

Article

Torrefied Biomass as an Alternative in Coal-Fueled Power Plants: A Case Study on Grindability of Agroforestry Waste Forms

Leonel J. R. Nunes ^{1,2,3,4} 

¹ PROMETHEUS—Unidade de Investigação em Materiais, Energia e Ambiente para a Sustentabilidade, Escola Superior Agrária, Instituto Politécnico de Viana do Castelo, Rua da Escola Industrial e Comercial de Nun'Alvares, 4900-347 Viana do Castelo, Portugal; leonelnunes@esa.ipv.pt; Tel.: +351-258-909-740

² GOVCOPP—Unidade de Investigação em Governança, Competitividade e Políticas Públicas, DEGEIT-Departamento de Economia, Gestão, Engenharia Industrial e Turismo, Universidade de Aveiro, Campus Universitário de Santiago, 3810-193 Aveiro, Portugal

³ YGE—Yser Green Energy SA, Área de Acolhimento Empresarial de Úl/Loureiro, Lote 17, 3720-075 Loureiro OAZ, Portugal

⁴ AFS—Advanced Fuel Solutions SA, Área de Acolhimento Empresarial de Úl/Loureiro, Lote 17, 3720-075 Loureiro OAZ, Portugal

Received: 22 June 2020; Accepted: 16 July 2020; Published: 20 July 2020



Abstract: The use of biomass as a renewable energy source is currently a reality, mainly due to the role it can play in replacing fossil energy sources. Within this possibility, coal substitution in the production of electric energy presents itself as a strong alternative with high potential, mostly due to the possibility of contributing to the decarbonization of energy production while, at the same time, contributing to the circularization of energy generation processes. This can be achieved through the use of biomass waste forms, which have undergone a process of improving their properties, such as torrefaction. However, for this to be viable, it is necessary that the biomass has a set of characteristics similar to those of coal, such that its use may occur in previously installed systems. In particular, with respect to grindability, which is associated with one of the core equipment technologies of coal-fired power plants—the coal mill. The objective of the present study is to determine the potential of certain residues with agroforestry origins as a replacement for coal in power generation by using empirical methods. Selected materials—namely, almond shells, kiwifruit pruning, vine pruning, olive pomace, pine woodchips, and eucalyptus woodchips—are characterized in this regard. The materials were characterized in the laboratory and submitted to a torrefaction process at 300 °C. Then, the Statistical Grindability Index and the Hardgrove Grindability Index were determined, using empirical methods derived from coal analysis. The results obtained indicate the good potential of the studied biomasses for use in large-scale torrefaction processes and as replacements for coal in the generation of electrical energy. However, further tests are still needed, particularly relating to the definition of the ideal parameters of the torrefaction process, in order to optimize the grindability of the materials.

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

1. Introduction

At present, the search for renewable energy sources that can serve as substitutes for traditional sources of energy of fossil origin has presented itself as one of the greatest objectives in science and technology, with an emphasis on those that are capable of supplying large amounts of energy and, above all, on those sources that are capable of presenting a real alternative for the decarbonization of the

economy [1–3]. Obviously, it has already been noted that the change from an energy matrix sustained by the consumption of fossil fuels to a renewable one will not be an easy task, especially with regard to the production of electricity as, despite the potential of several possibilities such as wind, solar, and water to contribute significantly to such decarbonization, the electrical demand at present still maintains a very high dependence on generation from coal, given the intermittency of the other sources [4,5]. The intermittency of such renewable sources, which is related to and dependent on climatic factors, necessitates an alternative to coal with the same type of behavior and availability [6,7]. In other words, it is necessary to obtain a type of fuel that behaves like coal and, at the same time, exists in quantities capable of supplanting the enormous reserves and availability of coal, or at least supplementing them, thus contributing to the reduction of greenhouse gas emissions [8]. The sustainable use of biomass for the production of bioenergy increasingly calls for the use of biomass waste, considering the use of dedicated biomass, which competes with other land-uses [9]. However, biomass waste often has low bulk density, high moisture or ash content, and mechanical resistance to crushing, which limits its use for energy production or material recovery [10]. Biomass, which is considered a neutral fuel from the point of view of CO₂ emissions, although presenting a number of disadvantages (namely, its lower calorific value, high moisture content, and low density), can be transformed into a product with greater added value if pre-processed using thermochemical conversion technologies such as torrefaction [11].

Torrefaction is a thermal pre-treatment which can contribute to improving the physical and chemical properties of biomass, facilitating its mechanical processing and increasing its stability and energy density [12]. In the case of species attacked by pests, torrefaction also acts as a sterilization process that allows for limiting the risk of spreading these pests during storage [13]. In Portugal, the demand for forest-based biomass for energy production has increased significantly due to incentives that have been introduced for the construction and operation of thermoelectric plants with subsidized tariffs [14]. The recent national growth of the pellet market for the production of heat in domestic or industrial boilers has resulted in a further increase in demand for biomass [15]. However, the 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, particularly the residual biomass from agricultural activities and food processing (agroindustry), as well as from other woody species and shrubs [16]. These alternative biomass sources have different characteristics from good quality 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 [17,18].

This thermochemical conversion process, which occurs in a temperature range between 220 and 320 °C in an environment with a low oxygen content at atmospheric pressure, is capable of transforming different types of biomass—mainly those that are available in larger quantities and are considered to be unusable waste forms—into energy products with greater added value, of which several byproducts originating from forest cleaning operations, such as sanitary thinning or cleaning to reduce the fuel load, can be highlighted, as well as residues from the agribusiness sector [12,13,19]. 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 [20]. The increase in research in this area, as well as the development of standards and technical documents, have highlighted the political, social, and economic relevance of solid biofuels [21]. The intensive use of wood-based fuels in co-combustion processes has put enormous pressure on forests [22]. To alleviate this pressure, and to simultaneously increase the use of biomass in co-combustion processes (and, thus, reduce CO₂ emissions), it is necessary to increase the use of alternative residual fuels; namely, agricultural waste [15]. The 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, enhancing the corrosion of metallic surfaces and the emission of small particles. This can limit the variety of residual biomass that can actually be used in co-combustion processes [17,21,23].

Portugal is a country with a large production capacity for these types of materials, being associated, on the one hand, with its large forest area and strong forestry industries; and, on the other hand, with the growing development of mechanized and modern agriculture, which has significant production capacities for several products [17]. However, such an abundance of potential resources can also pose problems, given the heterogeneity in the properties and composition (both physically and chemically) of the different products in question. It is in this aspect that torrefaction can provide a viable alternative, allowing for the homogenization of different materials and bringing their physico-chemical properties closer to those of mineral coal; namely, their heating value and lower moisture content, as well as other properties such as hydrophobicity and grindability [24]. In fact, the latter is perhaps the most important, as it allows the torrefied residual materials to be used in existing coal pulverizers without theoretically requiring significant changes in the coal-fired power plants [22].

In order to allow the correct and efficient functioning of boilers using pulverized coal, it is necessary that the coal particles are reduced to a size of at least 75 μm [25]. When biomass is used together with pulverized coal, in a process called co-combustion where the two fuels are used simultaneously, their particles must also be ground until equivalent sizes are reached [26]. However, grinding biomass material (which is always more fibrous) is a process that consumes more energy, as the fibrous structure and tenacity of biomass hinders the grinding process, especially when it still has a high moisture content [27–30].

The use of pre-processing technologies, namely those that occur at temperatures capable of structurally modifying biomass, such as torrefaction, can be used to degrade the hemicellulose chains present in the biomass, which are primarily responsible for its fibrous nature [31–34]. In this way, it is now commonly recognized that thermochemical conversion processes such as torrefaction or pyrolysis can significantly reduce the amount of energy required for grinding biomass, making it possible to reach a final product with similar grinding characteristics to that of coal [35–38].

