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Thermal Properties of Residual Agroforestry Biomass of Northern Portugal

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Abstract: Biomass from forestry and agricultural sector provides an important contribution to encounter the government's targets for increasing bioenergy production and utilization. Characterization of agricultural and forest wastes are critical for exploiting and utilizing them for energy purpose. In the present work agricultural and forest wastes and shrubs were sampled in two sites in north Portugal (Ave and Sabor basin) and subjected to Higher Heating Value (HHV) and chemical composition quantification. The HHV was evaluated according to the methodology described in Standard DD CEN/TS14918:2005. For the lignin content, the procedure was made by the Klason method and the extractives content was determined with the Soxhlet method. For agricultural and forest wastes the HHV values are identical with a range of 17 to 21 MJ·kg^{-1}. However, shrubs biomass presentx slightly higher and statistically different values from agricultural and forest wastes, varying between 19 and 21 MJ·kg^{-1}. Forest wastes contain higher levels of holocellulose compared to agricultural wastes and, with respect to extractive contents, this trend is the reverse. There is a general tendency for the woody components present thermo-chemical properties more suited for energy purposes, than the residues formed by the branches and leaves.

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

1. Introduction

Portugal is a European Country with a strong suitability for forest biomass production, not only because of its geographical location, but also because it is essentially agroforestry. According to data from the 6th IFN [1], about 35% of the territory is occupied by forest, (placing Portugal in the average of the 27 countries of the European Union), 32% shrubs and pastures, and agriculture occupies about 24% of the territory. Thus, it can be observed that about 90% of the country is occupied by forests, weeds and agriculture, meaning an enormous biomass production potential.

Furthermore, the increasing rural population migration to large seaside cities or to county principal cities, led to an abandonment of land management and, thus, to forest biomass accumulation like to be burnt by wild fires during summer time. This way, a potential source of energy, which could contribute to economical elevation, results in an enormous expense in firefighting actions and a large contribution to the greenhouse gas effect (GGE) and global warming effects (GWE).

Although in Portugal a high percentage of highly fragmented forestland under private ownership exists, the phenomenon of collective organization of private forest owners began only approximately

30 years ago. These organizations appeared with rather minor involvement of the forest services in promoting forest owners' associations [2]

Forest fires are an old phenomenon in Portuguese forests. What is new, and has become more frequent, is the scale reached by these forest fires in 2003, 2005, 2016 and especially in 2017 when approximately 500,000 ha of area were burnt, and 116 victims died.

Due to Portugal's dependence on fossil fuels and a great availability of biomass in the country, 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.

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 [3]. As biomass is a hypothetically reliable and renewable energy resource, biomass-based energy fuel is being considered as one of the most promising energy mover of the future generation [4].

According to Rawat et al. [5], there are various possible conversion technologies for getting different products from biomass is broadly classified into three groups: (i) thermo-chemical conversion, (ii) bio-chemical conversion and (iii) oil extraction.

In the production of bioenergy from biomass, particular attention is given to energy crops that can be converted into energy for heating, electricity (from combustion or mechanization) and biofuels (e.g., bioethanol, biodiesel and biogas). Biomass combustion is the main method of converting biomass to energy, responsible for more than 90% of the global contribution to bioenergy.

The EU and 15 member countries have developed bioeconomy strategies (see [6]). Although not among the front runners, some Southern countries have developed their own strategy, as is the case of Spain, Italy and France [2].

In order to evaluate their potential as a biomass feedstock for combustion, there is a need for an integrated biomass characterization for the main native species in the shrubland areas of this country.

The properties of raw materials used as biomass fuels can be grouped into physical, chemical and thermal properties [7]. Among them we emphasize the HHV, which quantifies the gross heat of combustion and that conditions for the performance of the energetic system [8–11], Generally a heating value of a fuel may be reported on two basis: the higher heating value and the lower heating value. The higher heating value (HHV) refers to the heat released from the fuel combustion with the original and generated water in a condensed state, while the lower heating value (LHV) is based on gaseous water as the product [9,12]. Generally, the heating value of a fuel may be reported on two basis, the higher heating value and the lower heating value. The higher heating value (HHV) refers to the heat released from the fuel combustion with the original and generated water in a condensed state, while the lower heating value (LHV) is based on gaseous water as the product [9,12].

