill and *Pinus pinaster* Aiton (forest wastes—wood and residues) and *Pterospartum tridentatum* L.; *Erica* sp.; *Erica arborea* L.; *Cytisus* sp.; *Ulex europaeus* L. and *Hakea sericea* Scharader (shrubs). For each type of biomass, 12 samples were collected, of which three replicates were performed for each sample for further thermochemical analysis.

In the forest species two types of samples were collected: wood (chips and sawdust from wood lumber industries) and residues (bark (20.3% ± 6.7%), branches (48.1% ± 16.5%) and leaves (31.6% ± 18.7%)). For the agricultural wastes and shrubs, as there is no legal restriction to the full use for these types of biomass, the sample used was obtained from the milling of the pruning material (agricultural wastes) or the entire plant (shrubs). From each sample were taken three subsamples were taken that were used in all analyzes.

Samples of each species were stored in paper bags and brought to the Forest Products Laboratory at University of Trás-os-Montes e Alto Douro (UTAD). The samples were then oven-dried at 40 °C during about one week until they reached a constant weight. Before the analyses were carried out, the material was preliminarily milled in a Retsch SM 100 cutting mill (Retsch, Haan, Germany) with a 6-mm sieve and further milled with a Retsch Ultra Centrifugal Mill ZM 100 with a 1-mm screen sieve.

2.2. Higher Heating Value (HHV)

The HHV was determined according to the methodology described in Standard DD CEN/TS14918: [29], using Parr 6300 Automatic Isoperibol Calorimeter. Samples ranging from 0.7 to 0.9 g were used to avoid combustion failures. Three replicates of each wood sample were made. The mean value of the three replicates was taken as the final value for further analysis.

2.3. Elemental Analysis (C/H/O/N/S) and Ashes

The analytic method used to determine the carbon, hydrogen, and nitrogen contents was based on complete and instant oxidation of the sample by “flash” combustion that converts all organic and nonorganic compounds into combustion products, with the use of a CHON Elemental Analyzer for Combustion Chromatography brand Carlo Erba model EA-1108. Gases from combustion were transported by carrier gas through a reduction oven of chromatographic column, where they were separated from other elements and then passed through the thermal conductivity detector that indicated the concentration of the components in the sample. Three replicates were performed for each sample and the mean value was taken as a final value for further analysis.

The S content was obtained by technical with inductively coupled plasma optical emission spectrometry (ICP-OES).

The ash content was determined by 1 g of oven-dried sample in a platinum crucible in a muffle furnace model (Lenton Thermal Designs EF 11/8b) at 550 ± 25 °C. All the analyses were done in

triplicate and the results were expressed on a dry weight basis according to CEN/TS 147775 [29], according to Telmo et al. [30].

The oxygen content was obtained by subtracting from 100% the sum of (C, H, N, S and ash) contents in percentage.

2.4. Other Elements

In all samples, the presence of Mineral nutrients (Na, K, Ca, Mg and P); Trace Elements (Mn, Fe, Zn, Ni, Cu, Cr and Cd) and Halogen elements (F and Cl) was also evaluated. To determine this elements content, a method previously described by Gouvinhas et al. [31] was used. For each species (0.5 g) of sample was weighed directly into the test tube. The digestion was performed by adding HNO₃ (1.0 mL) and H₂O₂ (5.0 mL) to each sample. The mixture was left at room temperature with a marble preventing evaporation for 24 h, and afterwards, the marble was removed, and the samples were left overnight at room temperature. After this period the sample was heated using a block heater at 50 °C during 1 h followed by 100 °C during 1 h (temperature at which the release of Nitric Oxide brown fumes starts), 120 °C during 1 h and finally left overnight at 155 °C (usual time needed to obtain a clear digestion mixture), or until the solution was clear, with a glass marble on the top of the culture tube (to avoid drying before digestion and sample charring). After this period the glass marbles were removed, and the contents were dried at 155 °C. After cooling to room temperature, 10.0 mL of HNO₃ matrix solution (1.5 mL of acid to 1000 mL of water) was added to the digested samples and stirred. Some of the solutions were diluted in order to allow the determination of the respective elements.

Na and K were determined by flame atomic emission spectrometry (FAES) and Ca, Mg, Fe and P were analyzed by flame atomic absorption spectrometry (FAAS), both of hem using a Thermo Scientific ICE 3000 equipped with HGA graphite furnace. For flame measurements, a 7-cm-long slot-burner head, a lamp and an air-acetylene flame were used (1.2 L min⁻¹).

The trace elements (Mn, Zn, Ni, Cu, Cr, and Cd) were analyzed by graphite furnace (GF-AAS) using a Unicam GF 90 furnace.

According to Gouvinhas et al. [31], in these measurements, argon was used as inert gas (250 mL min⁻¹). Each run of samples was preceded by calibration using aqueous mixed standards prepared in 1.0 M HNO₃. The mineral standard solutions of the calibration elements were produced by diluting a stock solution prepared at the concentration of 1000 mg L⁻¹. All calibration curves were based on five standard concentrations, including a blank.

The spectrophotometric method using a UniSPEC 2-Spectrophotometer UV/Vis apparatus was used for the quantification of Cl.

For the F determination, the Selective Electrode Method was used by Direct Potentiometry using a Fluorimeter Model JENWAY 3510 pH Meter.

All analyses are performed on three repeats and averages presented.

2.5. Statistic Analysis

Duncan New Multiple Range Test used in conjunction with an ANOVA (one way), done with JMP (SAS Institute, Cary, NC, USA) software to find which group of means is significantly different from one another.

To perform the relationship between all variables analyzed, the Pearson's correlation matrix was obtained using the following significance level (42 obs.): *** highly significant ($r > 0.490$), ** very significant ($r > 0.393$) and * significant ($r > 0.304$).

The multiple regression stepwise backward developed using Higher Heating Value (HHV) as output dependent variable and elemental analysis (C, H, O, N and S), ashes and chemical analysis (Na, K, Ca, Mg, P, Mn, Fe, Zn, Ni, Cr, Cd, Cu, F, and Cl) as input independent variables.

Backward elimination, involves starting with all candidate variables and testing them one by one for statistical significance, deleting the ones that are not significant. That means deleting the minor significance "t" values of the variables statistically not significant.

Throughout the text the following statistical annotation was used:

n.s.: not significant ($p > 0.05$)

*: significant ($p < 0.05$)

**: very significant ($p < 0.01$)

***: highly significant ($p < 0.001$)

3. Results and Discussion

3.1. Higher Heating Value, Elemental Analysis and Ashes

3.1.1. Higher Heating Value

Table 2 shows the overall results of HHV tests and elemental analysis of the biomass of the different species. The additional values of minimum, maximum and median of each biomass properties are presented in Appendices A–D.

Table 2. Statistics of HHV, elemental analysis and ashes by type of biomass ($n = 36$ samples).