There are several types of mills and pulverizers for industrial applications on the market, adapted to different purposes and requirements of the final product, which can be divided into the categories presented below (shown in Figure 1) [39–43]:

- (a) A tumbling mill consists of a rotating deposit, where the loose material inside is set in motion by the rotation of the deposit, causing the collision and breaking of the particles. To facilitate the process, spheres or other similar shapes made up of harder materials are often added to the material to be ground;
- (b) Hammer and impact mills use hydraulic steel pistons (or suspended arms) which repeatedly hit the particles to be ground, breaking them until they reach the desired dimension. Normally, sizes are selected by using a graduated sieve or mesh, which the particles pass through when they reach the desired dimension;
- (c) Ring or disc mills consist of a rotating ring or disc, using the inner and outer surfaces of the rotating ring or disc to grind the material when it comes into contact with the moving surface. The degree of abrasiveness of the surface of the disk or ring, as well as the speed of rotation, determine the degree of grinding of the material;
- (d) High Pressure Grinding Rollers (HPGR), or roller mills, are equipment that pulverize material as it passes between two rollers or between a roll and a flat surface. The rollers may have different types of surfaces, commonly being serrated, toothed, or smooth;
- (e) Blade (or knife) granulators and shredders are equipment that use several equally spaced blades to crush the material. These blades (or knives) can be arranged horizontally or vertically;
- (f) Central rotor (or universal) mills are equipment in which an impact surface placed on a central axis rotates at high speed, breaking the falling material and projecting it against the mill walls, further increasing the grinding efficiency; that is, grinding is carried out through a combination of the high speed of rotation of the rotor and the action of the generated centrifugal force, which projects the particles;

- (g) Jet (or flow) mills are equipment that project a flow of particles against another flow, which is projected in the opposite direction to the first, or against a stationary surface; and
- (h) Friction mills (or millstones) are equipment where a stone (or metallic part) rotates on another stone (or metallic part), which is stationary and of similar hardness, grinding material which is introduced through a central hole.

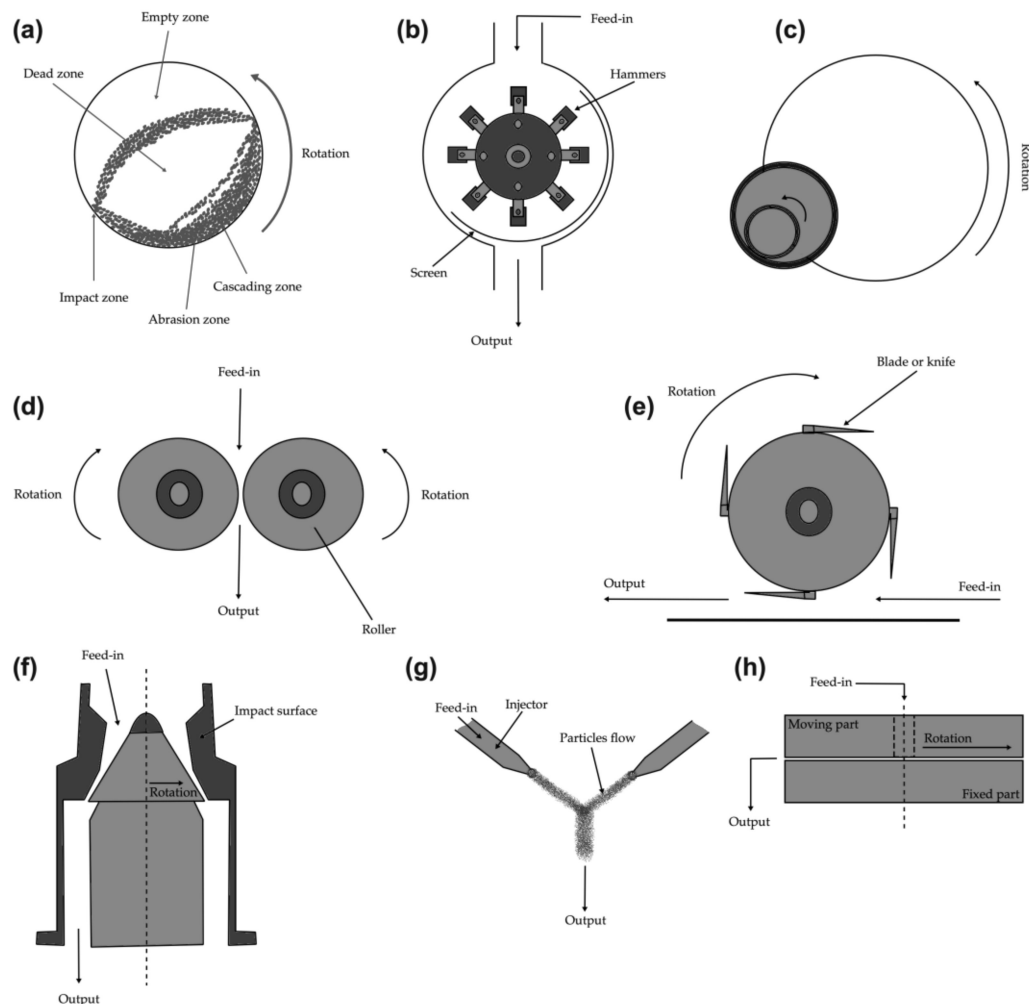


Figure 1. Schematic representation of the operating model of each of the mills described above: (a) Tumbling mill; (b) Hammer mill; (c) Disc mill; (d) High Pressure Grinding Rollers; (e) Blade breakers; (f) Universal mill; (g) Jet mill; and (h) Grinding wheels.

The selection of an appropriate mill to obtain a specific granulometry depends primarily on the type of material to be ground, but also on a varied set of factors that, when combined, determine how the process will develop [44]. Thus, the fundamental parameters for the selection of the type of mill and its design are the following [45]:

- (a) Desired output—with this parameter, it is possible to determine the dimension of the equipment based on the quantity to be processed;
- (b) Type of material, particle size when entering the mill, particle shape, presentation mode (e.g., if it comes loose or with some type of baling), and the hardness of the material (or, even better, its ability to resist grinding or grindability); and
- (c) Particle size of the output.

It should be noted that the particle size of the output has to be given in the form of an interval, as it is impossible to obtain all particles with a single dimension [46]. The grinding process of a given material (i.e., the reduction of particle size) is never a perfect tool, as it is not capable of producing only particles with a single dimension; rather, it is capable of producing a set of particles that present a distribution that, using the parameters defined in this process, fits within a certain range of values [47]. Figure 2 shows a schematic of the distributions of the different types of mills, according to the size of the desired outputs.

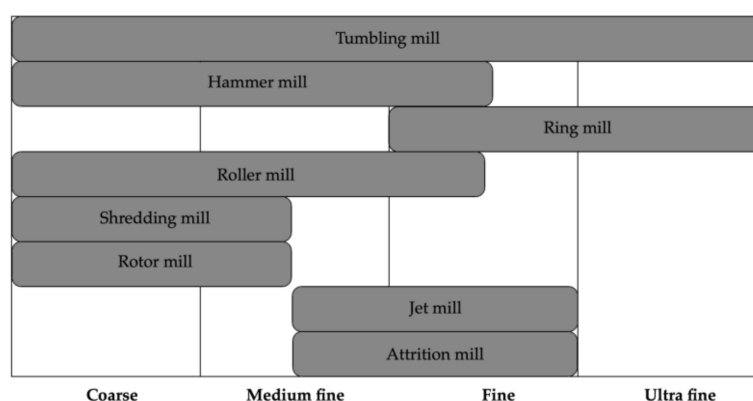


Figure 2. Schematic representation of the type of mill and the size ranges of the desired outputs.

Mills are fundamental equipment in coal-fired power plants, as there are a number of problems that occur during the combustion of the pulverized material which can be directly related to the use of poorly ground fuels; namely, the occurrence of excessively high temperatures in the flue gases, inefficient combustion in the furnace, overheating of the metal surfaces of the heat exchangers, water flows with excessive overheating, and heat losses through surfaces, among others [48]. Many scientific works and technical reports have indicated that approximately 75% of the improvements to be made in coal-fired power plants can be attributed to the mills, as they involve improvements in parameters, such as the particle size distribution, shape coefficient, and the control of air flows, which contribute to greater flame stability and, subsequently, greater process efficiency [49].

The improved particle size of the fuel, achieved only when the sprayers are operating at their best performance, leads to a better distribution of fuel and a larger surface area of each particle of coal, such that the nitrogen bound to the fuel is released into the devolatilization zone of the burner [50]. Larger coal particles have greater momentum when dragged through the air at a certain speed and are stratified more easily than finer coal particles, which have less mass and, therefore, less momentum. In addition, as the size of the coal particles decreases, their residence time in the furnace is used more effectively to complete the burning of coal before combustion products actively enter the overheating section of the boiler [51].

Grain size and hardness have a deeper effect on spray performance than moisture or feed capacity. This fact demonstrates that the common link between good combustion and good performance of the sprayer is the grain size of the fuel [52]. This is why it is important to have a properly adjusted sprayer, capable of providing a flow of fuel with satisfactory grain size [53]. The ideal air/fuel ratio and the ideal fuel grain size are essential for optimal combustion to occur [54]. The optimization of the sprayer is critical for optimum performance of the thermoelectric plant, lower NO_x emissions, and maximum efficiency [55].