The behavior of the biomass in the burning process is the sum of the behavior of each of its chemical components: cellulose, hemicellulose, lignin and extractives. As reported by Cintra [13], the structure of lignin can influence thermal degradation of the biomass, raising its upper heating value.

According to Sheng and Azevedo [9], the heating value is one of the most important properties of biomass fuels for design calculations or numerical simulations of thermal conversion systems for biomass. Several authors consider that the higher heating value is a key parameter for the evaluation of the energy content of the different types of biomass [7,11,14–16]. This occurs when the combustion takes place at constant volume and in which the water that forms during the combustion is condensed and the heat derived from that condensation is recovered.

The influence of chemical composition on the Higher Heating Value (HVV) derives from the fact that lignin has a higher heating value (about 6100 kcal/kg) in comparison to cellulose (4150–4350 kcal/kg), [17] and [18]. Besides the heating value analysis, the biomass chemical analysis is a very important information to consider in the reaction characteristics of solid fuels. In general, agroforestry biomass consists essentially of hollocelulose (hemicellulose and cellulose) and lignin. Thus, the quantification of these compounds is of extreme importance since these are what will influence the use of each of the substances as fuel.

The extractives (oils) are also constituent compounds of the biomass, however, they are structural compounds that are not part of the chemical structure of the cellular wall [19,20]. Extractives are compounds of varying chemical composition, such as gums, fats, waxes, resins, sugars, oils, starches, alkaloids and tannins. According Fengel and Wegner [21], the term "extractives" is used to identify non-structural components of biomass that can be extracted with solvents classified as neutral and lipophilic (water-insoluble) or hydrophilic (water-soluble).

Also important for energetic purposes is the content of some chemical elements with serious consequence for the emission of toxic gases into the atmosphere. In order to use these technologies, it is crucial to know the different types of biomass well and, therefore, it is essential to evaluate the thermochemical properties of this biomass in order to optimize its use. Therefore, the aims of this study are: thermochemical characterization of the different types of agroforestry biomass in Northern Portugal.

2. Materials and Methods

2.1. Study Area Characteristics

Portugal is a European Country with strong suitability for forest biomass production, due to its geographical location. This study was supported by samples collected in two distinct areas in North of Portugal, more specifically in the Sabor River basin and Ave River basin (Figure 1).

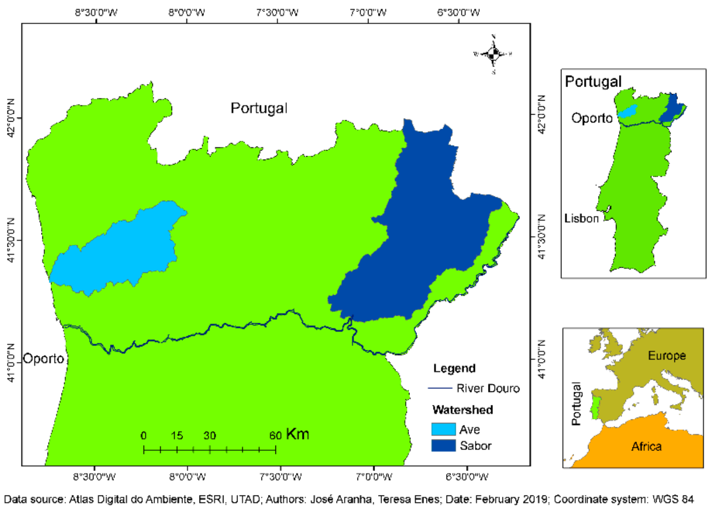

Figure 1. Portugal world geographical location. Sampling areas.