Type of Biomass	Statistics	HHV (MJ kg ⁻¹)	C (%)	H (%)	O (%)	N (%)	S (%)	Ashes (%)
Agricultural wastes								
<i>Olea europaea</i>	Mean	21.1 ^c	49.6 ^c	7.2 ^c	37.9 ^a	1.2 ^b	0.12 ^c	4.0 ^a
	SD	0.05	0.2	0.06	0.2	0.04	0.004	0.08
<i>Prunus dulcis</i>	Mean	18.2 ^b	44.2 ^a	6.1 ^a	41.6 ^b	1.2 ^b	0.07 ^a	6.8 ^b
	SD	0.07	0.1	0.02	0.2	0.05	0.001	0.08
<i>Vitis vinifera</i> (Sabor)	Mean	17.3 ^a	42.6 ^a	6.1 ^a	43.0 ^c	1.0 ^a	0.07 ^a	7.2 ^c
	SD	0.2	0.3	0.03	0.3	0.08	0.001	0.09
<i>Vitis vinifera</i> (Ave)	Mean	17.4 ^a	44.1 ^b	6.3 ^b	41.9 ^b	0.9 ^a	0.09 ^b	6.8 ^b
	SD	0.02	0.03	0.06	0.1	0.04	0.001	0.05
Forest wastes								
<i>Eucalyptus globulus</i> (residues)	Mean	18.7 ^b	48.7 ^c	6.6 ^c	37.5 ^a	1.0 ^c	0.08 ^c	6.2 ^d
	SD	0.04	0.2	0.07	0.3	0.04	0.003	0.05
<i>Pinus pinaster</i> (residues)	MED	19.5 ^b	48.7 ^c	6.9 ^d	39.9 ^b	1.2 ^d	0.09 ^d	3.2 ^c
	SD	0.04	0.1	0.01	0.1	0.04	0.002	0.00
<i>Eucalyptus globulus</i> (wood)	Mean	17.6 ^a	46.1 ^a	5.9 ^a	47.8 ^d	0.2 ^b	0.02 ^b	0.5 ^b
	SD	0.3	0.3	0.1	0.3	0.02	0.0001	0.03
<i>Pinus pinaster</i> (wood)	Mean	20.2 ^c	48.1 ^b	6.2 ^b	45.4 ^c	0.1 ^a	0.00 ^a	0.2 ^a
	SD	0.3	0.3	0.1	0.2	0.01	0.000	0.03
Shrubs								
<i>Pterospartum tridentatum</i>	Mean	20.9 ^c	50.4 ^f	6.5 ^b	41.0 ^a	1.1 ^d	0.06 ^b	1.0 ^a
	SD	0.3	0.2	0.1	0.3	0.05	0.001	0.01
<i>Erica</i> sp.	Mean	20.9 ^c	48.8 ^d	6.1 ^a	43.3 ^b	0.5 ^b	0.07 ^c	1.3 ^b
	SD	0.2	0.1	0.2	0.3	0.04	0.002	0.05
<i>Erica arborea</i>	Mean	21.4 ^c	49.7 ^e	6.5 ^b	41.3 ^a	0.7 ^c	0.08 ^d	1.8 ^e
	SD	0.2	0.2	0.04	0.2	0.02	0.007	0.04
<i>Cytisus</i> sp.	Mean	20.2 ^b	46.5 ^a	6.2 ^{a,b}	45.1 ^d	0.9 ^d	0.04 ^a	1.3 ^b
	SD	0.3	0.3	0.03	0.4	0.1	0.001	0.01
<i>Ulex europaeus</i>	Mean	19.4 ^a	46.9 ^b	6.5 ^b	43.8 ^{b,c}	1.1 ^d	0.06 ^{b,c}	1.6 ^d
	SD	0.3	0.1	0.1	0.3	0.07	0.003	0.01
<i>Hakea sericea</i>	Mean	20.3 ^b	47.6 ^c	6.3 ^b	44.2 ^c	0.4 ^a	0.05 ^a	1.5 ^c
	SD	0.3	0.3	0.1	0.4	0.07	0.001	0.01

Note: HHV—Higher Heating Value; SD—Standard Deviation; mean values with the same letter are not significantly different for $p < 0.05$ by Duncan New Multiple Range test.

In general, it is found that shrubs have the highest values of HHV, namely *Erica* sp., *Erica arborea* and *Pterospartum tridentatum* (20.9–21.4 MJ kg⁻¹) and the lowest value in the *Ulex europaeus* (19.41 MJ kg⁻¹).

For the latter species, the values presented are very similar to the HHV values presented by Rodríguez Añón et al. [32]. However, in general, the values obtained are relatively lower than those reported by Viana et al. [5] ranging from 21 to 24 MJ·kg⁻¹.

Concerning to forest wastes (Table 2), the highest values of HHV correspond to the woody part of *Pinus pinaster* (20.2 MJ kg⁻¹), followed by *Pinus pinaster* and *Eucalyptus globulus* residues (19.5 and 18.7 MJ kg⁻¹, respectively). Regarding the forest species, it is verified that woody biomass of *Pinus pinaster* have higher values of calorific value when compared to *Eucalyptus globulus*. This trend is in accordance with Telmo et al. [30], in which one of the main conclusions is that, in general, the softwood species present higher values of calorific value, compared with hardwood species.

Within this group, the wood of *Eucalyptus g.* is the type of biomass that present the lower HHV (17.6 MJ kg⁻¹). This result agrees with the study carried out by Viana et al. [5], where the higher heating value of each component (wood stem, bark stem, top, branches, and leaves) of the two species was evaluated. Concerning the *Pinus pinaster*, two studies carried out to in the north of Spain show that the HHV of woody component is slightly lower than branches and leaves [33,34].

Regarding to agricultural wastes, the highest values were observed in *Olea europaeus* biomass (21.1 MJ kg⁻¹), which is similar to the value obtained for *Erica arborea* and one of the highest values in comparison to the other species analyzed. These values are higher than two other similar studies carried out in the Mediterranean region by [35] (17.34 MJ kg⁻¹) and [36] (15.23 MJ kg⁻¹).

The lowest values observed (Table 2) correspond to the biomass of *Vitis vinifera* (17.3 and 17.4 MJ kg⁻¹). These HHV values are among the lowest among all types of biomass analyzed and are very similar to the values observed for woody wastes of *Eucalyptus g.* (17.6 MJ kg⁻¹). However, in other studies performed for the same species, HHV values are higher: Nasser and Salam [37] presented values between 18.75 and 19.9 MJ·kg⁻¹; Puglia et al. [38] between 18.54 and 19.0 MJ·kg⁻¹.

In a general analysis among the different groups (Table 3), there are differences between the HHV. The shrubs are those with the highest values (20.5 MJ kg⁻¹), followed by forest wastes (19.2 MJ kg⁻¹), and finally the agricultural wastes (18.5 MJ kg⁻¹), although the differences between forest and agricultural wastes are not statistically significant.

Table 3. Statistics of HHV, elemental analysis and ashes by biomass group.

Groups		<i>n</i>	HHV (MJ kg ⁻¹)	C (%)	H (%)	O (%)	N (%)	S (%)	Ashes (%)
Agricultural wastes	Mean	128	18.5 ^a	45.1 ^a	6.4 ^a	41.1 ^a	1.1 ^b	0.08 ^b	6.2 ^b
	SD		1.6	2.8	0.5	2.0	0.1	0.02	1.3
Forest wastes	Mean	128	19.2 ^a	47.9 ^a	6.4 ^a	42.6 ^a	0.7 ^a	0.05 ^a	2.5 ^a
	SD		1.0	1.1	0.4	4.3	0.5	0.04	2.5
Shrubs	Mean	192	20.5 ^b	45.8 ^a	6.3 ^a	45.6 ^a	0.8 ^a	0.06 ^a	1.4 ^a
	SD		0.7	10.2	0.2	10.2	0.3	0.01	0.3

Note: HHV—Higher Heating Value; SD—Standard Deviation; mean values with the same letter are not significantly different for $p < 0.05$ by Duncan New Multiple Range test.

3.1.2. Elemental Analysis (CHONS) and Ashes

The values of C, H, and O are very similar and not statistically different among the different types of biomass analyzed. Between the different groups of wastes, the values of C (Table 3) ranging between 45.1% and 47.9%, the H between 6.3% and 6.4%, the O between 41.1% and 45.6%, being these values within the range of CENS/TS 14961 [39].

Although forest residues were the group with the highest levels of C (47.9%), there were studies that presented higher content (Cuping et al. [7]: 49.4%; Lapuerta et al. [40]: 50.5% and Yin [41]: 53.2%).

In relation to the N, S and ashes, agricultural wastes showed statistically higher values (N = 1.1%, S = 0.08% and ashes = 6.2%) than forest wastes and shrubs (N between 0.7% and 0.8%; S between 0.05% and 0.06% and ashes between 1.4% and 2.5%).

In a global analysis of the biomass of all species (Table 2), it is verified that *Pterospartum tridentatum* (shrubs) is the species with the highest values of C (50.4%) and, within this group, *Cytisus* sp and *Ulex europaeus* are the ones with the lowest Carbon content (46.5% and 46.9%, respectively). However, in a study carried out by Rodríguez Añón et al. [32], the C contents of this last species are much higher (49.7%).