Grinding mills in a large-scale coal-fueled power plant are formed of four core parts: the coal dryer, the coal handling and transportation system, the coal sieve, and the grinding mill [56,57]. These coal grinding mills can be divided into four main types [58]: high speed mills, medium speed (or vertical spindle) mills, low speed mills, and very low speed mills, which use different grinding systems such as hammer mills, ball-race mills, liner mills, impact crushers, jaw crushers, and vertical spindle mills,

as described by Spero et al. (1991) [59]. In all situations found in the large-scale use of these mills, all are projected to increase grinding efficiency and output. These parameters are directly associated with the cost and maintenance needs of the mills, as stated by Peatfield (2003) [60].

Callcott (1956), in the early stages of modern coal science, defined grindability as the capacity of a material to be ground [61]. Initial discussions about coal grindability were conducted by R.N. Hardgrove in the early 1930s, after realizing that the performance of grinders was directly related to the properties of the materials being ground [62]. Coal grindability can be evaluated using a grinding machine, in accordance with certain procedures described in technical standards, in order to obtain the designated Hardgrove Grindability Index (HGI) [63]. This index indicates the resistance of a material to grinding, as compared to a standard sample with well-known resistance. A higher HGI indicates a lower resistance, while a lower HGI indicates a higher resistance to grinding. Standard values can be appointed as being below 55 for hard coals and above 60 for soft coals [64,65].

In the present work, a review of the different grinding technologies currently available is conducted, as well as a preliminary analysis of a set of residual biomasses available in Portugal—namely almond shells, kiwifruit pruning, vine pruning, olive pomace, pine woodchips, and eucalyptus woodchips—as candidates for use as coal replacements in thermal power plants, through the determination of grindability indices, namely the Statistical Grindability Index (SGI) and the Hardgrove Grindability Index (HGI) using empirical methods based on elemental analysis (CHNO) and thermogravimetric analysis (TGA) of the materials.

2. Materials and Methods

2.1. Samples Collection and Preparation

2.1.1. Torrefaction of the Samples

To verify the evolution of the properties of the residues and byproducts selected for this study resulting from the torrefaction process, several analyses were carried out to characterize them. Thus, different techniques were used, such as thermogravimetric analysis (fixed carbon content, volatiles, ash, and moisture), elemental analysis (C, H, O, and N), and heating value analysis.

Samples of almond shells, kiwifruit pruning, vine pruning, olive pomace, pine woodchips, and eucalyptus woodchips were collected and, when necessary, cut to obtain a granulometry that would allow for the best processing of the materials. These materials were selected because they are representative of the types of waste and byproducts that exist in great abundance, as available from agroforestry industries, and are therefore available to work, potentially, as alternatives to coal, if they are found to have physicochemical characteristics compatible with efficient energy recovery. The samples were subjected to drying in a laboratory oven at a temperature of 90 °C for 24 h.

Preparation of samples started with weighing approximately 250 g of material. Samples were prepared with conventional aluminum paper, in which the objective was to wrap the samples in a cylindrical shape. As the aluminum paper has two distinct sides, it should be noted that the opaque part of the sheet must be directed towards the outside such that, during the torrefaction process, the heat is not reflected.

In this work, the torrefaction protocol described by Ribeiro et al. (2018) was used [30], which proposed the use of a high-temperature oven, or ceramic muffle, for torrefaction. Its structure was composed of a metallic monobloc, covered inside by refractory bricks and with kaolin canvas for insulation. The heating of the muffle was caused by heat transfer produced by the electrical resistances found inside. Samples were torrefied in the muffle, which had a built-in controller with the ability to program four temperature thresholds and the residence time. There was a cavity on the top of the equipment, in order to facilitate the 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. Figure 3 presents an example of one of the torrefied materials obtained from the torrefaction test.

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

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



Figure 3. Example of one of the obtained materials, in this case torrefied pine woodchips.

2.1.2. Ultimate Analysis

To determine the elemental composition of the samples, an elemental carbon, hydrogen, and nitrogen analyzer was used. Its operation consisted of the incineration of samples at 900 °C, in an oxygen-rich atmosphere, such that all organic compounds were burnt with CO₂, H₂O, N₂, and SO₂ as final products. Subsequently, the levels of carbon, hydrogen, and nitrogen were obtained with a gas chromatography detector. 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 estimated based on Equation (1):

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

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

2.1.3. Proximate Analysis

Thermogravimetric analysis (TGA) is a method that is 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 [66]. For the TGA analysis, the equipment used consisted of an oven with a precision scale, where the melting pots were inserted. 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. 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 (8–10 s). When starting the process, the melting pots were inserted into the equipment to start weighing, where 1 g of sample was introduced into each of the melting pots. An empty reference melting pot was used as a blank sample.

2.1.4. Determination of Heating Value

Moran and Shapiro (2002) objectively defined the heating value of a fuel as being a positive number equal to its combustion enthalpy module, which can be used to define the High heating Value (HHV) and Low Heating Value (LHV) [67]. The HHV is obtained when all the water formed in combustion is liquid and the LHV is obtained when all the water formed in combustion is steam; the difference between these heating values is equivalent to the energy needed to vaporize the water formed in combustion [68]. These values have great relevance in the design of combustion equipment and the measurement of HHV is important for the characterization of a fuel. For solid fuels with certain previously known characteristics, HHV and LHV can be calculated using specific equations, using both elemental and thermogravimetric analyses [69]. It is common to find, in the literature, the calculation of HHV with an equation according to the elemental analysis of biomass fuels, as the variation of the main elements such as carbon, hydrogen, and oxygen is relatively small for any biomass. Observing this information, it is possible to use an equation to determine HHV, as long as the elemental analysis is known [70]; however, it should be noted that the moisture and ash content can cause great variation in the heating value of a biomass. Channiwala and Parikh (2002) presented a universal equation (Equation (2)) for calculating the HHV of several fuels [71]:

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

where C, H, O, and N is the carbon, hydrogen, oxygen, and nitrogen content, respectively; A is the ash content; and S is the sulphur content. Their validity ranges are: $0\% \leq \text{C} \leq 92.25\%$; $0.43\% \leq \text{H} \leq 25.15\%$; $0.00\% \leq \text{O} \leq 50.00\%$; $0.00\% \leq \text{N} \leq 5.60\%$; $0.00\% \leq \text{S} \leq 94.08\%$; $0.00\% \leq \text{Ash} \leq 71.4\%$; $4.75 \text{ MJ/kg} \leq \text{HHV} \leq 55.35 \text{ MJ/kg}$.

The validation of the correlation presented in Equation (2), developed by Channiwala and Parikh (2002), was performed through the comparison of measured and simulated HHV values, with error limits of $\pm 3\%$ [71]. The comparative study showed that the average absolute deviations for gaseous and liquid fuels, coals, biomasses, residues, chars and for the entire set of fuels analyzed, were, respectively, 0.588, 0.299, 0.295, 0.369, 0.406, 0.241 and 0.337 MJ/kg, while the bias deviations were of the order of -0.445 , 0.00 , 0.045 , -0.026 , 0.164 , 0.031 , and 0.00 MJ/kg, respectively [71]. Likewise, the average absolute error was 1.18, 0.772, 1.04, 1.94, 2.58, 0.951, and 1.45%, respectively, except for some gaseous fuels, such as C_2H_2 and C_2H_4 . The bias errors for these categories were -0.98 , 0.00 , 0.14 , -0.17 , 1.30 , 0.08 , and 0.00% , respectively. The validation of the correlation presented by Channiwala and Parikh (2002) was also validated using the comparison of the results obtained, with the results obtained with other correlations, namely those presented by Dulong (1880), whose formula was maybe the first correlation to estimate the HHV of coals [72], Vondracek (1927), Grummel and Davis (1933), Boie (1953), IGT (1976), Tillman (1978), Jenkins (1980), Jenkins and Ebeling (1985), and Niesson (1995) [71,73–75]. However, in the same work, the authors refer that these correlations are only valid for the fuels for which they were derived. Thus, it was observed that, except for some materials that have some special characteristics, namely particularly high levels of ash, Equation (2) presents results with a margin of $\pm 3\%$ [71].