Sabor River Basin is located in the north eastern corner of the country. Presents a territorial area of approximately 3297 km^2, largely concentrated in the Portuguese territory (2742 km^2) and the remaining in Spanish territory [22]. This region is characterized as having sub-continental prevailing climate conditions with long cold winters and short, but very hot and dry summers. The other sampling area is Ave River Basin with approximately 1390 km^2, also located in the north of Portugal with distinctly Atlantic characteristics.

2.2. Plant Material

Samples collected divided into three distinct groups: agricultural wastes (*Olea europaea* L.; *Prunus dulcis* Miller and *Vitis vinifera* L.); Forest wastes *Eucalyptus globulus* Labill and *Pinus pinaster* Aiton (wood and residues) and shrubs (*Pterospartum tridentatum* L.; *Erica* sp.; *Erica arborea* L.; *Cytisus* sp.; *Ulex europaeus* L. and *Hakea sericea* Scharader). In the forest species two types of samples were collected: wood (chips and sawdust from wood lumber industries) and residues (branches and leaves). Samples of each species were stored in paper bags and brought to Forestry Sciences and Landscape Architecture of the UTAD laboratory. The samples were then oven dried at 40 °C for one week until reaching a constant weight. Before the analyzes 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.

2.3. Heating Value and Macromolecules

2.3.1. Higher Heating Value (HHV)

HHV is an important trait in wood utilization for energy. It can be determined either by the use of a bomb calorimeter or by using calculations in accordance with the lignin and extractives content of the specimen [23]. The HHV was determined according to the methodology described in Standard DD CEN/TS14918:2005 (Solid Biofuels-Method for the Determination of Calorific Value), using a 6300 Automatic Isoperibol Calorimeter (Parr, Molene, IL, USA). 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.

2.3.2. Macromolecules

For the determination of the lignin content, a chemical procedure was used, using the Klason method. The amount was determined by hydrolyzing pre-extracted samples on 0.35 g of extracted wood sample T222 om-06 [24]. Samples were put into precipitation glasses, 3 mL of H_2SO_4 (72%) was added and the sample was shaken at 30 °C water bath during 1 h. The mixture was put in Erlenmeyer flasks and the glasses washed with 84 mL of distilled water, added to the mixture on the Erlenmeyer and placed in an autoclave for 1 h at 120 °C. The content in the Erlenmeyer was sucked through a glass filter by a Foss hydrolyzing unit. The dissolved cellulose passed through the glass filter but the lignin residue was trapped. Finally, the glass filters with the lignin were dried at 105 °C for 24 h, cooled in a desiccator and weighed. From the weight differences, the lignin content was calculated [10].

For determination of extractives content we distinguished two categories. Non-polar solvents soluble extractives (ethanol: dichloromethane) and polar (water) solvent soluble extractives. The sum of polar and non-polar solvent soluble extractives contents constituted total of extractives content. Approximately 3 g of oven dry ground wood of particle size 180–250 mm. The bags were placed into Soxhlet extraction apparatus following the methodology presented by Sluiter et al. [25]. The samples were extracted with 250 mL of dichloromethane for 4 h, followed by another 5 h extraction with 250 mL of 95% ethanol. The alcohol was then drained and evaporated to constant weight. Finally, water was extracted in a manner similar to the previous ones, with only the organic solvent being replaced with water for 6 h and then oven dried at 105 °C to constant weight. The extractive contents were determined as (%) weight losses after Soxhlet and boiling water bath extractions, respectively.

2.3.3. Statistical Analisys

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.

3. Results

3.1. General Higher Heating Value an Chemical Composition

Table 1 shows mean and standard deviation; of HHV, and macromolecules contents for all the samples. For agricultural and forestry wastes the HHV values are identical, with a range of 17 to 21 $MJ \cdot kg^{-1}$ (Table 1). However, shrubs biomass present slightly higher and statistically different values of agricultural and forest wastes (Table 2), varying between 19 and 21 $MJ \cdot kg^{-1}$ (Table 1). The variability of HHV among species within each of the groups (agricultural, forestry and shrubs) is very low, presenting standard deviation values between 0.7 and 1.6 (Table 2).