Among all species analyzed, *Vitis vinifera* was the waste with the lowest C content (42.6 and 44.1%), being these lower values lower to the levels presented by Jenking and Ebeling [20] (46.6%) for the same species.

As for H, the differences between species are very small, only ranging between 5.9% and 7.2% (Table 2). It should be noted that this lower value of H was observed in the species that showed the lowest value of HHV (*Eucalyptus* g. woody), while the highest value (7.2%) was observed in *Olea europaeus*, which presented highest values of HHV. Thus, the positive correlation between the contents of H and the HHV presented in the Section 3.3 ($r = 0.43$), which is according to Ref. [42–44]. However, there are authors who argue that the component that most influences HHV values is C, e.g., [19,24,25,30]. Tillman [19] observed that the Heating Value has a very strong influence of its carbon content and accordingly he derived the correlation for calorific value of biomass and its elementary components.

Also, Jenkins [18], noted that HHV is very well correlated with the amounts of C, with each 1% increase in carbon elevating the heating value by approximately 0.39 MJ kg^{-1}

On the other hand, there are also studies in which the HHV of biomass increases with the increase in carbon content but decreases at high hydrogen and oxygen contents [25].

Although N, S and Ashes are generally very low in biomass, these values may compromise the use of biomass for energy purposes, and they are key relevance regarding ash melting, deposit and slag formation as well as corrosion and environmental detriments, such as the formation and release to the atmosphere of NO_x and SO_x [9,20,45–49].

Therefore, it should be noted that agricultural waste presents N, S and ashes values much higher than most other types of biomass (Table 3). For example, while agricultural wastes have N values ranging from 0.9% to 1.2%, the woody component of *Pinus p.* and *Eucalyptus* g. is only 0.1% and 0.2%, respectively (Table 2). Concerning the shrub species, it can be seen that, as it might be expected, having the leguminous species (*Fabaceae* latin family) such as the *Pterospartum tridentatum*, *Cytisus* sp., and *Ulex europaeus*, the N-fixing capacity through symbiosis with *Rhizobium* sp. bacteria, these species present high N values (between 0.9% and 1.1%), identical to agricultural wastes.

The values of S, which in the agricultural residues range from 0.07% to 0.12%, in the woody components of *Eucalyptus* g. and *Pinus pinaster* are only 0.02% and 0.00%. As far as ash is concerned, the pattern is exactly the same, i.e., while agricultural waste presents values between 4.0% and 7.2%, woody components of the two forest species present values much lower (0.5% and 0.2%), and residues present values ranging (3.2% and 6.2%), much higher than those presented by Fanco et al. [50] (0.5% and 0.7 %). This trend is in line with the study by Cupping et al. [7] which verified that forestry species have much lower ash content comparing to agricultural species. Royo et al. [51] also refers to this difference in values between agricultural and forest residues, emphasizing that one of the great differences between these two types of biomass for energy use is related to the characteristics of its ashes (quantity and composition) which increase certain problematic phenomena during combustion, among them bottom ash sintering and fly ash deposition.

Thus, in general we can conclude that the woody biomass of the softwood species contains higher levels of C and lower levels of ashes. Also, among the forest wastes, the woody component has a different behavior to the residues, both in *Pinus pinaster* and in *Eucalyptus* g. In the N content the values are significantly lower in the woody component of *Eucalyptus* g. and *Pinus pinaster* (0.2% and 0.1%, respectively) compared to the residues (1.0% and 1.2%). In a study by Ref. [9], the N content in hardwoods was very similar to the value obtained for *Eucalyptus* g. wood (0.2%).

Identical behavior was verified for the S, which woody component presents values of 0.02% and 0%, while residues from 0.08% to 0.09%, as well as for the ash content in which the wood component showed 0.05% and 0.02% and the residues 6.2% and 3.2%. Thus, we can infer that the woody component of *Eucalyptus g.* and *Pinus pinaster* are of the biomass types with better characteristics, namely, high values of HHV and low levels of N, S and ashes, to take advantage of energy, while the residual component presents characteristics much lower and identical to the agricultural residues, since they present low values of HHV and high values of N, S and ashes.

3.2. Elements—Chemical Analysis

3.2.1. Mineral Nutrients—Na, K, Ca, Mg, and P

Table 4 shows the mean and standard deviation of each chemical elements and the test comparison means by biomass species, and Table 5 shows the mean and standard deviation of each chemical elements and the test comparison means by group.

In general, the quantities of these elements are statistically lower in the shrubs and forest wastes than agricultural (Table 5). The only exception found was in the amounts of Na, whose concentration in agricultural wastes is lower than the other groups. In the shrubs group, the lowest values of these elements are usually found in the *Pterospartum tridentatum*, *Erica sp.* and *Hakea sericea* (Table 4). In forest wastes group, the *Pinus pinaster* wood is noteworthy which always has the lowest values of mineral nutrients, followed by *Eucalyptus globulus* wood. These values agree with the values presented by Telmo et al. [30] for *Pinus pinaster* wood, as well as by Cuiping et al. [7] and Jazac et al. [10] for other *Pinus sp.* wood, and within the ranges defined in CEN/TS 14961 [39] Standard.

On the other hand, the mineral elements values present in the residues (bark, branches, and leaves) of the forest species are much higher than the woody component, whose values are relatively similar to those observed in the biomass of agricultural wastes and usually exceed the limits defined in the previously mentioned Standard.

Regarding agricultural wastes, it was verified that, except for the Na content, they usually presented the highest values of mineral elements. So, we can conclude that agricultural wastes and *P. pinaster* and *E. globulus* residues are not the most suitable types of biomass for energy purposes, namely through combustion processes, given the high risk of formation of sintering and corrosion problems in the boilers.

3.2.2. Trace Elements—Mn, Fe Zn, Ni, Cu, Cr, and Cd

In general, the lowest content of Mn, Fe, and Zn is present in the agricultural wastes, the Ni and Cr content in the shrubs and the Cu in the forestry wastes (Table 5).

Concerning the Mn it is notable that the amounts of this element present in the agricultural and forest wastes range from 13.2 to 120.4 mg/kg, while in the shrubs these values are much higher, 632.0 mg kg⁻¹ in *Erica arborea* and 3908 mg kg⁻¹ in *Ulex europaeus* biomass (Table 4), exceeding the limit value (147 mg kg⁻¹) referred by the CEN/TS 14961 [39] standard. The same tendency was observed for the Fe, in mg kg⁻¹ which in the agricultural and forest wastes range from 0 to 52.7 mg kg⁻¹, being within the range (10–100 mg kg⁻¹) established by the previous standard, while the shrubs present values between 145.4 and 843.5 mg kg⁻¹.

It is also verified that the values of Mn for *Eucalyptus globulus* and *Pinus pinaster* woody are similar to the values reported by Telmo et al. [30] and still lower than the values presented by Viana et al. [5] and Jazac et al. [10].

For the forest residues, in general the values of trace elements are within the range defined by Vassilev et al., [8] and lower than obtained by Jazac et al. [10].

About Zn contents, although forest wastes and shrubs presented higher values than agricultural wastes, all the values fall within the range of the CEN/TS 14961 [39] standard (5–100 mg kg⁻¹).

As regards to Ni, Cu and Cr, the quantities present in the shrubs and woody component of the forest species are very low (Table 4), not reaching the limits imposed by the same standard ($0.1 < \text{Ni} < 10$; $0.2 < \text{Cr} < 10.0$ and $0.5 < \text{Cu} < 10.0$). Agricultural wastes and forest residues usually exceed these limits. Comparing these two types of wastes, it can be seen from Table 5 that the agricultural wastes present larger amounts of these 3 elements, compared to forest wastes, which is in accordance to Cuiping et al. [7]. Also, it should be highlighted that most of these trace elements, being heavy metals, have great influence on gas emission and ash composition characteristics.

