

Article

Waste Recovery through Thermochemical Conversion Technologies: A Case Study with Several Portuguese Agroforestry By-Products

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Received: 11 June 2020; Accepted: 4 September 2020; Published: 10 September 2020



Abstract: Agroforestry waste stores a considerable amount of energy that can be used. Portugal has great potential to produce bioenergy. The waste generated during agricultural production and forestry operation processes can be used for energy generation, and it can be used either in the form in which it is collected, or it can be processed using thermochemical conversion technologies, such as torrefaction. This work aimed to characterize the properties of a set of residues from agroforestry activities, namely rice husk, almond husk, kiwi pruning, vine pruning, olive pomace, and pine woodchips. To characterize the different materials, both as-collected and after being subjected to a torrefaction process at 300 °C, thermogravimetric analyses were carried out to determine the moisture content, ash content, fixed carbon content, and the content of volatile substances; elementary analyses were performed to determine the levels of carbon, nitrogen, hydrogen, and oxygen, and the high and low heating values were determined. With these assumptions, it was observed that each form of residual biomass had different characteristics, which are important to know when adapting to conversion technology, and they also had different degrees of efficiency, that is, the amount of energy generated and potentially used when analyzing all factors.

Keywords: biomass waste; torrefaction; energy recovery; circular economy

1. Introduction

The use of biomass as an energy source currently presents itself as an alternative to fossil fuels in the generation of different forms of energy, namely in the generation of electrical and thermal energy [1–3]. There are several research works that have characterized the main forms of biomass commonly used in energy generation [4–6]. However, given the growing demand for these traditional forms of biomass, there has been an increasing pressure on resources, which are beginning to suffer a sharp decrease in availability, leading to the need to find other alternatives, namely those forms of biomass that are considered waste or by-products [7].

Among this group of residues or by-products, it is possible to identify a wide range of materials that, if properly framed and processed, can be presented as alternatives to traditional forms of biomass, both for the characteristics they present and the quantities available [8]. The fact these by-products exist in abundance is also problematic in some situations, mainly from an environmental perspective, since the volume generated from some waste is significant enough that, if an alternative is not found for its use and recovery, simple placement and landfilling does not appear to be a viable solution [9].

In this way, energy recovery is an alternative to landfilling since it can dispose large quantities of waste and by-products that, until now, have had no use (or when they do, it has been the limited use of a small amount of the total produced and, therefore, is not a definitive solution to the problem) [10]. This group of residual biomass forms includes those from the agroforestry industry, and Portugal has a number of examples that can be introduced into the supply chain of units dedicated to the production of energy from biomass [11].

However, from accumulated experience and the information made available by various previous works, it is possible to identify a diverse set of disadvantages and problems associated with the energy recovery of these materials, namely problems related to the low density, low calorific value, high moisture content, and geographic dispersion, but also issues related to extensive contamination with inert materials, high levels of chlorine, or even the presence of high levels of alkali metals [12].

The use of thermochemical conversion technologies, namely torrefaction, presents itself as a potential solution to pre-process these forms of residual biomass since it has shown good results in improving properties related to the combustibility of materials, namely those related to increasing energy density, or to the elimination of chlorine [13]. In the specific case of Portugal, there are several residues and by-products of agricultural and forestry origin. For the present study, six types of residual biomass or by-products were chosen that were readily available in terms of quantity and geographical dispersion. The selected residues or by-products were rice husk, almond husk, kiwi pruning, vine pruning, olive pomace, and pine woodchips.

This work aims to characterize these forms of waste and by-products for energy generation through laboratory tests, namely elemental, thermogravimetric, and energy analyses of materials, both in thermally untreated versions and with the materials submitted to torrefaction at 300 °C. In this way, we intend to effectively compare potential improvements before and after heat treatment and, thus, assess whether waste and by-products have potential use in energy recovery or any other application.