Table 1. Mean ± SD of Higher Heating Values and Macromolecules contents, of the samples. Note: mean values with the same letter within waste group are not significantly different for p < 0.05 by Duncan New Multiple Range test. Number of samples used in each species (n = 12).

Species	Higher Heating Value ($MJ \cdot kg^{-1}$)	Extractives (%)	Klason Lignin (%)	Holocellulose (%)
Agricultural wastes				
Olea europaea	21.09 ± 0.05 [c]	38.2 ± 2.4 [b]	22.6± 0.2 [b]	39.2 ± 2.4 [a]
Prunus dulcis	18.21 ± 0.07 [b]	24.6 ± 2.1 [a]	20.9 ± 0.1 [a]	54.4 ± 2.1 [b]
Vitis vinifera (Sabor)	17.29 ± 0.24 [a]	28.8 ± 2.4 [a]	20.3 ± 0.4 [a]	50.8 ± 2.1 [b]
Vitis vinifera (Ave)	17.39 ± 0.02 [a]	25.6 ± 2.1 [a]	20.3 ± 0.4 [a]	54.1 ± 2.4 [b]
Forest wastes				
Eucalyptus globulus (residues)	19.67 ± 0.04 [b]	30.9 ± 2.1 [c]	19.4 ± 0.1 [a]	49.7 ± 2.2 [a]
Pinus pinaster (residues)	19.45 ± 0.04 [b]	33.6 ± 3.3 [c]	19.5 ± 0.2 [a]	46.9 ± 3.4 [a]
Eucalyptus globulus (Wood)	17.60 ± 0.26 [a]	3.2 ± 0.3 [a]	25.9 ± 0.2 [b]	70.9 ± 0.4 [c]
Pinus pinaster (Wood)	20.15 ± 0.31 [c]	1 12.6 ± 0.8 [b]	29.6 ± 0.3 [c]	57.8 ± 0.9 [b]
Shrubs				
Pterospa rtum tridentatum	20.87 ± 0.26 [c]	18.6 ± 1.2 [b]	24.4 ± 0.1 [e]	57.0 ± 1.1 [b]
Erica sp.	20.95 ± 0.22 [c]	9.7 ± 1.0 [a]	25.1 ± 0.3 [f]	65.2 ± 1.1 [c]
Erica arborea	21.35 ± 0.19 [c]	24.4 ± 2.2 [c]	23.2 ± 0.2 [d]	52.4 ± 2.3 [a]
Cytisus sp.	20.20 ± 0.32 [b]	16.2 ± 1.3 [b]	17.8 ± 0.1 [a]	66.0 ± 1.4 [c]
Ulex europaeus	19.41 ± 0.30 [a]	12.5 ± 1.1 [a]	20.0 ± 0.1 [b]	67.5 ± 1.0 [c]
Hakea sericea	20.26 ± 0.27 [b]	10.3 ± 1.0 [a]	22.2 ± 0.2 [c]	67.5 ± 1.2 [c]

Table 2. Mean, SD in brackets, test comparison of means of HHV and chemical composition by biomass group. Note: mean values with the same letter are not significantly different for $p < 0.05$ by Duncan New Multiple Range test HHV–Higher Heating Value; n = number of samples used in each group.