Finally, for Cd, whose range defined by CEN/TS 14961 [39] between 0.05 to 0.5 mg kg⁻¹, presents null or practically null values in all types of biomass, except for *Pinus pinaster* residues whose value amounts to 202.8 mg kg⁻¹. However, these results agree with the results obtained by Osteras et al. [52], with values of this element between 200–300 mg/kg in the biomass of *Pinus sylvestris*. In another study [53], where the Cd amount in *Pinus halepensis* residues is also evaluated, the results showed that the amounts could reach 186 mg/kg, being very similar to the present study.

3.2.3. Halogen Elements—F and Cl

Analyzing the halogen elements, the highest values are those of the group of shrubs compared to agricultural and forest wastes (Table 5). The higher values were found in *Pterospartum tridentatum* (2843 mg kg⁻¹), *Cytisus* sp. (352.7 mg kg⁻¹) as well as *Ulex europaeus* (277.3 mg kg⁻¹). These values should be taken into account since the main effect of Cl is the corrosive effect of chloride salts and HCl on metal parts in furnace and boiler [30,46,50,52–58].

Moreover, chlorine is a major factor in ash formation. Chlorine facilitates the mobility of many inorganic compounds, in particular, potassium. Chlorine concentration often dictates the amount of alkali vaporized during combustion as strongly as does the alkali concentration [59].

Concerning F, the quantities are relatively high in the shrubs, in particular *Cytisus* sp. (19.3 mg kg⁻¹) and *Erica* sp. (6.0 mg kg⁻¹). As for this element, it is also worth noting that the values found in the woody component of *Eucalyptus globulus* and *Pinus pinaster* (0.9 mg kg⁻¹) are much lower than the values found in the residues of these two species, 6.7 and 1.4 mg kg⁻¹, respectively.

3.3. Multiple Regression Analysis

Table 6 contain the correlation coefficient between all variables. HHV was found to be significantly positively statistic related to H (0.43**); Mn (0.43**); Fe (0.47**) and negatively to ashes (−0.37*); K (−0.59***); Ca (−0.38*); P (−0.33*); Mg (−0.37*); Ni (−0.42**) and Cu (−0.38*).

Regarding H, although it presents a positive correlation (0.43) with HHV, which is advantageous from the point of view of its use for energy purposes, it presents high positive correlation with N (0.57), S (0.67) and Cr (0.62) also. So, the species with a high H content should be used with special care to minimize possible environmental problems, such as the NO_x and SO_x emissions.

Concerning to Mn, it was found to be positively correlated with HHV (0.43) and negatively correlated with ashes content (−0.53), which is very advantageous. Furthermore, although the increase of Mn is associated with the increase of Fe ($r = 0.75$) and Zn ($r = 0.61$), these two elements being environmentally harmless, their effect can be neglected. So, in general the species with high Mn contents are good indicators for energy purposes. In this way, we can conclude that among all biomass groups, the shrubs present the higher values of Mn, HHV and the lower values of ashes, becoming thus the most suitable group for energetic uses, and the worst being the agricultural wastes. The same behavior was found in Fe, that present positive correlation with HHV (0.47) and negative with ashes (−0.53), and positive with Mn (0.75) and Zn (0.48). Thereby, the shrubs group continues to be the best, as well as the woody component of forest species, and the agricultural wastes the worst for these uses.

Table 4. Statistics of Mineral nutrients (Na, K, Ca, Mg, and P); Trace Elements (Mn, Fe Zn, Ni, Cu, Cr, and Cd) and Halogen elements (F and Cl) by type of biomass (mg kg⁻¹) (n = 36 samples).

Type of Biomass	Statistics	Elements (mg Kg ⁻¹)													
		Na	K	Ca	Mg	P	Mn	Fe	Zn	Ni	Cr	Cd	Cu	F	Cl
Agricultural wastes															
<i>Olea europaea</i>	Mean	217.0 ^a	5586.3 ^a	2216.0 ^a	1082.9 ^a	420.0 ^b	13.2 ^a	18.9 ^c	17.9 ^c	313.6 ^b	158.6 ^c	0.0 ^a	29.5 ^b	1.3 ^a	30.4 ^c
	SD	8.6	462.7	136.2	45.8	13.8	0.7	1.8	2.0	19.0	12.4	0.0	1.8	0.01	2.8
<i>Prunus dulcis</i>	Mean	359.6 ^c	5057.9 ^a	6436.9 ^c	2030.2 ^c	239.2 ^a	25.9 ^b	14.0 ^b	9.8 ^b	400.3 ^c	100.4 ^b	0.0 ^a	14.1 ^a	1.4 ^b	48.3 ^d
	SD	10.2	361.2	150.1	101.9	1.8	0.5	1.0	2.7	12.9	14.8	0.0	2.3	0.01	1.6
<i>Vitis vinifera</i> (Sabor)	Mean	233.3 ^a	7848.0 ^b	5507.9 ^b	2431.1 ^d	409.5 ^b	38.7 ^c	6.6 ^a	0.0 ^a	456.8 ^c	1.8 ^a	0.0 ^a	6.6 ^a	1.3 ^a	15.25 ^b
	SD	4.7	559.6	327.5	4.6	12.5	4.9	0.8	0.0	42.4	0.5	0.0	0.7	0.01	2.1
<i>Vitis vinifera</i> (Ave)	Mean	259.1 ^b	7005.5 ^b	5108.8 ^b	1761.4 ^b	421.9 ^b	37.2 ^c	15.8 ^b	19.3 ^c	144.3 ^a	2.5 ^a	0.0 ^a	136.6 ^c	3.9 ^c	9.1 ^a
	SD	5.7	233.7	371.9	40.7	10.8	1.6	1.1	3.4	23.4	1.1	0.0	7.9	0.02	1.2
Forest wastes															
<i>Eucalyptus globulus</i> (residues)	Mean	1478.0 ^b	2772.7 ^b	6959.0 ^c	870.2 ^b	276.4 ^b	120.4 ^d	0.0 ^a	14.4 ^a	175.5 ^b	0.0 ^a	0.0 ^a	5.6 ^b	6.7 ^c	21.7 ^c
	SD	77.1	489.8	26.1	166.6	17.3	3.8	0.0	3.2	141.4	0.0	0.0	1.0	0.005	2.6
<i>Pinus pinaster</i> (residues)	Mean	1641.7 ^c	4850.3 ^c	1740.2 ^b	1615.6 ^c	351.6 ^b	82.9 ^c	10.3 ^b	29.6 ^b	634.5 ^c	76.5 ^b	202.8 ^b	4.6 ^b	1.4 ^b	6.6 ^a
	SD	54.9	136.8	135.5	78.4	26.9	1.8	0.8	3.1	33.5	5.5	109.6	0.4	0.01	0.8
<i>Eucalyptus globulus</i> (wood)	Mean	19.6 ^a	3106.0 ^b	107.3 ^a	83.6 ^a	1279.4 ^c	32.6 ^a	52.7 ^c	80.3 ^c	0.32 ^a	0.62 ^a	0.016 ^a	0.4 ^a	0.9 ^a	11.5 ^b
	SD	0.4	135.7	5.1	2.9	58.5	1.0	3.3	9.5	0.03	0.07	0.002	0.05	0.07	1.0
<i>Pinus pinaster</i> (wood)	Mean	98.7 ^a	492.2 ^a	1.0 ^a	57.3 ^a	5.9 ^a	71.8 ^b	49.3 ^c	30.4 ^b	1.54 ^a	0.45 ^a	0.003 ^a	0.3 ^a	0.9 ^a	22.7 ^c
	SD	2.2	13.7	0.08	2.9	0.2	3.2	3.5	4.1	0.15	0.05	0.001	0.02	0.04	2.5
Shrubs															
<i>Pterospartum tridentatum</i>	Mean	256.2 ^a	1012.5 ^a	2102.3 ^b	576.1 ^a	10.3 ^a	2693.0 ^b	503.1 ^b	42.3 ^b	0.0 ^a	1.7 ^b	0.070 ^b	6.6 ^b	1.5 ^a	2843.0 ^c
	SD	7.1	26.6	92.8	19.6	0.4	100.2	32.6	5.5	0.0	0.2	0.012	1.0	0.2	159.4
<i>Erica</i> sp.	Mean	810.4 ^d	1213.2 ^a	1526.1 ^a	710.7 ^b	152.3 ^d	3564.0 ^c	803.4 ^c	53.2 ^{b,c}	0.0 ^a	1.3 ^b	0.050 ^a	9.2 ^c	6.0 ^b	36.8 ^a
	SD	16.8	65.2	53.9	12.5	4.2	107.9	50.0	5.8	0.0	0.2	0.006	0.8	0.7	2.5
<i>Erica arborea</i>	Mean	463.1 ^b	2824.3 ^b	2936.7 ^c	1503.0 ^f	116.6 ^c	632.0 ^a	145.4 ^a	15.4 ^a	0.0 ^a	5.2 ^c	0.030 ^a	8.0 ^b	2.7 ^a	38.2 ^a
	SD	11.9	117.5	116.3	31.5	3.3	29.1	9.9	2.9	0.0	0.6	0.006	0.6	0.2	3.9
<i>Cytisus</i> sp.	Mean	607.4 ^c	5482.4 ^d	3512.4 ^d	1403.4 ^e	475.3 ^e	3811.2 ^{d,e}	174.6 ^a	77.6 ^d	0.0 ^a	0.27 ^a	0.120 ^c	6.4 ^b	19.3 ^c	352.7 ^b
	SD	9.9	146.4	140.8	32.3	19.8	93.8	16.2	8.0	0.0	0.03	0.018	0.6	1.3	44.3
<i>Ulex europaeus</i>	Mean	2132.8 ^f	3535.5 ^c	3561.8 ^d	936.9 ^c	61.5 ^b	3908.0 ^e	161.6 ^a	41.9 ^b	0.0 ^a	1.5 ^b	0.070 ^b	9.8 ^c	2.4 ^a	277.3 ^b
	SD	56.0	115.3	175.9	22.2	2.4	86.4	12.6	4.2	0.0	0.2	0.011	1.2	0.2	44.0
<i>Hakea sericea</i>	Mean	1923.1 ^e	1050.7 ^a	2311.7 ^b	1124.7 ^d	25.2 ^a	3635.0 ^{c,d}	843.5 ^c	63.4 ^c	0.0 ^a	0.6 ^a	0.070 ^b	3.3 ^a	2.9 ^a	102.3 ^a
	SD	10.1	42.3	112.8	37.5	0.8	120.5	30.3	4.7	0.0	0.09	0.011	0.3	0.3	8.5