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 vaporization of the water vapor formed during combustion is discounted [76]. The formula for calculating the LHV is as follows (Equation (3)) [71]:

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

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

The mass of water formed during combustion is calculated using the 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, as determined from the elementary analysis presented above [68,71].

2.2. Grindability Indices

The properties of a material, such as strength, elasticity, or hardness, reflect its ability to be ground and the ease with which grinding can occur. R.N. Hardgrove developed a procedure that allowed for the quantification of this capacity of resistance to grinding, which became known as the Hardgrove Grindability Index (HGI), with the objective of measuring how different types of coals behave in the grinding process, such that they can be efficiently used in industrial-scale sprayers. The test works by placing a sample of coal in a ball mill that, through a pre-determined number of rotations, grinds the material, followed by sieving and determining its granulometric distribution. Subsequently, by comparison with the results obtained for standard samples, an HGI value is determined for the sample under study. A material with higher HGI value is considered easier to grind, while a lower HGI value indicates greater resistance to efficient grinding. In this context, greater or lesser resistance to grinding is understood as the greater or lesser consumption of energy in this process, indicating a greater or lesser ease in achieving the desired granulometries during the grinding process. The easiest materials to grind are those that have volatile material content in the range of 14–30%, analyzed on a dry basis. Sengupta (2002) noted the following correlation between the statistical grindability index (SGI) and proximate analysis of coal, which can be presented as follows (Equation (5)) [77]:

$$\text{SGI} = 93.25 + (0.256 M + 0.196 M^2) + (3.291 A - 0.027 A^2) - (3.495 \text{VM} - 0.087 \text{VM}^2) - (5.515 \text{FC} - 0.083 \text{FC}^2), \quad (5)$$

where M, A, VM, and FC are the percentages of moisture, ash, volatile matter, and fixed carbon, respectively, determined on an air-dried basis. This equation of statistical nature relates the four parameters obtained through the thermogravimetric analysis. The first factor, where moisture comes in, is always positive. It can be noted that, for a moisture content of 1% and 10%, the calculated values of the factor are 0.5 and 22.2, respectively [77]. Therefore, only 0.5 will be added to the constant 93.25 of the equation, compared to 22.3 for the latter. This increase, obviously, indicates that the increase in moisture content makes the material softer if considered alone. However, the increase in humidity is always associated with the increase in oxygenated functional groups, responsible for cross-linking through the hydrogen bond to make these materials more difficult to grind and, therefore, should have a lower SGI [77]. The next factor in the equation deals with ashes, and it can be noted that the factor tends to increase, for example with 10% and 60% ash, the value of the factor is calculated at 30.2 and 100.3, respectively, indicating that materials with 60% ash should have a higher grindability. Therefore, the equation at least justifies that the increase in mineral matter will make the material softer. The next factors, VM and A, are both negative, indicating that both tend to decrease the SGI value. Considering the VM in the first instance, it can be noted that for 20% of the VM, the factor value is minimal (35.1). Therefore, coal is the hardest in this region, so the hardness decreases and, with 40% of VM, the factor is less 0.6 and, again, with 40.2%, the factor becomes positive. Subsequently, for 45%, its value is 18.9. Thus, it can be concluded that the factor becomes additive, that is, it increases the value of the SGI to make it softer from 40.2%. It can also be noted that for 10% and 30% of VM, the factor values are the same (26.3). This indicates that the equation cannot differentiate the effects of VM in certain ranges of values. A similar trend is also observed in the FC factor in the ranges of 15% to 66%, with 35%, where the value is less than 91.4, indicating that the material is harder at this point. After this phase, the FC factor tends to decrease, and at 66.5% the factor becomes positive, that is, it tends to increase

the value of the factor or, in this case, it tends to make the material softer, increasing the SGI. Again, the FC factor cannot differentiate its effect on the SGI in certain ranges of values, for example 25% and 41%, since the SGI values are almost identical in these regions. It can be concluded that, in the general equation, the synergistic factor that covers all four components of the close analysis plays a vital role in establishing the final form of the equation, eliminating the masking effect of one item by another. Due to this synergistic effect, if any item of the thermogravimetric analysis is eliminated, the correlation coefficient will be lower. Herein lies the novelty of the equation, which can give more reliable and reproducible results [77].

Similar to this, another correlation was proposed by Mathews et al. (2014), in order to relate HGI with the ultimate analysis of coal (Equation (6)) [78]:

$$\text{HGI} = 77.162 + 3.994 \ln(S) - 10.920 H + 1.904 M - 0.424 A - 11.765 \ln\left(\frac{O + N}{C}\right), \quad (6)$$

where S, H, O, N, and C are the percentages of sulphur, hydrogen, oxygen, nitrogen, and carbon, respectively, and M and A are percentages of moisture and ash, respectively. In the specific case of the materials under study in the present work, all values determined for S were lower than the detection limit of the equipment. That is, were lower than 0.01%, this being the value used for all calculations. However, given the provenance of the analyzed samples, most likely, the values should tend to 0, so this may be an error factor associated with the determination of the HGI, predicting that a default approximation to the real value may occur.

3. Results

3.1. Elemental Analysis

The results obtained in the analysis of the elemental composition are shown in Table 2. The elemental analysis determines the contents of the elements C, H, N, and O. As can be seen, the dominant element in all analyzed materials is C. It is also verified, for this element, that there is an increase in its concentration after the torrefaction process. This increase in concentration, associated proportionally to the mass loss, is due to the fact that, during the torrefaction process, hydrogenated compounds, associated with the degradation of hemicellulose, are eliminated, while C, together with N, see their contents concentrated, respectively, with an increase of 42.90% and 81.09%, and it is not possible at the moment to define the reason for the reduction of the N content in the eucalyptus samples, which have always shown a tendency to reduce this value. For the levels of H and O, there was a decrease in the average values of, respectively, 31.31% and 51.31%.

Table 2. Elemental analysis for the different biomass waste forms.

Elements		Almond Shells	Kiwifruit Pruning	Vine Pruning	Olive Pomace	Pine Woodchips	Eucalyptus Woodchips
C (%)	Dried	58.40	49.40	48.30	56.20	50.20	57.44
	300 °C	79.90	75.50	73.40	81.70	80.10	63.67
H (%)	Dried	5.24	5.69	5.71	6.83	5.86	5.83
	300 °C	3.77	3.62	3.80	3.66	3.91	5.23
N (%)	Dried	0.242	0.559	0.748	1.210	0.100	0.236
	300 °C	0.470	1.600	1.320	1.560	0.227	0.174
O (%)	Dried	36.12	44.35	45.24	35.76	43.84	36.49
	300 °C	15.86	19.28	21.48	13.08	15.76	30.93

3.2. Thermogravimetric Analysis

The results obtained in the thermogravimetric analysis are shown in Table 3. The TGA analysis, as already mentioned, determines the content of Fixed Carbon, Moisture, the content of Ashes and the

content of Volatiles. As can be observed, there is an increase in the concentration of Fixed Carbon in all materials analyzed, with an average increase of 270%. For Moisture, as expected, there is a reduction of the content, going from an average value of 7.24% to 2.32%. The ash content increases proportionally to the loss of mass, going from an initial average value of 1.34% to 4.04%. The Volatiles content indicates a decrease, also directly related to the loss of mass, with an average decrease of 67.62%.

Table 3. Thermogravimetric composition for the different biomass waste forms.

Properties		Almond Shells	Kiwifruit Pruning	Vine Pruning	Olive Pomace	Pine Woodchips	Eucalyptus Woodchips
Fixed Carbon (%)	Dried	20.73	19.54	20.04	18.84	17.82	17.30
	300 °C	73.63	68.57	63.57	73.78	72.98	68.67
Moisture (%)	Dried	8.64	10.87	10.84	3.51	2.61	6.98
	300 °C	1.26	2.98	2.68	2.26	1.87	2.89
Ashes (%)	Dried	1.60	1.32	2.89	1.31	0.27	0.67
	300 °C	4.07	5.03	7.98	4.56	0.94	1.67
Volatiles (%)	Dried	77.67	79.14	77.06	79.85	81.91	82.02
	300 °C	22.30	26.40	28.46	21.66	26.08	29.76

3.3. Heating Value

The results obtained for the calculation of High Heating Value (HHV), Low Heating Value (LHV), and the verified mass loss for each of the tests carried out are shown in Table 4. As expected, the results indicate an upward trend for HHV values, and subsequently for LHV values in the same proportion, with an average increase in HHV and LHV values of, respectively, 36.21% and 44.53%. The average value of the mass loss was 68.02%, with the highest value corresponding to the samples of olive pomace, with 71.10%, and the lowest value to the samples of kiwi fruit pruning, with 66.00%.