Groups	n	HHV ($MJ \cdot kg^{-1}$)	Extractives (%)	Klason Lignin (%)	Holocellulose (%)
Agricultural wastes	48	18.5 [a] (1.61)	29.3 [b] (6.05)	21.0 [a] (1.05)	49.6 [a] (6.88)
Forest wastes	48	19.2 [a] (1.03)	20.1 [a] (13.38)	23.6 [b] (4.55)	56.3 [b] (9.97)
Shrubs	72	20.5 [b] (0.70)	15.3 [a] (5.47)	22.1 [ab] (2.60)	62.6 [c] (6.15)

The percentage of extractives is relatively high (24–38%), both in agricultural and forestry wastes, except for the very low values of *Eucalyptus globulus* wood (3.2%) and *Pinus pinaster* wood (12.6%). On the other hand, shrubs have much lower values, with values between 9.7 and 24.4% (Table 1). In addition, the variability of the extractive values within each of the 1 groups is relatively high, with *sd* values ranging from 5.5 to 13.4%, as can be seen in Table 2.

The contents of Klason lignin are globally identical, being between 18 and 23%, with the exception of the wood of *Eucalyptus globulus* (25.9 %) and *Pinus pinaster* (29.6%) as well as the *Pterospartum tridentatum* (24.4 %) and *Erica* sp. (25.1 %) (Table 1). For holocellulose contents, agricultural wastes have the lowest levels (39 to 54%), followed by forest wastes (47 to 71%) and the highest values in the shrub species (52 to 68%).

3.1.1. HHV and Chemical Composition–Agricultural Wastes

Regarding the biomass of the agricultural wastes, it is verified that Olea europaea and Prunus *dulcis* are the species that display higher HHV values than *Vitis vinifera*. As for the chemical composition, *Olea europaea* presents higher levels of extractives and lignin and lower contents of holocellulose, compared to *Prunus dulcis* and *Vitis vinifera* (Table 1). The variability between the biomass of the wastes of the different species is very low since the values of the standard deviation are between 0.02 and 2.96.

3.1.2. HHV and Chemical Composition–Forest Wastes

Comparing the biomass of the wastes of the forest species, the component with the lowest HHV is eucalyptus wood (17.6 MJ·kg^{-1}). The wastes of the two species listed in Table 1 show higher values (19.7 and 19.4 MJ·kg^{-1}), as well as *Pinus pinaster* wood (20.1 MJ·kg^{-1}). Regarding the chemical composition, wood contain less extractives and more lignin and holocellulose compared to residues (Table 1).

3.1.3. HHV and Chemical Composition–Shrub Biomass

In general, *Pterospartum tridentatum* and *Erica arborea* have higher values of extractives and lignin and less amount of holocellulose compared to the remaining shrub species, as can be seen in Table 1. The HHV is similar between species, in the range of 20.3 MJ·kg^{-1} to 21.3 MJ·kg^{-1}, with the exception of *Ulex* having a lower value (19.4 MJ·kg^{-1})

3.1.4. HHV and Chemical Composition–Correlation Analysis

Table 3 shows that there is a trend of positive dependence of the higher heating value with the Klason lignin contents in the biomass, than the other parameters evaluated. It can also be observed that there is a strong and statistically significant negative correlation between extractive amounts and holocellulose.

Table 3. Correlation coefficient matrix of HHV (MJ·kg^{-1}), and chemical composition analysis (%).

Components	HHV (MJ·kg^{-1})	Extractives (%)	Klason Lignin (%)	Holocellulose (%)
HHV (MJ·kg^{-1})	1.000			
Extractives (%)	0.007	1.000		
Klason Lignin (%)	0.242	–0.482	1.000	
Holocellulose (%)	–0.089	–0.954 ***	0.197	1.000

Correlation significance level for r > 0.532 *, r > 0.661 **, r > 0.780 ***

4. Discussion

4.1. Higher Heating Value

There are differences between the Higher Heating Values for the different analyzed groups and species. From the results obtained in the analysis between the different groups, it is verified that the shrub species present relatively higher heating value values (19 to 21 MJ·kg^{-1}) when compared with the agricultural and forest species (17 to 21 MJ·kg^{-1}). However, the values obtained are relatively lower than those reported by Viana et al. [26] in a study also performed in northern Portugal and Galicia (NW Spain), ranging from 21 to 24 MJ·kg^{-1}. Although the values were lower, in another recent study by Viana et al. [27], the trend was similar, *Pinus pinaster* wood presented higher calorific power values (21.6 MJ·kg^{-1}) compared to *Eucalyptus globulus* wood (19.18 MJ·kg^{-1}).