Note: SD—Standard Deviation; mean values with the same letter are not significantly different for $p < 0.05$ by Duncan New Multiple Range test.

Table 5. Statistics of Mineral nutrients (Na, K, Ca, Mg, and P); Trace Elements (Mn, Fe Zn, Ni, Cu, Cr, and Cd) and Halogen elements (F and Cl) by biomass group (mg kg⁻¹).

Groups	n		Na	K	Ca	Mg	P	Mn	Fe	Zn	Ni	Cr	Cd	Cu	F	Cl
Agricultural wastes	128	Mean	267.3 ^a	6374.5 ^b	4817.4 ^b	1826.4 ^b	372.6 ^b	28.7 ^a	13.8 ^a	11.7 ^a	328.8 ^b	65.8 ^b	0.0 ^a	46.7 ^b	1.9 ^a	25.7 ^a
		SD	58.3	1239.8	1671.0	516.6	81.4	11.1	4.9	8.4	126.5	70.6	0.0	55.1	1.2	16.0
Forest wastes	128	Mean	809.5 ^b	2805.3 ^a	2201.9 ^a	656.7 ^a	478.3 ^b	76.9 ^a	28.1 ^a	38.7 ^b	203.0 ^b	19.4 ^a	50.7 ^b	2.7 ^a	2.5 ^{a,b}	15.6 ^a
		SD	788.2	1643.3	2958.5	678.3	502.6	32.8	24.4	26.6	281.1	34.5	108.1	2.6	2.6	7.4
Shrubs	192	Mean	1032.2 ^b	2519.8 ^a	2658.5 ^a	1042.5 ^a	140.2 ^a	3040.5 ^b	438.6 ^b	49.0 ^b	0.0 ^a	1.8 ^a	0.1 ^a	7.2 ^a	5.8 ^b	608.4 ^b
		SD	747.3	1685.3	777.2	349.5	162.5	1184.4	308.3	20.8	0.0	1.7	0.03	2.4	6.4	1038.0

Note: SD—Standard Deviation; mean values with the same letter are not significantly different for $p < 0.05$ by Duncan New Multiple Range test.

Table 6. Pearson's correlation matrix between high heating value (HHV) and chemical elements (CHONS and ashes, mineral, trace, and halogen elements).

	HHV	C	H	O	N	S	Ashes	Na	K	Ca	P	Mg	Mn	Fe	Zn	Ni	Cr	Cd	Cu	F	Cl	
HHV	1.00																					
C	0.16	1.00																				
H	0.43	0.08	1.00																			
O	0.02	-0.92	-0.20	1.00																		
N	-0.04	-0.12	0.57	-0.17	1.00																	
S	0.10	0.06	0.67	-0.34	0.76	1.00																
Ashes	-0.56	-0.06	0.11	-0.33	0.56	0.59	1.00															
Na	0.18	0.18	0.29	-0.17	0.18	0.18	-0.09	1.00														
K	-0.59	-0.04	0.13	-0.25	0.56	0.49	0.71	-0.21	1.00													
Ca	-0.38	-0.08	0.01	-0.26	0.58	0.47	0.85	0.14	0.54	1.00												
P	-0.33	0.03	-0.42	0.15	-0.40	-0.42	-0.32	-0.30	0.03	-0.36	1.00											
Mg	-0.37	-0.06	0.10	-0.25	0.59	0.55	0.74	0.03	0.77	0.68	-0.36	1.00										
Mn	0.43	-0.05	-0.15	0.24	-0.08	-0.21	-0.53	0.48	-0.38	-0.17	-0.07	-0.19	1.00									
Fe	0.47	-0.03	-0.21	0.22	-0.35	-0.17	-0.47	0.31	-0.61	-0.32	-0.14	-0.26	0.75	1.00								
Zn	0.14	0.04	-0.31	0.34	-0.48	-0.55	-0.73	0.14	-0.39	-0.56	0.62	-0.54	0.61	0.48	1.00							
Ni	-0.42	-0.07	0.05	-0.13	0.18	0.37	0.51	-0.24	0.50	0.31	-0.13	0.31	-0.31	-0.26	-0.28	1.00						
Cr	0.11	0.11	0.62	-0.27	0.49	0.57	0.31	-0.12	0.34	0.05	-0.17	0.26	-0.39	-0.32	-0.35	0.08	1.00					
Cd	-0.02	0.09	0.37	-0.12	0.25	0.24	0.01	0.30	0.12	-0.17	-0.08	0.15	-0.18	-0.16	-0.07	-0.07	0.25	1.00				
Cu	-0.38	-0.07	0.04	-0.11	0.18	0.37	0.47	-0.22	0.47	0.30	-0.14	0.30	-0.23	-0.21	-0.25	0.99	0.04	-0.09	1.00			
F	0.19	0.08	-0.14	-0.03	0.09	-0.09	-0.12	0.08	0.13	0.19	0.16	0.08	0.48	0.10	0.43	-0.05	-0.26	-0.12	-0.01	1.00		
Cl	0.28	-0.44	0.05	0.49	0.21	-0.08	-0.28	-0.14	-0.32	-0.13	-0.14	-0.24	0.33	0.31	0.15	-0.14	-0.16	-0.09	-0.11	-0.03	1.00	

Note: Significance level (42 obs.): *** highly significant ($r > 0.490$), ** very significant ($r > 0.393$), * significant ($r > 0.304$).