2. State-of-the-Art

Sustainable biomass use for the production of bioenergy has increasingly called for the use of biomass waste, to the detriment of dedicated biomass, which competes with other land uses [14–17]. However, biomass waste often has a low bulk density, high moisture or ash content, and is mechanically resistant to crushing, which limits the use of the available biomass for energy or material recovery [18–20]. Torrefaction is a thermal pre-treatment that can contribute to improving the physical and chemical properties of biomass, facilitating its mechanical processing and increasing its stability and energy density [21–23]. In the case of species attacked by pests, torrefaction is also a sterilization process that limits the risk of these pests spreading during storage [24–26].

In Portugal, the demand for forest-based biomass in energy production has increased significantly due to incentives for the construction and operation of thermoelectric plants with subsidized tariffs [12,25,27,28]. The recent national growth in the pellet market for heat production in domestic or industrial boilers has resulted in a further increase in demand for biomass [25,29]. However, this growing use of biomass for energy production may lead to its scarcity; therefore, it is necessary to assess the potential use of other types of biomass available in Portugal, namely residual biomass from agricultural activities and food processing (agroindustry) and other woody species and shrubs [16,30,31]. These alternative biomasses have different characteristics due to the quality of woody biomasses, which can significantly influence the supply and pre-treatment chain, combustion processes, ash behavior

(slagging, fouling, and corrosion), and environmental constraints associated with energy conversion processes [32–34].

The use of solid biofuels for energy production plays an important role in reducing greenhouse gas emissions, as well as in the diversification of energy sources, thereby reducing dependence on external sources [35–37]. The increase in research in this area, as well as the development of standards and technical documents, highlight the political, social, and economic relevance of solid biofuels [38,39]. Intensive use of wood-based fuels in co-combustion processes has put enormous pressure on forests [40,41]. To alleviate this pressure and simultaneously increase the use of biomass in co-combustion processes, thereby reducing CO₂ emissions, it is necessary to increase the use of alternative residual fuels, namely agricultural waste [29,42]. Co-combustion of these alternative biomasses can cause operational problems due to the presence of alkali metals, chlorine, and other elements in the ashes of these materials, and it can enhance the corrosion of metallic surfaces and the emission of small particles [43,44]. This can limit the variety of residual biomass that can actually be used in co-combustion processes [32,38,45].

From an economic perspective, the use of residues of agroforestry origin has a set of very significant advantages, since they constitute an alternative to the use of other types of biomass that already have other uses [46–48]. In this way, when other supply chains are created, competition between traditional industries is avoided, such as pulp and paper or the production of wood pellets, with the production of energy [49–51]. This non-competition allows, first, the use of resources that until now have not been used, and therefore, with low market value, its cost depending only on the complexity of its supply chain; and, second, the creation of a truly sustainable option, in a perspective of circular economy, where all resources are valued, to the detriment of the intensive exploitation of forest resources [52–54].

3. Materials and Methods

3.1. Sample Collection and Preparation

To verify the evolution of the properties of the residues and by-products resulting from the torrefaction process, several analyses were carried out. Thus, different techniques were used such as thermogravimetric (fixed carbon content, volatiles, ash, and moisture), elemental (C, H, O, and N), and heating value analyses.

Samples of rice husk, almond shells, kiwi pruning, vine pruning, olive pomace, and pine woodchips were collected and, when necessary, cut to obtain a granulometry that would allow the materials to be efficiently processed. These materials were selected because they are representative of types of waste and by-products from the agroforestry industry. They exist in great abundance and are, therefore, available to potentially work as alternatives if they are found to have physicochemical characteristics compatible with efficient energy recovery. After collection, the samples were dried in a laboratory oven at 90 °C for 24 h.

Samples were prepared by weighing approximately 250 g of the material. Preparations were made with the aid of conventional aluminum foil in which the objective was to wrap the samples in a cylindrical shape. Since aluminum foil has two distinct sides, it should be noted that the opaque part of the sheet was directed towards the outside so that during the torrefaction process the heat was not reflected.