Table 4. High Heating Value calculated for the different biomass waste forms.

Properties		Almond Shells	Kiwifruit Pruning	Vine Pruning	Olive Pomace	Pine Woodchips	Eucalyptus Woodchips
HHV (MJ/kg)	Dried	22.79	19.33	18.84	23.92	19.89	23.13
	300 °C	30.60	28.50	27.69	31.36	30.92	25.15
LHV (MJ/kg)	Dried	20.71	17.07	16.58	21.22	17.57	20.82
	300 °C	29.11	27.07	26.19	29.91	29.37	23.08
Mass loss (%)		68.00	66.00	63.50	71.10	69.50	70.04

3.4. Grindability Indices

The results obtained for the calculation of the Statistical Grindability Index (SGI) and Hardgrove Grindability Index (HGI) for each of the tests carried out with torrefied material are shown in Table 5. To facilitate reading, and because the results for each group of samples corresponding to each of the analyzed materials showed variations of $\pm 5\%$, there followed a methodology for presenting the results through their distribution in intervals, defined as those commonly used in coal science studies and reports. As can be seen in the results presented in Table 5, the values obtained for the SGI indicate a high grindability, with the values all above 80, while the values presented for the HGI indicate values that are in the range of 30–55, indicating an average value close to 55, which corresponds to materials that have good grindability after torrefaction.

Table 5. Grindability indices calculated for the different biomass waste forms.

Properties	Almond Shells	Kiwifruit Pruning	Vine Pruning	Olive Pomace	Pine Woodchips	Eucalyptus Woodchips
SGI	80–100	80–100	<80	80–100	80–100	80–100
HGI	30–55	30–55	30–55	30–55	30–55	30–55

4. Discussion

Biomass has been presented as a promising alternative for the renewable generation of energy, mainly as it is able to solve the problem of intermittency present in other renewable forms, therefore being able to serve as an alternative to coal in the generation of electric energy. However, for this substitution to be possible, it is necessary that biomass (of whatever type) presents a set of parameters similar to those of mineral coal, in order to allow for its use in the same systems previously installed in coal-fueled power plants. One of the most important sections, which defines most of the parameters that lead to combustion efficiency, is the grinding section. This industrial procedure, as shown above, can be carried out using different technologies and is extremely important, as it defines the size distribution of the particles to be introduced into the combustion chamber, which can contribute to more efficient energy conversion.

Torrefaction presents itself as a biomass pre-processing technology capable of converting heterogeneous products with low density, low calorific value, and high moisture content into improved products with properties similar to those found in mineral coal. For this reason, it is a technology that must be taken into account for the energy conversion of residual biomass. Above all, this technology is able to improve the two most important properties for the replacement of coal: Hydrophobicity, as it allows for the storage of torrefied products in outdoor yards, and grindability, because it allows for the use of the same mills previously used for grinding coal, avoiding additional investments. This parameter is crucial for the fuels to reach a particle size that allows for efficient combustion.

The results obtained in the elementary analysis differed slightly from other studies; however, these differences were not significant [79–83]. It is understood that these results are related to the fact that the elementary analyses in other works could have been determined by using different methodologies from that used in the present work. Another reason may be related to the fact that the geographic origin of the forms of residual biomass used in the characterizations differed, not originating from the same soil; this may have interfered in the chemical composition of the residues and, consequently, in the results obtained [84]. The results obtained showed, however, a common trend to what would be expected and described in the analyzed bibliography; that is, there was an increase in the levels of carbon and nitrogen in all analyzed materials, consistent with the concentration of the components not eliminated during the process—usually oxygenated and hydrogenated compounds, which lowered their content in all materials after thermal processing by torrefaction.

The fixed carbon content present in a given fuel is directly related to the amount of energy it is able to supply: the higher this content, the slower the fuel will burn. It can also, in this way, guarantee total combustion and more efficient energy recovery [85–87]. The values obtained for the fixed carbon content for the six materials studied, even without the thermal treatment at 300 °C, were in the range between 17.30% and 20.73% (with the minimum value for eucalyptus woodchips and the highest value for almond shells). For the remaining materials, there was a certain proximity between the values obtained, with an average value of $19.06 \pm 0.86\%$. The values obtained were in line with the values presented in previous studies, namely those by Demirbaş (2002) for almond husks [88], by Torreiro et al. (2020) for kiwifruit pruning [89], by San José et al. (2013) for vine pruning [90], by Nunes et al. (2020) for olive pomace [91], Nunes et al. (2019) for the pine chip [92], and Sá et al. (2020) [93]. 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) [94–96]—with the smallest

percentage increase corresponded to the increase seen in vine pruning, which stood at 63.57%, while the remaining materials had an average of $70.51 \pm 3.96\%$. These values were also in line with the values obtained in previous studies, namely those developed by Chiou et al. (2018) for almond shells [97], by Margaritis et al. (2020) for vine pruning [98], by Volpe et al. (2015) for olive pomace [99], Phanphanich and Mani (2011) for pine chip [35], and Sá et al. (2020) [93]. In the case of kiwifruit pruning, the only works found in the bibliographic research referred to its characterization as a fuel after drying, without any other type of thermal processing such as torrefaction (see, e.g., the works developed by Dyjakon and García-Galindo (2019) or Boumancher et al. (2019) [100,101]). With reference to works carried out on the application of thermochemical conversion technologies (in this case, pyrolysis), we found a work developed by Rene et al. (2020), which was carried out with the aim of studying the production of biochar from kiwifruit pruning employed as an amendment aiming to evaluate its remediation potential in smelter- and mining-contaminated soils [102]; therefore, the data from this study was not used for comparison, as 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 waste material from pruning kiwifruit orchards for energy purposes, after pre-treatment using torrefaction, is a novelty that appears in this work; furthermore, 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 kiwifruit is a growing crop, given the excellent edaphoclimatic conditions for this species [103].

When the biomass to be used as a fuel has a high moisture content, the combustion process is less efficient when compared to material with a lower moisture content. This is because, with higher moisture content present in the biomass, more energy is required to start the combustion process; that is, more energy is needed to vaporize the water present in the fuel and less energy is provided for the endothermic reaction, which is responsible for maintaining combustion [104–106]. Several authors have reported that the presence of moisture makes combustion difficult as the calorific value is reduced, thereby increasing fuel consumption [107,108]. Other studies have also claimed that the presence of a high moisture value generates environmental pollution due to an increase in the volume of combustion products and particulate material, not to mention that the corrosion process is accelerated at the final part of the steam generator and particles are accumulated on the heating surfaces [109,110]. In the case of a process for converting biomass into fuel, or as an intermediate pre-processing step for other processes (specifically for use in gasification processes), Lucena Tavares and dos Santos (2013) stated that a high moisture content does not generate technical difficulties in gasification, but instead leads to a reduction in the efficiency of the process, as the energy needed to evaporate the water and maintain the operating temperature is only obtained by feeding more fuel and oxidants [111]. In short, moisture is a limiting factor in the choice of fuel, and fuels with values above 50% should not be used as, above this point, there is not enough energy released to ensure the maintenance of combustion and, consequently, the production of heat [112]. In the present work, all the analyzed materials were submitted to a drying process in the laboratory immediately after collection, in order to reduce their initial moisture content, which varied between 25% and 60% depending on the materials. After this period of forced drying, during the performance of the thermogravimetric analysis, the materials presented values between 2.61% (verified for pine woodchips) and 10.84% (verified for the vine pruning). After the torrefaction test, there was a profound reduction in the moisture content of the products under analysis, with the almond shell showing the lowest value (at 1.26%), while the kiwifruit pruning showed a value of 2.98%. These values are clearly low, allowing high potential for the combustion of the waste under analysis. These results are in line with the results presented in previous studies, such as those carried out by Demirbaş (2002) with almond husks, Manzone et al. (2019) with kiwifruit pruning, San José et al. (2013) with vine pruning, Nunes et al. (2020) with olive pomace, Nunes et al. (2019) with pine chips, and Sá et al. (2020); indicating a good potential for energy recovery in all works [88,90–93,113,114].