Regarding the forest species, it is verified that woody biomass of *Pinus pinaster* have higher values of calorific value when compared to eucalyptus residues. This trend confirms in the reference [10] in which one of the main conclusions is that, in general, the softwood species presents higher values of calorific value when compared with hardwood species.

However, this is not always the case. For example, Franco et al. [28], presented a study of reactions influencing the biomass steam gasification process, in which the higher heating value of the pine wood is lower than *Eucalyptus globulus* wood. This trend may be in line with the White 1986 conclusion that HHV differences between hardwood and softwood may be more related to the presence of extractives than to the lignin content.

Regarding the residues biomass (branches and leaves), there were no significant differences of HHV values between species, with mean values between the calorific value of *Eucalytpus globulus* and *Pinus pinaster* wood.

Within each species, it was found that the woody *Pinus pinaster* component has comparatively higher HHV compared to *Pinus pinaster* residues, while for the *Eucalyptus globulus* there is the opposite.

This results agrees with the study carried out by Viana et al. [29], where the higher heating value of each component (wood stem, bark stem, top, branches and leaves) of the two species was evaluated. However, in two studies carry out to *Pinus pinaster* in the north of Spain show that the HHV of woody component is slightly lower than branches and leaves [30,31].

Some of these results conflicts may be due to the different proportion of each component (branches, needles, bark and top) in the analysed samples, whose HHV values are in some cases different. For example Viana et al. [27] obtained the following values of HHV: Top = 20.65 MJ·kg^{-1}; Branches = 20.92 MJ·kg^{-1}; Needles=21.61 MJ·kg^{-1}; Álvarez-Álvarez et al. [30] Crown = 19.96 MJ·kg^{-1}, Bark = 19.84 MJ·kg^{-1} and Torres [31]: Bark = 20.72 MJ·kg^{-1}; Branches + Needles = 20.75 MJ·kg^{-1}.

Relative to the values of higher heating value in shrub species, *Pterospartum tridentatum* and *Ulex europaeus* were the lowest species (20.2 MJ·kg^{-1} and 19.41 MJ·kg^{-1}, respectively), being very similar values to the study by Martinez-Gonzalez et al. [32] in Galicia (Spain).

As regards the agricultural waste it is verified that the *Olea europaea* is the species with the highest heating value, followed by the *Prunus dulcis*, 21.1 and 18.2 MJ·kg^{-1}, respectively. This values are higher than two other similar studies carry out in the Mediterranean region [33] and [34] which refer HHV values for *Olea europaea* of 17.34 MJ·kg^{-1} and 15.23 MJ·kg^{-1} respectively, and for *Prunus dulcis* of 17.55 MJ·kg^{-1} and 15.84 MJ·kg^{-1}, respectively. Nevertheless, the authors of both studies warned about the fact that these values are slightly lower than those proposed in the bibliography references, which assign as a possible cause the adoption of different methodologies used by them. However, references [35] and [36] presented values of 18.2 MJ·kg^{-1} and 18.4 MJ·kg^{-1}, respectively, for the wastes of *Prunus dulcis*, as well as Sanchez and Miguel [37] and Woods et al. [38] presented HHV values of 21.1 MJ·kg^{-1} and 21.2 MJ·kg^{-1}, respectively for *Olea europaea* wastes, which are very similar to the values of the present study.

In the *Vitis vinifera* samples of the two study areas, it is verified that the HHV presents very similar values (about 17.3 MJ·kg^{-1}). Taking into account the fact that the two basins under study have very different soil and climatic conditions, we can deduce that the geographic location has a very small contribution to the HHV differences in this type of waste. However, in other studies performed for the same species, HHV values are higher (e.g., Reference [39] presented values between 18.75 and 19.9 MJ·kg^{-1}; Puglia et al. [40] between 18.54 and 19.0 MJ·kg^{-1}).