In this work, the torrefaction protocol used was the one described by Ribeiro et al. (2018) [55], in which a high-temperature oven or ceramic muffle was used. The oven was composed of a metallic monobloc, covered inside by refractory bricks, and had a kaolin canvas for insulation. The muffle was heated by the heat transfer produced from the electrical resistances found inside. The samples were torrefied in a muffle, which had a built-in controller and the ability to program the residence time and four temperature thresholds. There was a cavity on top of the equipment in order to facilitate extraction of the torrefaction gases. The muffle was then programmed according to the desired temperature

(°C) and residence time (minutes), with each level corresponding to different torrefaction phases, as presented in Table 1.

Table 1. Correspondence of the four programmable levels with the different torrefaction phases, depending on the temperature and residence time.

Level	Torrefaction Phase	Temperature (°C)	Residence Time (min)
1	Heating/Drying	T _{room} (18 °C) to T ₁	Rt ₁
2	Drying/Torrefaction	T ₁ to T ₂	Rt ₂
3	Torrefaction	T ₂	Rt ₃
4	Cooling	T ₂ to 50 °C	Rt ₄

Table 2 defines the parameters used for each series of torrefaction tests, and the materials obtained in the torrefaction process are shown in Figure 1.

Table 2. Torrefaction tests.

Temperature (°C)	Residence Time (min)
18–180	30
180–300	60
300	90
300–50	The time needed to safely collect the material

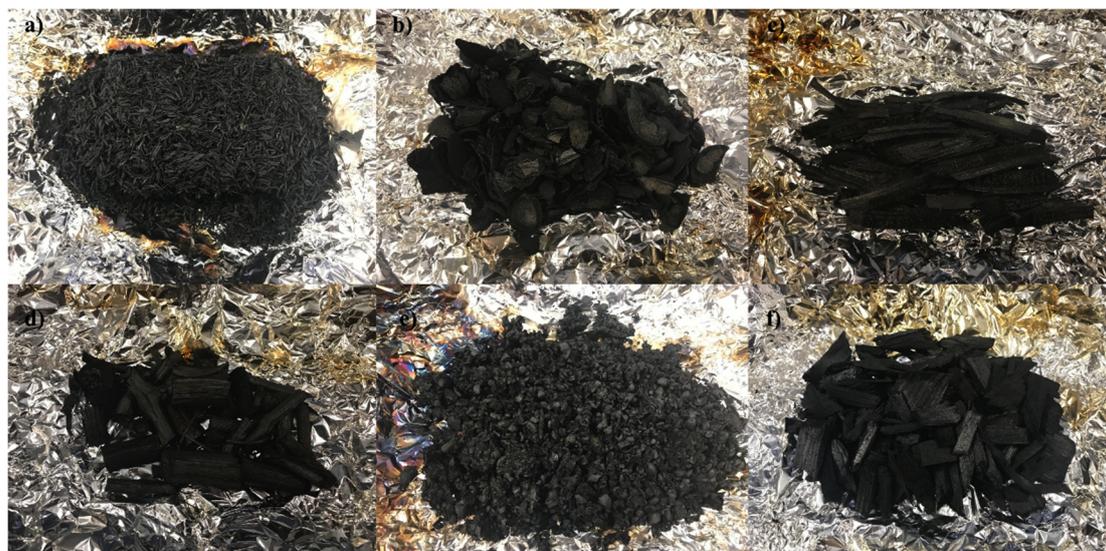


Figure 1. Obtained materials: (a) rice husk; (b) almond shells; (c) kiwi pruning; (d) vine pruning; (e) olive oil pomace; and (f) pine woodchips.