For several authors, such as Nunes et al. (2016) or Kalemekiewicz and Chmielarz (2012), high ash content led to a decrease in efficiency due to the increased consumption of oxygen in order to melt the ash and the loss of heat with ash leaving the reactor, which cannot be fully recovered [115,116]. Other studies have also reported that, for use as pre-processing for later gasification, lower ash content reduces the likelihood of equipment clogging and encrustation [117,118]. As with humidity, the ash content also interferes with the calorific value, causing energy losses in addition to impairing heat transfer [119,120]. Several authors have agreed on the removal of ash from the combustion site, as it also contributes to an increase in problems related to the corrosion of metal equipment; especially when a high content of alkali metals is associated with high ash content [121,122]. In the products analyzed in the present work, the materials presented values in accordance with those previously determined by previous works, with values ranging from 0.27% (for pine woodchips) and 2.89% (for vine pruning). After torrefaction, the values fluctuated between 0.94% (for pine woodchips) and 7.89% (for vine pruning), thus maintaining compliance due to mass losses. The values determined were also in accordance with previous works; namely, those mentioned above for the previous parameters.

When biomass has a high volatile content, it is easier to start combustion and to maintain it. However, for this reason, the combustion process may be faster or may become difficult to control, leading to a greater consumption of fuel; therefore, a high content of volatile materials can also affect the combustion process in general [123]. The volatile content determined for the materials under analysis in the present study showed great uniformity, presenting an average value around $77.04 \pm 4.93\%$ for products not thermally processed, while products submitted to the torrefaction process presented an average value of $24.44 \pm 2.66\%$, in total agreement with the works of García et al. (2012) and Sun et al. (2017), where several residual biomasses without thermal treatment were characterized [124,125], or with the work of Singh and Zondlo (2017), where samples of torrefied residual biomass were treated [126].

Regarding the lower calorific value, there was an increase in line with what was expected, according to previous experiences, for all materials [17,19,127–130]. All values determined for the lower calorific value indicated good potential for the energetic valorization of the analyzed materials.

The indices calculated using the empirical methods presented by Sengupta (2002) and by Mathews et al. (2014) provided quite different results and indicated a trend that points to the high grindability of all tested materials [77,78]. No references were found in the bibliography to allow a comparative analysis with the same type of indices and with the same (or, at least, similar) materials. It was found that, with SGI calculation for all materials, all had values above 80 (with the exception of vine pruning), indicating high grindability. In the case of HGI, although the values presented were clearly below 55, this may be related to the presence of a relatively large amount of volatile compounds in the materials, which may indicate that the torrefaction did not reach the optimum temperature or, at least, that the residence time was not long enough to lower the volatile content in all materials. In any case, it should be noted that these materials were not densified, a situation that should increase the grindability of all materials, as the density increases.

5. Conclusions

In the present work, it was found that torrefaction is capable of producing materials with grindability indices comparable to those obtained in mineral coal, such that the potential for use and feasibility of this process was demonstrated in this preliminary approach. However, it is still necessary to develop further studies and tests; namely, to determine the ideal torrefaction parameters (temperature and residence time), such that the highest possible grindability values are achieved. The SGI derived from thermogravimetric analysis is perhaps more useful to understand and compare the behavior of all types of materials. It can be calculated from a simple thermogravimetric analysis and, therefore, eliminates the use of the laboratory method usually used to determine the Hardgrove Grindability Index. The SGI can be used to predict HGI with reasonable accuracy when the ease of determining HGI is not available.

It is also of particular importance to use residual forms of biomass, especially those that have large quantities available. In this way, in addition to decarbonizing the energy generation process, it also contributes to the circularization of the process, through the inclusion of a set of residual forms of biomass. It also contributes to solving a set of environmental problems; for example, those associated with the elimination of olive pomace. In the case of forest residues, such as those resulting from sanitary thinning operations in pine forests or the selection of sticks in eucalyptus forests, in addition to the biomass resulting from operations to control invasive species, there may also be an important role in reducing the existing load of forest fuel, thus contributing to reducing the risk of rural fires occurring, while creating a value chain for products that have had no (or very little) value to date and, therefore, have been neglected by forestry operators.

Funding: This research received no external funding.

Acknowledgments: The author 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 author declares no conflict of interest.

References

1. Bunn, D.W.; Redondo-Martin, J.; Muñoz-Hernandez, J.I.; Diaz-Cachinero, P. Analysis of coal conversion to biomass as a transitional technology. *Renew. Eng.* **2019**, *132*, 752–760. [\[CrossRef\]](#)
2. Proskurina, S.; Heinimö, J.; Schipfer, F.; Vakkilainen, E. Biomass for industrial applications: The role of torrefaction. *Renew. Eng.* **2017**, *111*, 265–274. [\[CrossRef\]](#)
3. Roni, M.S.; Chowdhury, S.; Mamun, S.; Marufuzzaman, M.; Lein, W.; Johnson, S. Biomass co-firing technology with policies, challenges, and opportunities: A global review. *Renew. Sustain. Eng. Rev.* **2017**, *78*, 1089–1101. [\[CrossRef\]](#)
4. Stirling, R.J.; Snape, C.E.; Meredith, W. The impact of hydrothermal carbonisation on the char reactivity of biomass. *Fuel Proc. Technol.* **2018**, *177*, 152–158. [\[CrossRef\]](#)
5. Melikoglu, M. Vision 2023: Status quo and future of biomass and coal for sustainable energy generation in Turkey. *Renew. Sustain. Eng. Rev.* **2017**, *74*, 800–808. [\[CrossRef\]](#)
6. Gowrisankaran, G.; Reynolds, S.S.; Samano, M. Intermittency and the value of renewable energy. *J. Political Econ.* **2016**, *124*, 1187–1234. [\[CrossRef\]](#)
7. Aflaki, S.; Netessine, S. Strategic investment in renewable energy sources: The effect of supply intermittency. *Manuf. Serv. Oper. Manag.* **2017**, *19*, 489–507. [\[CrossRef\]](#)
8. Engeland, K.; Borga, M.; Creutin, J.-D.; François, B.; Ramos, M.-H.; Vidal, J.-P. Space-time variability of climate variables and intermittent renewable electricity production—A review. *Renew. Sustain. Eng. Rev.* **2017**, *79*, 600–617. [\[CrossRef\]](#)
9. Elum, Z.; Modise, D.; Nhamo, G. Climate change mitigation: The potential of agriculture as a renewable energy source in Nigeria. *Environ. Sci. Pollut. Res.* **2017**, *24*, 3260–3273. [\[CrossRef\]](#) [\[PubMed\]](#)
10. Creutzig, F.; Ravindranath, N.H.; Berndes, G.; Bolwig, S.; Bright, R.; Cherubini, F.; Chum, H.; Corbera, E.; Delucchi, M.; Faaij, A. Bioenergy and climate change mitigation: An assessment. *GCB Bioenergy* **2015**, *7*, 916–944. [\[CrossRef\]](#)
11. Niu, Y.; Lv, Y.; Lei, Y.; Liu, S.; Liang, Y.; Wang, D. Biomass torrefaction: Properties, applications, challenges, and economy. *Renew. Sustain. Eng. Rev.* **2019**, *115*, 109395. [\[CrossRef\]](#)
12. Shankar Tumuluru, J.; Sokhansanj, S.; Hess, J.R.; Wright, C.T.; Boardman, R.D. A review on biomass torrefaction process and product properties for energy applications. *Ind. Biotechnol.* **2011**, *7*, 384–401. [\[CrossRef\]](#)
13. Chen, W.-H.; Peng, J.; Bi, X.T. A state-of-the-art review of biomass torrefaction, densification and applications. *Renew. Sustain. Eng. Rev.* **2015**, *44*, 847–866. [\[CrossRef\]](#)
14. Nunes, L.; Matias, J.; Catalão, J. Biomass in the generation of electricity in Portugal: A review. *Renew. Sustain. Eng. Rev.* **2017**, *71*, 373–378. [\[CrossRef\]](#)
15. Nunes, L.; Matias, J.C.; Catalao, J.P. Wood pellets as a sustainable energy alternative in Portugal. *Renew. Eng.* **2016**, *85*, 1011–1016. [\[CrossRef\]](#)