4.2. Chemical Composition

4.2.1. Holocellulose (Cellulose and Hemicelluloses)

Holocellulose is a water-insoluble carbohydrate fraction of wood materials. From the results obtained it is verified that the agricultural species show the lower amounts of this compound (49.6%) and the shrubs the greater (62.6%). The lower values of the agricultural species could be related to a partial decomposition of organic matter that occurs when biomass is exposed for a long time to weathering and the action of natural micro-organisms. Between agricultural wastes, the Olea europaea present the lowest holocellulose contents (39.2%), may be due to the expressive amounts of extractives.. In a study with same species carried out by Garcia-Maraver [41] in Granada (Spain), the quantities of holocellulose are still smaller (31%) compared to this study (39%), although the methodology used was different. However, part of this difference in results may be due not only to differences in the method used, but also to differences in the proportion of leaves present in the samples. For example, in the aforementioned study in [41] in which the chemical composition in the different components of *Olea europaea* was evaluated, it was verified that higher percentage of holocellulose were found in the wood component (47%), followed by pruning residues (partially composed of leaves) with 30%, and olive leaf samples only 10%, confirming, therefore, that one of the main sources of variation of holocellulose contents of this type of wastes are due to the presence of leaves.

Regarding forest species, the results obtained reflect higher levels of holocellulose in Eucalyptus globulus wood (70.9%), too much higher than values of 46.9% to 57.8% present in the other forest wastes. Requejo et al. [42] presented a study carried out in Córdova (Spain), where holocellulose values for *Eucalytus globulus* species were very similar, about 72%.

This values are in agreement with the literature that states that the hardwoods present higher values of holocellulose to the softwoods ones [10,43–46]. Another situation that can be highlighted in the forest wastes, is the contents of holocellulose in leaves and branches (*Eucaliptus globulus* 49.7% and *Pinus pinaster*, 46.9%) are much lower than the woody component (70.9% from *Eucalyptus globulus* and 57.8% from *Pinus pinaster*).

4.2.2. Lignin

Lignin is a natural biopolymer found in lignocellulosic biomass. The structure and chemical composition of lignin vary in different plant species, or while using different extraction processes and subsequent treatments, thus increasing the complexity of lignin processing and decreasing its applicability in industrial processes [47]. In an overall analysis of the results it is verified that the highest values of lignin content were observed in the forest wastes, in which the leaves and branches component showed much lower levels of lignin (19.4% and 19.5%) compared to woody component (25.9% and 29.6%), whose values are identical to those reported by references [48–51].

Moreover, it is possible to verify that the softwood species contain higher levels of lignin relative to the hardwood species, as reported by Sorec et al. [52] and Iskjorard et al. [53].

The agricultural wastes were the group that presented lower levels of lignin, with a small variation of values between them (20.3% to 22.6%). The *Olea europaea* wastes presented the highest lignin contents (22.6%), being this value comparatively to two studies carried out in Spain, slightly higher than the values obtained by Requejo et al. [42] (19.71%) and lower then [41] (27.43%), but identical to that referred to reference [54] (21.5%). The same trend is observed for *Prunus dulcis* wastes, which results obtained (20.9%) are lower than other similar work in Greece (26.5%) [54].

From shrub species studied, *Cytisus* sp. and *Ulex europaeus* were the ones with the lowest lignin levels (17.8% and 20.0%, respectively). However, in other studies performed for the same species, the contents of this macromolecule were higher, e.g., in [32,55–57] with values that comprised between 22% to 24% for *Cytisus* spp and [32,58–60] with lignin content between 21 and 30% for *Ulex europaeus*).

4.2.3. Extractives

Contrary to the trend of lignin content in the different groups analyzed, the agricultural wastes are those with the highest values of extractives. In relation to shrubs, agricultural wastes present almost double of the extractives amounts.