3.2. Ultimate Analysis

To determine the elemental composition of the samples, an elemental carbon, hydrogen, and nitrogen analyzer was used. Its operation consisted of incinerating the samples at 900 °C in an atmosphere rich in oxygen so that all organic compounds were burnt using CO₂, H₂O, N₂, and SO₂ as final products. Subsequently, through a gas chromatography detector, the levels of carbon, hydrogen, and nitrogen were obtained. The calibration line used for this procedure was obtained from the analysis of barley (barley sample calibration method for CHNS, LECO®) with known concentrations of carbon,

hydrogen, and nitrogen. After obtaining the results, the oxygen content of the samples was then estimated based on Equation (1):

$$w(\text{O}) = 100 - w(\text{C}) - w(\text{H}) - w(\text{N}), \quad (1)$$

where $w(\text{O})$ is the oxygen content (%), $w(\text{C})$ is the carbon content (%), $w(\text{H})$ is the hydrogen content (%), and $w(\text{N})$ is the nitrogen content (%).

3.3. Proximate Analysis

Thermogravimetric analysis (TGA) is a method used to analyze the loss of mass of a given sample of organic, inorganic, or synthetic origin, depending on the evolution of temperature in a controlled atmosphere defined by the user [56]. For the TGA analysis, the equipment used consisted of an oven with a precision scale inside where melting pots for measuring the samples were inserted. The analyses were conducted in an atmosphere with a nitrogen flow of 150 mL/min and a heating rate of 50 °C/min, from room temperature to 900 °C, in accordance with the standards EN 14775:2009, Solid Biofuels—Determination of Ash Content; EN 15148:2009, Solid Biofuels—Determination of Volatiles Content; and EN 14774-3:2009, Solid Biofuel—Determination of Moisture Content. During the heating process, the moisture content, volatile content, and fixed carbon content were determined precisely in this sequential order. Finally, the ash content was determined from the final residue present in the sample. This procedure required the samples to be previously ground before being introduced into the melting pots. The grinding process was carried out for short periods of time of 8 to 10 s. When starting the process, the melting pots were inserted into the equipment, where 1 g of sample was introduced in each of the melting pots. An empty reference melting pot was used as a blank sample.

3.4. Determination of Heating Value

Moran and Shapiro (2002) objectively defined the heating value of a fuel as a positive number equal to its combustion enthalpy module, and this can be further defined as the high heating value (HHV) and the low heating value (LHV) [57]. The HHV is obtained when all the water formed in the combustion is liquid, and the LHV is obtained when all the water formed in the combustion is steam; the difference between these heating values is equivalent to the energy needed to vaporize the water formed in the combustion [58]. These values have great relevance in designing combustion equipment, and the measurement of HHV is important to characterize a fuel. For solid fuels with certain previously known characteristics, the HHV and LHV can be calculated with specific equations, using both elemental and thermogravimetric analyses [59]. In the literature, the HHV is commonly calculated with an equation according to the elemental analysis of biomass fuels, as variations of the main elements such as carbon, hydrogen, and oxygen are relatively small for any biomass. Observing this information, it is possible to use an equation to determine the HHV as long as the elemental analysis is known [60]. Large variations in the heating value of a biomass are caused by its moisture and ash content. Channiwala and Parikh (2002) presented a universal equation (Equation (2)) for calculating the HHV of several fuels [61]:

$$\text{HHV} = 0.3491 \times \text{C} + 1.1783 - 0.1034 \times \text{O} - 0.0151 \times \text{N} - 0.0211 \times \text{Ashes} + 0.1005 \times \text{S}, \quad (2)$$

whose validity range is $0\% \leq \text{C} \leq 92.25\%$; $0.43\% \leq \text{H} \leq 25.15\%$; $0.00\% \leq \text{O} \leq 50.00\%$; $0.00\% \leq n \leq 5.60\%$; $0.00\% \leq \text{S} \leq 94.08$; $0.00\% \leq \text{Ashes} \leq 71.4\%$; and $4.75 \text{ MJ/kg} \leq \text{HHV} \leq 55.35 \text{ MJ/kg}$. Normally, for solid fuels, the value determined in the laboratory is the HHV of the dry material. The LHV of the dry material is calculated from the HHV and the elemental analysis, where the enthalpy of water vaporized during combustion is discounted [62]. The formula for calculating the LHV is shown as follows (Equation (3)) [61]:

$$\text{LHV} = \text{HHV} - m_{\text{H}_2\text{O}} \times \Delta H_{\text{H}_2\text{O}_{\text{vap}}} (25 \text{ }^\circ\text{C}), \quad (3)$$

where $\Delta H_{\text{H}_2\text{O}_{\text{vap}}}$ (25 °C) is the enthalpy of water vaporization at 25 °C.