Although the correlation between Zn and HHV is relatively low (0.14^{n.s.}), the correlation is positive. Additionally, Zn is negatively correlated with the elements that could cause major environmental problems, namely N (−0.48), S (−0.55), ashes (−0.73), K (−0.39), Ca (−0.56), Mg (−0.54) and Cr (−0.35). So, the species with high Zn content are good markers for the energetic uses of agroforestry biomass. In this way, it was verified that shrubs and the woody component of forest species continue being the best group, since they present high contents of Zn and low of N, S, ashes, K, Ca, Mg, and Cr, and the worst being the agricultural wastes.

On the other hand, the K is one of the most undesirable elements, since it shows a negative correlation with HHV (−0.59) and positive correlations with N (0.56), S (0.49), ashes (0.71) and Ca (0.85). Identical trend was reported by Telmo et al. [30]. In this way, it is expected that the species with high K present low calorific power, with high propensity to form ashes and high harmful emissions of NO_x and SO_x. Between all species analyzed, the agricultural wastes presented the highest K values, while the shrubs and forestry group presented the lowest.

For the ashes, these are positively correlated with the N (0.56), S (0.59), K (0.71), Ca (0.85) and Mg (0.74), being this group of elements one of the major responsible for the ashes production.

It can also be verified that the correlation between HHV with H, as well as HHV with C was positive, while between HHV with O it was negative, coinciding with the results obtained by [15,30,42,44,45].

Since the biomass features could be affected by multiple independent variables, and the multiple regression models can accommodate many explanatory variables that can be correlated, which are sometimes mislead in simple regression analysis [24], multiple regression was used to predict the calorific power through the chemical elements.

Table 7 represents the multiple regression using HHV as dependent variable and the Elemental analysis, (CHONS), ashes, mineral nutrients (Na, K, Ca, Mg and P), trace elements (Mn, Fe Zn, Ni, Cu, Cr and Cd) and halogen elements (Cl and F) as independent variables to identify the variables of greater importance for HHV variation, using the stepwise backward procedure.

With all the variables in the model, the determination coefficient to predict HHV variation was 0.975.

With the elimination of all the statistically non-significant variables (K, Na, O, C, Cd, P, Cu, Mn), the coefficient of determination decreased slightly from 0.975 to 0.967.

Forcing to exclude the variables (Mg, Ni, Cl, S, N, and Ca) it is verified that, although the coefficient of determination decreases to 0.907, the model becomes much simpler, with only 6 of the initial 20.

Thus, the final six variables of the model with the greatest contribution to the explanation of HHV variation with positive effect are H, Fe, Zn, Cr and F and, with negative effect on the ashes.

The ashes and Zn were revealed as having greater relative weight (Beta value) in the HHV variation. The ashes in the negative sense and the Zn in positive sense, explaining respectively 29.6% and 25.4% of the total variation of HHV. The F, Fe, H, and Cr explain 14.6%, 14.5%, 9.7% and 5.9%, respectively of HHV in the positive sense. This regression suggested that energy content of this agroforest wastes increase with F, Fe, H, and Cr contents.

These results from negative correlation from HHV and ashes content agree with those obtained from other authors, [15,42,45,60]. For example, Livingstone [60] has demonstrated that heating values are negatively related to ash content, with every 1% increase in ash concentration decreasing the heating value by 0.2 MJ kg^{−1}.

It is also possible to verify that H is one of the variables that most contributes (positively) to HHV variation, as in the recent studies [43,44], and previously by Bunckley and Domalsk [42].

Although several authors claim that the C along with the H have a strong contribution to HHV variation, this did not occur with these types of wastes, that not only have a low correlation coefficient of 0.16 (not significant, Table 6), but are also one of the variables with lower weight in multiple regression (Table 7), being the 4th variable to be eliminated from the Model.

Table 7. Multiple regression analysis between the dependent variable HHV and the independent variables, chemical analysis (CHONS and ashes, Na, K, Ca, P, Fe, Mn, Cd, Cu, F, and Cl).

STEP	C	H	O	N	S	Ashes	Na	K	Ca	Mg	P	Mn	Fe	Zn	Ni	Cr	Cd	Cu	F	Cl	R ²
1	-9.1	2.3	-9.7	-4.4	5.2	-16.8	-0.8	-0.5	4.4	-1.5	-2.6	-3.4	3.9	5.0	-11.3	2.8	-0.5	9.1	5.4	1.0	0.975
2	-8.9	2.2	-9.5	-4.2	4.9	-16.8	-0.7	-	4.7	-1.7	-2.6	-3.8	4.2	5.0	-11.7	2.8	-0.5	9.5	5.2	0.9	0.975
3	-6.2	2.3	-6.5	-4.5	4.5	-14.6	-	-	3.8	-1.6	-2.2	-4.0	4.1	5.5	-15.6	3.2	-0.6	13.5	5.7	1.5	0.975
4	-0.1	3.2	-	-5.0	5.3	-15.0	-	-	4.6	-1.9	-2.4	-4.5	5.1	7.1	-17.5	3.8	-0.7	15.1	6.9	1.7	0.975
5	-	3.2	-	-5.0	5.3	-14.7	-	-	4.5	-1.8	-2.5	-4.5	5.0	6.9	-17.9	3.8	-0.7	15.5	6.8	1.8	0.975
6	-	3.3	-	-5.3	4.4	-12.8	-	-	4.4	-1.8	-1.8	-3.7	4.5	6.8	-20.6	3.8	-	18.4	6.3	1.9	0.974
7	-	4.4	-	-4.8	2.9	-12.8	-	-	4.6	-1.6	-	-3.2	5.7	8.8	-20.4	3.8	-	18.6	6.5	1.8	0.971
8	-	5.2	-	-7.1	6.8	-24.4	-	-	8.5	-2.4	-	-3.2	8.3	14.7	-1.6	5.6	-	-	9.8	2.6	0.969
9	-	5.3	-	-9.8	8.2	-22.6	-	-	7.2	-2.6	-	-	6.2	15.8	-2.2	6.1	-	-	10.1	3.6	0.967
10	-	5.9	-	-11.5	8.3	-23.7	-	-	7.8	-	-	-	5.4	15.0	-2.2	6.2	-	-	9.6	4.3	0.962
11	-	5.9	-	-10.4	6.9	-26.3	-	-	9.2	-	-	-	6.0	15.5	-	6.8	-	-	9.2	3.7	0.956
12	-	6.8	-	-6.9	5.3	-30.0	-	-	9.4	-	-	-	8.5	17.5	-	6.3	-	-	9.2	-	0.940
13	-	9.7	-	-5.4	-	-28.6	-	-	8.6	-	-	-	11.0	19.4	-	6.9	-	-	10.4	-	0.930
14	-	8.6	-	-	-	-32.1	-	-	6.0	-	-	-	13.0	22.3	-	6.5	-	-	11.5	-	0.910
15	-	9.7	-	-	-	-29.6	-	-	-	-	-	-	14.5	25.4	-	5.9	-	-	14.6	-	0.907

4. Conclusions

Among all the types of biomass analyzed, in general, shrubs are those with better characteristics for energy uses, namely through combustion processes. Not only they contain high heating value (HHV), but less undesirable elements such as N, S, K, Ca, Cr, and Ashes. The greatest limitation of this type of biomass for these purposes is the high values of the halogen elements (F and Cl), which may raise serious problems of sintering and corrosive effect of chloride salts and HCl on metal parts in furnace and boiler.

In forest wastes, it was verified that, in general, these present intermediate features between the shrubs and agricultural group. However, when the two components of forest wastes were analyzed separately, it was concluded that woody component has thermochemical properties much more suited and identical to shrubs group for energy purposes than the residual component (branches and leaves). On the other hand, the forest residues have high values of undesirable elements of N, S, K, Na, Ca, Ni, Cr, Cu, F, and ashes. So, if this residual component is used in combustion processes, special care will be required in the treatment of gaseous emissions as well as solutions to minimize sintering and corrosion problems.

The agricultural wastes have lower HHV, higher ash and some undesirable chemical elements (S, N, K, Ca, Ni, Cr, Cu, and ashes). Its application for energy purposes by combustion may be limited due to its lower energy capacity, the risks of emission of volatile compounds toxic to the atmosphere, sintering, and corrosion of the firing systems.