Among the agricultural species, the *Olea europaea* wastes were those that presented higher values (38.2%). In a study conducted by Cara et al. [61], lower extractive amount values were observed (31.4%). As these authors point out *Olea europaea* pruning is lignocellulosic agricultural residue generated yearly, widely available especially in Mediterranean countries and lacking economic alternatives. A typical *Olea europaea* pruning lot includes thin branches (70% by weight, with approximately one third of leaves) and wood (branches >5 cm diameter) although variable amounts and compositions of pruning are possible, depending on culture conditions, production and local uses. This difference in extractive contents may thus be a consequence of the differences in the proportion of each pruning component (thin branches, leaves and wood), different conditions of culture, location and production of the specie.

In the quantification of the extractive contents in the forest species, it was verified that the residues (branches and leaves), both of the *Eucalyptus globulus* and of the *Pinus pinaster*, contain much higher values with respect to the wood, being able to generalize both in the hardwoods and in the resinous ones. This trend is reflected in other studies, for example, [62] and [63].

Among the shrub species, it was verified that these were the ones that presented lower values and, within this group, the outstanding species is the *Erica arborea*, with contents very close to 25%. Compared with other similar works, namely Carriou-Prieto [64], Tsounamis [65] and Leroy et al. [66], it was found that the content obtained is overestimated. However, it is judged that the significant difference of contents is due to the difference in extraction method. In the present work, three polar and non-polar solvents (dichloromethane, ethanol and water) were used with degrees of increasing polarity, which increased the extraction capacity.

4.3. HHV and Chemical Composition Correlation

Although there is a tendency for HHV to be positively dependent on the amounts of lignin, its predictive capacity is relatively low (r = 0.242), which means that there are other characteristics with significant weight in the variation of HHV. The same trend was observed in 2012 in a study presented by Khider and Elsaki [67].

There was also a strong correlation (r = –0.954) and statistically significant between extractive content and holocellulose. Paula et al. [68], in a study carried out in Brazil with agricultural and forestry wastes, showed a very similar trend to this study, that is, a high and negative correlation (-0.694) between the extractive contents and the holocellulose. In 1997, Ona et al. [69] found a negative and highly significant correlation (r = –0.614) between holocellulose contents and extractives from woody residues of hardwood species. In the same study, these authors verified a negative and non-significant correlation between the lignin and holocellulose contents.

5. Conclusions

The possibility of exploiting different residual agroforestry biomass wastes for energy purposes was investigate in this work. The biomass was analyzed to assess if its thermo-chemical characteristics are suitable for this utilization. In general, softwood species tend to have higher HHV, extractives and lignin contents than hardwood species.

The chemical properties of the different biomass wastes affect their thermal behavior. In general, the heating value of biomass increases with the Klason lignin content. In the case of forest wastes, in both studied species (*P. pinaster* and *E. globulus*), the woody component always presented higher levels of holocellulose, and lignin and lower extractive content, compared to the corresponding waste component (leaves and branches). In addition, the calorific value of the woody component of *P. pinaster* is also higher than the component of the residues, although, in the case of *E. globulus*, the opposite occurs. In this way, it can be concluded that there is a general tendency for the woody components present thermo-chemical properties more suited for energy purposes, than the residues formed by the branches and leaves. That is, although the residual biomass from pruning can be used for bioenergy, this product will not perform as good as the corresponding woody component coming from the stem of the trees.

Regarding the agricultural wastes, when compared to the other two groups (forest wastes and shrubs), they are the ones with lower HHV values, higher extractive contents and lower lignin and holocellulose contents. Within this group, *Olea europaea* differs from the other species because it presents the highest values of HHV, the highest contents of extractives and lignin, and the lowest values of holocellulose.

Finally, regarding the shrub species, it can be concluded, when compared to agricultural and forest wastes, that they are the ones that present the highest values of HHV, lower values of extractives and the highest values of holocellulose, thus presenting good thermochemical properties to be used for energy purposes, such as the woody component of the forest wastes.

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