The mass of water formed during combustion is calculated using the following expression (Equation (4)):

$$m_{\text{H}_2\text{O}} = 9 \times H \quad (4)$$

where H is the hydrogen content in the dry solid fuel, determined from the elementary analysis presented above [58,61].

4. Results

4.1. Elemental Analysis

The results obtained from the elemental composition analysis are shown in Table 3.

Table 3. Ultimate analysis for the different products.

Elements		Rice Husk	Almond Shells	Kiwi Pruning	Vine Pruning	Olive Pomace	Pine Woodchips
C (%)	Dried	48.60	58.40	49.40	48.30	56.20	50.20
	300 °C	52.60	79.90	75.50	73.40	81.70	80.10
H (%)	Dried	4.42	5.24	5.69	5.71	6.83	5.86
	300 °C	2.91	3.77	3.62	3.80	3.66	3.91
N (%)	Dried	0.574	0.242	0.559	0.748	1.210	0.100
	300 °C	0.833	0.470	1.600	1.320	1.560	0.227
O (%)	Dried	46.41	36.12	44.35	45.24	35.76	43.84
	300 °C	43.66	15.86	19.28	21.48	13.08	15.76

From the results, it can be seen that the carbon content increases in all samples analyzed, varying for dry material from 48.30%, from vine pruning, up to a maximum of 58.40%, from almond shell. The dry samples of rice husk, kiwi pruning, olive pomace, and pine woodchips showed values, respectively, of 48.60%, 49.40%, 56.20%, and 50.20%. After the torrefaction test, the carbon content rose in all samples, with gains between 8% for rice husk and 60% for pine woodchips. The samples of almond shells, kiwi pruning, vine pruning, and olive pomace, showed gains, respectively, of 37%, 53%, 52%, and 45%. Hydrogen and oxygen showed a decrease in the levels quantified in the dry samples, for the roasted samples. Thus, there are decreases of, respectively, 34%, 28%, 36%, 33%, 46%, and 33%, for hydrogen contents. For oxygen levels, there are decreases of 6%, 56%, 57%, 53%, 63%, and 64%, respectively. For nitrogen levels, there are percentage increases of 45%, 94%, 186%, 76%, 29%, and 127%, respectively.

4.2. Thermogravimetric Analysis

The results obtained from the proximate composition analysis are shown in Table 4.

Fixed carbon showed a percentage increase from the dry to the torrefied state, in all samples analyzed, being, respectively, 157%, 255%, 251%, 217%, 292%, and 310%. On the other hand, moisture shows a decrease of 62%, 85%, 73%, 75%, 36%, and 28%, respectively. Ashes have a contrary trend, clearly increasing, and are related to the loss of mass, as will be analyzed in more detail, with a percentage increase in the content of, respectively, 109%, 154%, 281%, 176%, 248%, and 248%. On the other hand, the volatile content decreases, with decreasing values of 67%, 71%, 67%, 63%, 73%, and 68%, respectively.

Table 4. Thermogravimetric composition for the different products.

Properties		Rice Husk	Almond Shells	Kiwi Pruning	Vine Pruning	Olive Pomace	Pine Woodchips
Fixed Carbon (%)	Dried	17.55	20.73	19.54	20.04	18.84	17.82
	300 °C	45.10	73.63	68.57	63.57	73.78	72.98
Moisture (%)	Dried	11.55	8.64	10.87	10.84	3.51	2.61
	300 °C	4.37	1.26	2.98	2.68	2.26	1.87
Ashes (%)	Dried	15.86	1.60	1.32	2.89	1.31	0.27
	300 °C	33.19	4.07	5.03	7.98	4.56	0.94
Volatiles (%)	Dried	66.59	77.67	79.14	77.06	79.85	81.91
	300 °C	21.71	22.30	26.40	28.46	21.66	26.08

4.3. Heating Value

The results obtained from the high heating value calculations are shown in Table 5.