Author Contributions: Conceptualization, J.L. and A.B.; methodology, J.L., A.B., T.E. and C.M.; investigation, T.E., J.L., A.B.; resources, J.L., T.F., J.A., A.B., and T.E.; writing—original draft preparation, T.E. and J.L.; writing—review and editing, J.L., T.E., J.A., T.F. and A.B.; supervision, J.L., T.F., A.B. and J.A.; project administration, J.L., J.A. and T.F.; funding acquisition, J.L., J.A., A.B. and T.E.

Funding: This research was funded by the INTERACT project—“Integrated Research in Environment, Agro-Chain and Technology”, no. NORTE-01-0145-FEDER-000017, in its line of research entitled BEST, co-financed by the European Regional Development Fund (ERDF) through NORTE 2020 (North Regional Operational Program 2014/2020). For authors integrated in the CITAB research centre, it was further financed by the FEDER/COMPETE/POCI—Operational Competitiveness and Internationalization Programme, under Project POCI-01-0145-FEDER-006958, and by National Funds by FCT—Portuguese Foundation for Science and Technology, under the project UID/AGR/04033/2019.

Conflicts of Interest: The authors declare no conflict of interest

Appendix A

Table A1. Minimum, Maximum and Median values of HHV, elemental analysis and ashes, by biomass species.

Specie	Statistics	HHV	C	H	O	N	S	Ashes
		(MJ kg ⁻¹)	(%)					
Agricultural wastes								
<i>Olea europaea</i>	Min	21.02	49.39	7.11	37.66	1.16	0.1124	3.9
	Max	21.15	49.88	7.26	38.20	1.25	0.1217	4.1
	Median	21.10	49.47	7.19	37.88	1.21	0.1140	4.0
<i>Prunus dulcis</i>	Min	18.12	44.01	6.12	41.39	1.09	0.0679	6.7
	Max	18.27	44.31	6.17	41.77	1.21	0.0692	6.9
	Median	18.26	44.25	6.14	41.75	1.18	0.0682	6.8
<i>Vitis vinifera</i> (Sabor)	Min	17.12	42.24	6.09	42.70	0.91	0.0684	7.1
	Max	17.63	42.87	6.16	43.50	1.10	0.0704	7.3
	Median	17.13	42.73	6.13	42.90	0.96	0.0685	7.1
<i>Vitis vinifera</i> (Ave)	Min	17.37	44.00	6.20	41.77	0.87	0.0861	6.7
	Max	17.40	44.08	6.35	42.00	0.97	0.0890	6.8
	Median	17.40	44.06	6.28	41.94	0.91	0.0884	6.8

Table A1. Cont.

Specie	Statistics	HHV	C	H	O	N	S	Ashes
		(MJ kg ⁻¹)	(%)					
Forest wastes								
<i>Eucalyptus globulus</i> (residues)	Min	19.63	48.53	6.47	37.09	0.99	0.0796	6.1
	Max	19.73	48.97	6.65	37.65	1.08	0.0863	6.2
	Median	19.64	48.61	6.57	37.64	1.00	0.0844	6.2
<i>Pinus pinaster</i> (residues)	Min	19.42	48.52	6.88	39.79	1.18	0.0890	3.2
	Max	19.50	48.83	6.91	40.07	1.29	0.0942	3.2
	Median	19.43	48.62	6.89	39.91	1.24	0.0936	3.2
<i>Eucalyptus globulus</i> (wood)	Min	17.31	45.78	5.81	47.46	0.19	0.0180	0.5
	Max	17.94	46.37	6.05	48.08	0.23	0.0210	0.6
	Median	17.56	46.25	5.84	47.84	0.21	0.0200	0.5
<i>Pinus pinaster</i> (wood)	Min	19.73	47.75	6.09	45.08	0.10	0	0.1
	Max	20.46	48.33	6.38	45.66	0.13	0	0.2
	Median	20.26	48.22	6.15	45.46	0.11	0	0.2
Shrubs								
<i>Pterospartum tridentatum</i>	Min	20.65	50.24	6.31	40.67	1.02	0.0576	1.0
	Max	21.24	50.70	6.57	41.38	1.13	0.0598	1.0
	Median	20.71	50.31	6.47	40.98	1.09	0.0578	1.0
<i>Erica</i> sp.	Min	20.70	48.58	5.81	42.92	0.47	0.0650	1.3
	Max	21.24	48.88	6.34	43.63	0.56	0.0694	1.4
	Median	20.91	48.78	6.01	43.43	0.52	0.0667	1.3
<i>Erica arborea</i>	Min	21.14	49.45	6.40	41.17	0.70	0.0682	1.7
	Max	21.61	49.83	6.49	41.50	0.74	0.0834	1.8
	Median	21.30	49.81	6.45	41.19	0.72	0.0820	1.8
<i>Cytisus</i> sp.	Min	19.95	46.16	6.19	44.54	0.80	0.0416	1.3
	Max	20.65	46.78	6.26	45.52	1.12	0.0435	1.3
	Median	20.01	46.47	6.21	45.08	0.91	0.0420	1.3
<i>Ulex europaeus</i>	Min	19.12	46.82	6.37	43.54	1.02	0.0582	1.6
	Max	19.82	47.03	6.61	44.16	1.18	0.0655	1.6
	Median	19.30	47.01	6.48	43.71	1.12	0.0613	1.6
<i>Hakea sericea</i>	Min	19.98	47.32	6.23	43.57	0.28	0.0462	1.5
	Max	20.62	47.96	6.47	44.58	0.45	0.0495	1.5
	Median	20.19	47.39	6.33	44.43	0.31	0.0487	1.5

Appendix B

Table A2. Minimum, Maximum and Median values of HHV, elemental analysis and ashes, by biomass group.

Groups	Statistic	HHV	C	H	O	N	S	Ashes
		(MJ kg ⁻¹)	(%)					
Agricultural wastes	Min	17.12	42.24	6.09	37.66	0.87	0.07	3.9
	Max	21.15	49.88	7.26	43.50	1.25	0.12	7.3
	Median	17.88	44.07	6.19	41.77	1.10	0.08	6.8
Forest wastes	Min	17.31	45.78	5.81	37.09	0.10	0	0.1
	Max	20.46	48.97	6.91	48.08	1.29	0.09	6.2
	Median	19.57	48.43	6.43	42.58	0.61	0.05	1.9
Shrubs	Min	19.12	46.16	5.81	40.67	0.28	0.04	1.0
	Max	21.61	50.70	6.61	45.52	1.18	0.08	1.8
	Median	20.65	48.27	6.36	43.56	0.77	0.06	1.4

Appendix C

Table A3. Minimum, Maximum and Median values of Mineral nutrients (Na, K, Ca, Mg and P), Trace Elements (Mn, Fe, Zn, Ni, Cu, Cr and Cd) and Halogen elements (F and Cl), by biomass species.