16. Nunes, L.J.R.; Meireles, C.I.R.; Pinto Gomes, C.J.; de Almeida Ribeiro, N.M.C. Socioeconomic Aspects of the Forests in Portugal: Recent Evolution and Perspectives of Sustainability of the Resource. *Forests* **2019**, *10*, 361. [\[CrossRef\]](#)
17. Rodrigues, A.; Loureiro, L.; Nunes, L. Torrefaction of woody biomasses from poplar SRC and Portuguese roundwood: Properties of torrefied products. *Biomass Bioenergy* **2018**, *108*, 55–65. [\[CrossRef\]](#)
18. Nunes, L.J.; Raposo, M.A.; Meireles, C.I.; Pinto Gomes, C.J.; Ribeiro, N.; Almeida, M. Control of Invasive Forest Species through the Creation of a Value Chain: Acacia dealbata Biomass Recovery. *Environments* **2020**, *7*, 39. [\[CrossRef\]](#)
19. Batidzirai, B.; Mignot, A.; Schakel, W.; Junginger, H.; Faaij, A. Biomass torrefaction technology: Techno-economic status and future prospects. *Energy* **2013**, *62*, 196–214. [\[CrossRef\]](#)
20. Nunes, L.; Matias, J.; Catalão, J. Analysis of the use of biomass as an energy alternative for the Portuguese textile dyeing industry. *Energy* **2015**, *84*, 503–508. [\[CrossRef\]](#)
21. Rodrigues, A.; Nunes, L. Evaluation of ash composition and deposition tendencies of biomasses and torrefied products from woody and shrubby feedstocks: SRC poplar clones and common broom. *Fuel* **2020**, *269*, 117454. [\[CrossRef\]](#)
22. Nunes, L.; Matias, J.; Catalão, J. Biomass waste co-firing with coal applied to the Sines Thermal Power Plant in Portugal. *Fuel* **2014**, *132*, 153–157. [\[CrossRef\]](#)
23. Ribeiro, J.P.; Vicente, E.D.; Gomes, A.P.; Nunes, M.I.; Alves, C.; Tarelho, L.A. Effect of industrial and domestic ash from biomass combustion, and spent coffee grounds, on soil fertility and plant growth: Experiments at field conditions. *Environ. Sci. Pollut. Res.* **2017**, *24*, 15270–15277. [\[CrossRef\]](#) [\[PubMed\]](#)
24. Nunes, L.J.; Matias, J.C. Biomass Torrefaction as a Key Driver for the Sustainable Development and Decarbonization of Energy Production. *Sustainability* **2020**, *12*, 922. [\[CrossRef\]](#)
25. Moon, C.; Sung, Y.; Ahn, S.; Kim, T.; Choi, G.; Kim, D. Thermochemical and combustion behaviors of coals of different ranks and their blends for pulverized-coal combustion. *Appl. Therm. Engineer.* **2013**, *54*, 111–119. [\[CrossRef\]](#)
26. Geier, M.; Shaddix, C.R.; Davis, K.A.; Shim, H.-S. On the use of single-film models to describe the oxy-fuel combustion of pulverized coal char. *Appl. Energy* **2012**, *93*, 675–679. [\[CrossRef\]](#)
27. Visona, S.; Stanmore, B. Modelling NO formation in a swirling pulverized coal flame. *Chem. Eng. Sci.* **1998**, *53*, 2013–2027. [\[CrossRef\]](#)
28. Wang, L.; Barta-Rajnai, E.; Skreiberg, Ø.; Khalil, R.; Czégény, Z.; Jakab, E.; Barta, Z.; Grønli, M. Effect of torrefaction on physiochemical characteristics and grindability of stem wood, stump and bark. *Appl. Energy* **2018**, *227*, 137–148. [\[CrossRef\]](#)
29. Correia, R.; Gonçalves, M.; Nobre, C.; Mendes, B. Impact of torrefaction and low-temperature carbonization on the properties of biomass wastes from *Arundo donax* L. and *Phoenix canariensis*. *Bioresour. Technol.* **2017**, *223*, 210–218. [\[CrossRef\]](#) [\[PubMed\]](#)
30. Ribeiro, J.M.C.; Godina, R.; Matias, J.C.d.O.; Nunes, L.J.R. Future perspectives of biomass torrefaction: Review of the current state-of-the-art and research development. *Sustainability* **2018**, *10*, 2323. [\[CrossRef\]](#)
31. Tchapda, A.H.; Pisupati, S.V. A review of thermal co-conversion of coal and biomass/waste. *Energies* **2014**, *7*, 1098–1148. [\[CrossRef\]](#)
32. Kambo, H.S.; Dutta, A. Comparative evaluation of torrefaction and hydrothermal carbonization of lignocellulosic biomass for the production of solid biofuel. *Energy Convers. Manag.* **2015**, *105*, 746–755. [\[CrossRef\]](#)
33. Zheng, A.; Jiang, L.; Zhao, Z.; Huang, Z.; Zhao, K.; Wei, G.; Wang, X.; He, F.; Li, H. Impact of torrefaction on the chemical structure and catalytic fast pyrolysis behavior of hemicellulose, lignin, and cellulose. *Energy Fuels* **2015**, *29*, 8027–8034. [\[CrossRef\]](#)
34. Thrän, D.; Witt, J.; Schaubach, K.; Kiel, J.; Carbo, M.; Maier, J.; Ndibe, C.; Koppejan, J.; Alakangas, E.; Majer, S. Moving torrefaction towards market introduction—Technical improvements and economic-environmental assessment along the overall torrefaction supply chain through the SECTOR project. *Biomass Bioenergy* **2016**, *89*, 184–200. [\[CrossRef\]](#)
35. Phanphanich, M.; Mani, S. Impact of torrefaction on the grindability and fuel characteristics of forest biomass. *Bioresour. Technol.* **2011**, *102*, 1246–1253. [\[CrossRef\]](#)
36. Acharya, B.; Sule, I.; Dutta, A. A review on advances of torrefaction technologies for biomass processing. *Biomass Convers. Biorefinery* **2012**, *2*, 349–369. [\[CrossRef\]](#)