Table 5. High heating values calculated for the different torrefaction temperatures.

Properties		Rice Husk	Almond Shells	Kiwi Pruning	Vine Pruning	Olive Pomace	Pine Woodchips
HHV (MJ/kg)	Dried	17.03	22.79	19.33	18.84	23.92	19.89
	300 °C	16.56	30.60	28.50	27.69	31.36	30.92
LHV (MJ/kg)	Dried	15.28	20.71	17.07	16.58	21.22	17.57
	300 °C	15.41	29.11	27.07	26.19	29.91	29.37
Mass loss (%)		56.90	68.00	66.00	63.50	71.10	69.50

The values of HHV and LHV, with the exception of the values corresponding to the rice husk samples, which suffered a decrease from the dry to the torrefied state, showed a significant increase, which reached its maximum value in the samples of pine woodchips, with a 55% gain for HHV. Mass losses were significant in all samples, with the lowest value corresponding to the rice husk sample, with 56.90%, and the highest value corresponding to the olive pomace sample, with a mass loss of 71.10%.

5. Discussion

The fixed carbon content present in a given fuel is directly related to the amount of energy it is able to supply [63]. The higher this content, the slower the fuel will burn, and this can guarantee total combustion and more efficient energy recovery [64–66]. The values of fine carbon content for the six materials studied, even without thermal treatment at 300 °C, were in the range between 17.55% for rice husks and 20.73% for almond shells. For the remaining materials, the fixed carbon contents were around an average of $19.06 \pm 0.83\%$. The values obtained were in line with those presented in previous studies, namely by Kalderis et al. (2014) for rice husk [67], Demirbaş (2002) for almond husk [68], Torreiro et al. (2020) for kiwi pruning [69], San José et al. (2013) for vine pruning [70], Nunes et al. (2020) for olive pomace [71], and Nunes et al. (2019) for pine chips [72]. For the same materials, after being subjected to the heat treatment process by torrefaction, there was an expected increase in the fixed carbon content as described in several previous works for biomass materials, namely the works of Faizal et al. (2018), Lau et al. (2018), and Conag et al. (2017) [73–75]. The smallest percentage increase corresponded to rice husk, which stood at 45.10%, a value 25% lower than the average value obtained for the remaining materials, which was $70.51 \pm 3.96\%$. These values were also in line with those obtained in previous studies, namely Chen et al. (2020) for rice husk [76], Chiou et al.

(2018) for almond shell [77], Margaritis et al. (2020) for vine pruning [78], Volpe et al. (2015) for olive pomace [79], and Phanphanich and Mani (2011) for pine chips [80]. This significant difference in fixed carbon content for rice husk is certainly related to the very high ash content, which was also demonstrated during product characterization. This ash content, as also demonstrated in the works by Pode (2016), Prasara and Gheewala (2017), Raisi et al. (2018), or da Silva et al. (2019), results from the amount of silica that accumulates during the plant's growth in wet soils with a deeply clayey and silty nature [81–84]. This factor is almost entirely eliminated when using rice husk for the purposes of energy recovery. However, this can be of great interest if, in association with energy recovery, the recovery of silica is the main objective, for example, in the production of abrasive products. In the case of kiwi pruning, the only works found in the literature refer to its characterization as a fuel after drying, without any other type of thermal processing such as torrefaction, including works developed by Dyjakon and García-Galindo (2019) or by Boumancher et al. (2019) [85,86]. With reference to works carried out on the application of thermochemical conversion technologies, in this case pyrolysis, Rene et al. (2020) studied the production of biochar from pruning kiwi, employed as an amendment, aiming to evaluate its remediation potential on smelter and mining contaminated soils [87]; however, the data from this study were not used for comparison because the methodological assumptions related to sample preparation were significantly different from those used in the present work. In this way, it can be said quite safely that the characterization of material from pruning kiwi orchards for energy purposes, after pre-treatment using torrefaction, is novel in this work. In the case of Portugal, this may contribute to the creation of a value chain for waste produced annually in large quantities, since the production of kiwi is growing given the excellent edaphoclimatic conditions for this species [88].