Species	Statistics	Elements (mg Kg ⁻¹)													
		Na	K	Ca	Mg	P	Mn	Fe	Zn	Ni	Cr	Cd	Cu	F	Cl
Agricultural wastes															
<i>Olea europaea</i>	Min	206.42	4945.05	2061.49	1018.31	401.49	12.30	16.60	15.54	290.64	143.63	0	26.91	1.26	26.72
	Max	227.47	6019.80	2392.83	1118.92	434.70	13.97	20.99	20.45	337.08	173.95	0	31.14	1.29	33.49
	Median	217.20	5794.10	2193.72	1111.43	423.78	13.38	19.12	17.80	313.11	158.14	0	30.35	1.27	30.91
<i>Prunus dulcis</i>	Min	345.53	4668.62	6225.67	1886.06	236.71	25.21	13.01	5.99	387.50	79.81	0	11.45	1.42	47.12
	Max	369.21	5539.02	6560.57	2103.10	241.10	26.52	15.40	12.18	417.98	114.09	0	17.06	1.45	50.52
	Median	363.94	4966.18	6524.33	2101.37	239.83	25.81	13.53	11.14	395.51	107.17	0	13.81	1.42	47.32
<i>Vitis vinifera</i> (Sabor)	Min	228.51	7071.60	5127.58	2424.92	394.08	32.26	5.96	0.00	409.78	1.46	0	5.82	1.24	12.60
	Max	239.61	8368.79	5927.01	2436.07	424.65	44.15	7.79	0.00	512.59	2.50	0	7.51	1.26	17.74
	Median	231.76	8103.70	5469.18	2432.41	409.75	39.80	6.08	0.00	447.94	1.49	0	6.59	1.24	15.17
<i>Vitis vinifera</i> (Ave)	Min	252.39	6741.34	4583.02	1706.43	412.87	35.62	14.80	15.54	113.80	1.18	0	126.13	3.82	7.59
	Max	266.41	7309.49	5379.46	1803.73	437.04	39.42	17.26	23.81	170.79	3.86	0	145.36	3.87	10.51
	Median	258.60	6965.76	5364.01	1773.93	415.73	36.46	15.40	18.42	148.31	2.55	0	138.27	3.86	9.20
Forest wastes															
<i>Eucalyptus globulus</i> (residues)	Min	1423.51	2081.05	6922.55	634.72	253.86	115.75	0	10.88	49.94	0	0	4.27	6.71	18.09
	Max	1587.06	3150.08	6982.02	995.43	295.95	125.08	0	18.64	373.03	0	0	6.72	6.72	24.11
	Median	1423.51	3087.00	6972.33	980.46	279.45	120.48	0	13.59	103.37	0	0	5.93	6.72	22.87
<i>Pinus pinaster</i> (residues)	Min	1569.92	4698.63	1565.10	1515.22	313.84	80.41	9.61	25.25	600.72	72.04	112.77	4.27	1.35	5.43
	Max	1703.12	5030.06	1895.06	1706.43	374.21	84.47	11.44	32.35	680.15	84.29	357.10	5.14	1.37	7.23
	Median	1652.15	4822.09	1760.30	1625.28	366.88	83.80	9.81	31.27	622.75	73.08	138.49	4.27	1.36	7.11
<i>Eucalyptus globulus</i> (wood)	Min	19.09	3001.24	102.12	79.55	1220.30	31.25	48.36	68.31	0.29	0.53	0.01	0.37	0.82	10.66
	Max	19.96	3297.66	114.32	86.21	1359.10	33.53	56.48	91.56	0.35	0.71	0.02	0.50	0.99	12.85
	Median	19.74	3019.05	105.53	85.03	1258.80	33.02	53.26	81.03	0.30	0.62	0.02	0.44	0.89	10.99
<i>Pinus pinaster</i> (wood)	Min	96.80	480.24	0.92	54.68	5.70	67.56	46.13	25.11	1.35	0.41	0	0.26	0.85	19.88
	Max	101.70	511.35	1.11	61.35	6.20	75.15	54.11	35.04	1.71	0.52	0	0.30	0.95	25.99
	Median	97.60	485.01	0.97	55.87	5.80	72.69	47.69	31.06	1.55	0.42	0	0.30	0.90	22.23

Table A3. Cont.

Species	Elements (mg Kg ⁻¹)														
	Statistics	Na	K	Ca	Mg	P	Mn	Fe	Zn	Ni	Cr	Cd	Cu	F	Cl
Shrubs															
<i>Pterospartum tridentatum</i>	Min	250.65	980.93	2010.35	548.95	9.81	2568.99	464.20	37.59	0	1.44	0.06	5.50	1.24	2651.20
	Max	266.23	1045.92	2229.31	594.51	10.78	2814.34	544.01	49.95	0	1.93	0.09	7.91	1.64	3041.40
	Median	251.81	1010.68	2067.25	584.91	10.31	2695.65	501.10	39.36	0	1.67	0.07	6.54	1.63	2836.50
<i>Erica</i> sp.	Min	790.21	1138.13	1463.03	701.38	147.77	3445.20	749.81	46.26	0	1.12	0.04	8.12	5.16	33.34
	Max	831.35	1297.18	1594.63	728.39	157.80	3706.30	870.11	60.35	0	1.59	0.05	9.73	6.91	39.04
	Median	809.67	1204.28	1520.70	702.29	151.32	3540.61	790.28	52.99	0	1.35	0.05	9.70	5.96	38.02
<i>Erica arborea</i>	Min	451.28	2698.34	2830.04	1461.02	114.04	600.25	131.41	12.03	0	4.55	0.02	7.10	2.46	34.04
	Max	479.36	2981.24	3098.38	1536.72	121.21	670.55	153.24	19.05	0	5.93	0.04	8.46	2.99	43.33
	Median	458.69	2793.31	2881.65	1511.33	114.56	625.25	151.56	15.12	0	5.22	0.03	8.33	2.65	37.24
<i>Cytisus</i> sp.	Min	599.64	5300.25	3341.95	1368.04	450.24	3700.98	156.35	69.19	0	0.23	0.11	5.61	17.42	290.25
	Max	621.33	5658.68	3686.89	1446.11	498.64	3930.13	195.69	88.31	0	0.30	0.15	7.13	20.46	388.62
	Median	601.24	5488.28	3508.35	1396.05	477.02	3801.95	171.76	75.31	0	0.28	0.11	6.38	20.03	379.21
<i>Ulex europaeus</i>	Min	2065.31	3400.02	3329.98	905.94	59.46	3799.04	144.96	38.59	0	1.22	0.05	8.03	2.18	224.51
	Max	2202.43	3681.86	3755.89	956.86	64.81	4010.32	175.32	47.81	0	1.71	0.08	10.77	2.63	332.30
	Median	2130.64	3524.61	3599.49	947.87	60.24	3914.65	164.51	39.32	0	1.48	0.07	10.52	2.38	275.10
<i>Hakea sericea</i>	Min	1915.35	1002.02	2171.61	1079.32	24.01	3546.18	801.18	58.26	0	0.45	0.05	2.86	2.49	90.32
	Max	1937.31	1105.19	2447.90	1171.16	25.80	3805.31	870.14	69.62	0	0.68	0.08	3.67	3.11	109.36
	Median	1916.61	1044.89	2315.60	1123.61	25.78	3553.45	859.15	62.31	0	0.55	0.07	3.26	3.10	107.21

Appendix D

Table A4. Minimum, Maximum and Median values of Mineral nutrients (Na, K, Ca, Mg and P), Trace Elements (Mn, Fe, Zn, Ni, Cu, Cr and Cd) and Halogen elements (F and Cl), by biomass group.

Groups	Statistic	Elements (mg Kg ⁻¹)													
		Na	K	Ca	Mg	P	Mn	Fe	Zn	Ni	Cr	Cd	Cu	F	Cl
Agricultural wastes	Min	206.42	4668.62	2061.49	1018.31	236.71	12.30	5.96	0	113.80	1.18	0	5.82	1.24	7.59
	Max	369.21	8368.79	6560.57	2436.07	437.04	44.15	20.99	23.81	512.59	173.95	0	145.36	3.87	50.52
	Median	246.00	6380.57	5371.73	1844.89	411.31	29.39	15.10	13.86	362.29	41.83	0	21.98	1.35	22.23
Forest wastes	Min	19.09	480.24	0.92	54.68	5.70	31.25	0	10.88	0.29	0	0	0.26	0.82	5.43
	Max	1703.12	5030.06	6982.02	1706.43	1359.10	125.08	56.48	91.56	680.15	84.29	357.10	6.72	6.72	25.99
	Median	762.60	3053.02	839.71	360.46	304.89	77.78	28.78	31.16	25.82	0.52	0.01	2.38	1.17	15.47
Shrubs	Min	250.65	980.93	1463.03	548.95	9.81	600.25	131.41	12.03	0	0.23	0.02	2.86	1.24	33.34
	Max	2202.43	5658.68	3755.89	1536.72	498.64	4010.32	870.14	88.31	0	5.93	0.15	10.77	20.46	3041.44
	Median	705.77	1997.76	2638.97	1018.09	89.42	3549.81	329.94	48.88	0	1.39	0.06	7.52	2.82	166.93

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