When the biomass has a high moisture content, the combustion process is less efficient when compared to a material with a lower moisture content. This is because the higher the moisture content present in the biomass, the greater the energy needed to start the combustion process; in other terms, if more energy is needed to vaporize the water present in the fuel, then less energy will be provided for the endothermic reaction responsible for maintaining combustion [89–91]. Several authors reported that the presence of moisture makes combustion difficult, as the calorific value is reduced, and this increases fuel consumption [92,93]. Other studies also claimed that high humidity generates environmental pollution due to an increase in the volume of combustion products and particulate material, not to mention the corrosion process is accelerated in the final part of the steam generator, and particles accumulate on the heating surfaces [94,95]. In the case of converting biomass into fuel, or as an intermediate pre-processing step specifically for use in gasification processes, Lucena Tavares and dos Santos (2013) stated that a high moisture content does not lead to technical difficulties in gasification, but instead a reduction in the efficiency of the process, since the energy needed to evaporate water and maintain the operating temperature is obtained by increasing the fuel and oxidants [96]. In short, humidity is a limiting factor when choosing fuel, and fuels with values above 50% should not be used because there is not enough energy released to ensure the maintenance of combustion and, consequently, the production of heat [97]. In the present work, all analyzed materials were submitted to a drying process in the laboratory immediately after collection in order to reduce the initial moisture content, which varied between 25% and 60% depending on the material. After this period of forced drying, the thermogravimetric analysis showed values between 2.61% for pine chips and 11.55% for rice husk. After the torrefaction test, there was a profound reduction in the moisture content of the products, with almond shells showing the lowest value at 1.26%, while rice shells showed a value of 4.37%. These values are clearly low and indicate a high potential for the combustion of this waste. These results are in line with those presented in previous studies, such as those carried out by Bazargan et al. (2014) with rice husks, Demirbaş (2002) with almond husks, Manzone et al. (2019) with kiwi pruning, San José et al. (2013) with vine pruning, Nunes et al. (2020) with olive pomace, and Nunes et al. (2019) with pine chips, and all works indicated a good potential for energy recovery [68,70–72,98,99].

Several authors, such as Nunes et al. (2016) or Kalemekiewicz and Chmielarz (2012), found that a high ash content led to a decrease in efficiency due to both the increased consumption of oxygen to melt the ash as well as the loss of heat from ash leaving the reactor, which cannot be fully recovered [100,101]. Other studies also reported that, for use in pre-processing for later gasification, a lower ash content reduced the likelihood of equipment getting clogged and encrusted [102,103]. As with humidity, the ash content also interferes with the calorific value, which causes energy losses in addition to impairing heat transfer [104,105]. Several authors agreed on removing ash from the combustion site, as ash also worsens problems related to the corrosion of the metal equipment, especially if there is a high ash content or high content of alkali metals [106,107]. In the products analyzed in the present work, only the rice husk showed values much higher than acceptable for use in combustion processes: 15.86% and 33.19%, respectively, for samples before and after the torrefaction process. This increase is related to the loss of mass, which in this specific case was 56.90%. The remaining materials presented values in accordance with those determined by previous works, with values ranging from 0.27% for pine chips to 2.89% for vine pruning. After torrefaction, the values fluctuated between 0.94% for pine chips and 7.89% for wine pruning, thus maintaining compliance due to mass losses.

When biomass has a high volatile content, it is easier to start and maintain combustion. For this reason, the combustion process may be faster or become difficult to control, leading to greater fuel consumption; thus, a high content of volatile materials can also affect the combustion process in general [108]. The volatile contents in the present study showed great uniformity. Products not thermally processed presented an average value around $77.04 \pm 4.93\%$, while products submitted to the torrefaction process presented an average value of $24.44 \pm 2.66\%$. This is in agreement with the works of García et al. (2012) or by Sun et al. (2017), where several residual biomasses without thermal treatment are characterized [6,109], or with the work of Singh and Zondlo (2017), where samples of torrefied residual biomass are treated [110].

The results obtained in the elementary analysis differed slightly and insignificantly from other studies [111–115]. These differences are related to the fact that the elementary analysis could have been determined using different methodologies from the one used in the present work. Another reason may be related to the different geographic origins of residual biomass forms used in this characterization, or different soils, a fact that alters the chemical composition of the residues and, consequently, the results [116]. The present work showed, however, a common trend to what would be expected and described in the literature, that is, there was an increase in the levels of carbon and nitrogen in all analyzed materials, and this was consistent with the concentration of the components not eliminated during the process, usually oxygenated and hydrogenated compounds, which lowered the content in all materials after thermal processing by torrefaction.

Regarding the low heating value, there was an increase in line with what was expected, according to previous experiences for all materials, with the exception of rice husk, which showed a very small increase in LHV [32,117–121]. This situation is due to the high ash and mineral content in the rice husk, which will in no way contribute to increasing the energy density after the torrefaction process, a fact that is in line with the verified loss of mass, which was only 56.90%, while for the remaining materials it was $67.62 \pm 2.66\%$. All low heating values indicated a good potential for energetic valorization of the analyzed materials.

6. Conclusions

The growing demand for alternative forms of energy has led to biomass becoming increasingly used as an alternative to fossil fuels. However, different forms of biomass have a number of disadvantages when used as fuels, mainly due to factors such as a lower heating value, low density, high moisture content, or geographic dispersion. In this way, thermochemical conversion technologies, such as torrefaction, can be used as an alternative to improve the properties of these materials, especially if residual forms of biomass are used.

Residual forms of biomass are interesting, as they allow new flows to be incorporated in the supply chain for energy recovery. The agroforestry sector may contribute to this supply chain with various residues and by-products, of which the materials used in this study can be used as an example: rice husks, almond husks, kiwi pruning, vine pruning, olive pomace, and pine woodchips.

We showed an improvement in the properties of the materials after being subjected to the torrefaction process at 300 °C, mainly with regard to the calorific value, reduction in volatile content, and increase in the fixed carbon content. However, in all cases, there was an increase in ash content associated with a loss of mass. In the specific case of rice husks, because they are a form of biomass that, even without thermal treatment, already has a high ash content, the increase in ash after torrefaction renders it unusable as a fuel, except if the ash is extracted and the combustion systems are frequently cleaned, which would help to deter ash encrustation and vitrification.

Despite the viable uses of biomass for energy production, further tests are needed to confirm this potential, including chemical characterizations of different types of waste, namely with regard to the levels of halogens, such as chlorine, or alkali metals, such as sodium and potassium, since these wastes are mainly responsible for the corrosion of combustion equipment, fouling, or slagging.

Author Contributions: Conceptualization, L.J.R.N.; methodology, L.J.R.N. and H.F.C.S.; validation, L.J.R.N., L.C.R.S. and L.M.E.F.L.; formal analysis, L.J.R.N.; investigation, L.J.R.N., L.C.R.S., L.M.E.F.L.; resources, H.F.C.S.; data curation, L.J.R.N., L.C.R.S. and L.M.E.F.L.; writing—original draft preparation, L.J.R.N.; writing—review and editing, L.J.R.N. and H.F.C.S.; supervision, L.J.R.N.; funding acquisition, H.F.C.S. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Acknowledgments: The authors would like to acknowledge the Portuguese companies YGE—Yser Green Energy SA and AFS—Advanced Fuel Solutions SA, both in Portugal, that allowed the execution of the laboratory tests.

Conflicts of Interest: The authors declare no conflict of interest.

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