37. Van der Stelt, M.; Gerhauser, H.; Kiel, J.; Ptasiński, K. Biomass upgrading by torrefaction for the production of biofuels: A review. *Biomass Bioenergy* **2011**, *35*, 3748–3762. [[CrossRef](#)]
38. Nunes, L.; Matias, J.; Catalão, J. A review on torrefied biomass pellets as a sustainable alternative to coal in power generation. *Renew. Sustain. Eng. Rev.* **2014**, *40*, 153–160. [[CrossRef](#)]
39. Miao, Z.; Grift, T.E.; Hansen, A.C.; Ting, K.C. Energy requirement for comminution of biomass in relation to particle physical properties. *Ind. Crops Prod.* **2011**, *33*, 504–513. [[CrossRef](#)]
40. Bitra, V.S.; Womac, A.R.; Chevanan, N.; Miu, P.I.; Igathinathane, C.; Sokhansanj, S.; Smith, D.R. Direct mechanical energy measures of hammer mill comminution of switchgrass, wheat straw, and corn stover and analysis of their particle size distributions. *Powder Technol.* **2009**, *193*, 32–45. [[CrossRef](#)]
41. Temmerman, M.; Jensen, P.D.; Hebert, J. Von Rittinger theory adapted to wood chip and pellet milling, in a laboratory scale hammermill. *Biomass Bioenergy* **2013**, *56*, 70–81. [[CrossRef](#)]
42. Bitra, V.S.; Womac, A.R.; Igathinathane, C.; Miu, P.I.; Yang, Y.T.; Smith, D.R.; Chevanan, N.; Sokhansanj, S. Direct measures of mechanical energy for knife mill size reduction of switchgrass, wheat straw, and corn stover. *Bioresour. Technol.* **2009**, *100*, 6578–6585. [[CrossRef](#)] [[PubMed](#)]
43. Schell, D.J.; Harwood, C. Milling of lignocellulosic biomass. *Appl. Biochem. Biotechnol.* **1994**, *45*, 159–168. [[CrossRef](#)]
44. Suryanarayana, C. Mechanical alloying and milling. *Prog. Mater. Sci.* **2001**, *46*, 1–184. [[CrossRef](#)]
45. Ulusoy, U.; Igathinathane, C. Particle size distribution modeling of milled coals by dynamic image analysis and mechanical sieving. *Fuel Proc. Technol.* **2016**, *143*, 100–109. [[CrossRef](#)]
46. Afoakwa, E.O.; Paterson, A.; Fowler, M.; Vieira, J. Relationship between rheological, textural and melting properties of dark chocolate as influenced by particle size distribution and composition. *Eur. Food Res. Technol.* **2008**, *227*, 1215–1223. [[CrossRef](#)]
47. Burmeister, C.F.; Kwade, A. Process engineering with planetary ball mills. *Chem. Soc. Rev.* **2013**, *42*, 7660–7667. [[CrossRef](#)]
48. Hanak, D.; Kolios, A.; Biliyok, C.; Manovic, V. Probabilistic performance assessment of a coal-fired power plant. *Appl. Energy* **2015**, *139*, 350–364. [[CrossRef](#)]
49. Goodarzi, F. Assessment of elemental content of milled coal, combustion residues, and stack emitted materials: Possible environmental effects for a Canadian pulverized coal-fired power plant. *Int. J. Coal Geol.* **2006**, *65*, 17–25. [[CrossRef](#)]
50. Basu, P.; Butler, J.; Leon, M.A. Biomass co-firing options on the emission reduction and electricity generation costs in coal-fired power plants. *Renew. Energy* **2011**, *36*, 282–288. [[CrossRef](#)]
51. Odgaard, P.F.; Lin, B.; Jorgensen, S.B. Observer and data-driven-model-based fault detection in power plant coal mills. *IEEE Trans. Energy Convers.* **2008**, *23*, 659–668. [[CrossRef](#)]
52. Hussain, T.; Dudziak, T.; Simms, N.; Nicholls, J. Fireside corrosion behavior of HVOF and plasma-sprayed coatings in advanced coal/biomass co-fired power plants. *J. Therm. Spray Technol.* **2013**, *22*, 797–807. [[CrossRef](#)]
53. Qi, H.; Guo, Y.; He, Y.; Wang, D. High temperature corrosion in boilers of coal fired power plants. *Corros. Sci. Protect. Technol.* **2002**, *14*, 113–116.
54. Chao, C.Y.; Kwong, P.C.; Wang, J.; Cheung, C.; Kendall, G. Co-firing coal with rice husk and bamboo and the impact on particulate matters and associated polycyclic aromatic hydrocarbon emissions. *Bioresour. Technol.* **2008**, *99*, 83–93. [[CrossRef](#)]
55. Starke, M.; Schulpin, H.J.; Haug, M.; Schreiber, M. Measuring coal particles in the pipe. *Power Eng.* **2007**, *111*, 44–49.
56. Joseph, T.J.; Thapa, D.S.; Patel, M. Review on Combustion Optimization Methods in Pulverised Coal Fired Boiler. *Int. J. Eng. Dev. Res.* **2017**, *5*, 70–77.
57. Bose, D.; Chattopadhyay, S.; Bose, G.; Adhikary, D.; Mitra, S. RAM investigation of coal-fired thermal power plants: A case study. *Int. J. Ind. Eng. Comput.* **2012**, *3*, 423–434.
58. Sligar, J. Component wear in vertical spindle mills grinding coal. *Int. J. Miner. Proc.* **1996**, *44*, 569–581. [[CrossRef](#)]
59. Spero, C.; Hargreaves, D.; Kirkcaldie, R.; Flitt, H. Review of test methods for abrasive wear in ore grinding. *Wear* **1991**, *146*, 389–408. [[CrossRef](#)]
60. Peatfield, D. Coal and coal preparation in South Africa—A 2002 review. *J. S. Afr. Inst. Min. Metall.* **2003**, *103*, 355–372.

61. Callcott, T. Coal grindability—A standardized procedure for the determination of coal grindability and a survey of the grindabilities of British coals. *J. Inst. Fuel* **1956**, *29*, 207–217.
62. Tiryaki, B. Practical assessment of the grindability of coal using its hardness characteristics. *Rock Mech. Rock Eng.* **2005**, *38*, 145–151.
63. Zuo, W.; Zhao, Y.; He, Y.; Shi, F.; Duan, C. Relationship between coal size reduction and energy input in Hardgrove mill. *Int. J. Min. Sci. Technol.* **2012**, *22*, 121–124. [[CrossRef](#)]
64. Snyman, C.; Barclay, J. The coalification of South African coal. *Int. J. Coal Geol.* **1989**, *13*, 375–390. [[CrossRef](#)]
65. Snyman, C. The role of coal petrography in understanding the properties of South African coal. *Int. J. Coal Geol.* **1989**, *14*, 83–101. [[CrossRef](#)]
66. Materazzi, S. Mass Spectrometry Coupled to Thermogravimetry (TG-MS) for Evolved Gas Characterization: A Review. *Appl. Spectrosc. Rev.* **1998**, *33*, 189–218. [[CrossRef](#)]
67. Baratieri, M.; Baggio, P.; Fiori, L.; Grigiante, M. Biomass as an energy source: Thermodynamic constraints on the performance of the conversion process. *Bioresour. Technol.* **2008**, *99*, 7063–7073. [[CrossRef](#)]
68. Friedl, A.; Padouvas, E.; Rotter, H.; Varmuza, K. Prediction of heating values of biomass fuel from elemental composition. *Anal. Chim. Acta* **2005**, *544*, 191–198. [[CrossRef](#)]
69. Yin, C.-Y. Prediction of higher heating values of biomass from proximate and ultimate analyses. *Fuel* **2011**, *90*, 1128–1132. [[CrossRef](#)]
70. Annamalai, K.; Sweeten, J.; Ramalingam, S. Technical Notes: Estimation of gross heating values of biomass fuels. *Trans. ASAE* **1987**, *30*, 1205–1208. [[CrossRef](#)]
71. Channiwal, S.; Parikh, P. A unified correlation for estimating HHV of solid, liquid and gaseous fuels. *Fuel* **2002**, *81*, 1051–1063. [[CrossRef](#)]
72. Kieseler, S.; Neubauer, Y.; Zobel, N. Ultimate and proximate correlations for estimating the higher heating value of hydrothermal solids. *Energy Fuels* **2013**, *27*, 908–918. [[CrossRef](#)]
73. Selvig, W.; Gibson, F. *Chemistry of Coal Utilization*; John Wiley: New York, NY, USA, 1945; Volume 132, p. 170.
74. Nhuchhen, D.R.; Afzal, M.T. HHV predicting correlations for torrefied biomass using proximate and ultimate analyses. *Bioengineering* **2017**, *4*, 7. [[CrossRef](#)]
75. Parikh, J.; Channiwal, S.; Ghosal, G. A correlation for calculating HHV from proximate analysis of solid fuels. *Fuel* **2005**, *84*, 487–494. [[CrossRef](#)]
76. Prins, M.J.; Ptasiński, K.J.; Janssen, F.J. Torrefaction of wood: Part 2. Analysis of products. *J. Anal. Appl. Pyrolysis* **2006**, *77*, 35–40. [[CrossRef](#)]
77. Sengupta, A.N. An assessment of grindability index of coal. *Fuel Proc. Technol.* **2002**, *76*, 1–10. [[CrossRef](#)]
78. Mathews, J.P.; Krishnamoorthy, V.; Louw, E.; Tchaptada, A.H.; Castro-Marciano, F.; Karri, V.; Alexis, D.A.; Mitchell, G.D. A review of the correlations of coal properties with elemental composition. *Fuel Proc. Technol.* **2014**, *121*, 104–113. [[CrossRef](#)]
79. Picchio, R.; Spina, R.; Sirna, A.; Monaco, A.L.; Civitarese, V.; Giudice, A.D.; Suardi, A.; Pari, L. Characterization of woodchips for energy from forestry and agroforestry production. *Energies* **2012**, *5*, 3803–3816. [[CrossRef](#)]
80. Rosales, E.; Ferreira, L.; Sanromán, M.Á.; Tavares, T.; Pazos, M. Enhanced selective metal adsorption on optimised agroforestry waste mixtures. *Bioresour. Technol.* **2015**, *182*, 41–49. [[CrossRef](#)]
81. Enes, T.; Aranha, J.; Fonseca, T.; Lopes, D.; Alves, A.; Lousada, J. Thermal Properties of Residual Agroforestry Biomass of Northern Portugal. *Energies* **2019**, *12*, 1418. [[CrossRef](#)]
82. Enes, T.; Aranha, J.; Fonseca, T.; Matos, C.; Barros, A.; Lousada, J. Residual Agroforestry Biomass—Thermochemical Properties. *Forests* **2019**, *10*, 1072. [[CrossRef](#)]
83. Nyakuma, B.B.; Oladokun, O.; Ivase, T.J.; Moveh, S.; Otitolaiye, V.O. Energy Potential of Malaysian Forestry Waste Residues. *Pet. Coal* **2020**, *62.1*, 238–243.
84. Garcia, D.P.; Caraschi, J.C.; Ventorim, G.; Vieira, F.H.A. Trends and challenges of Brazilian pellets industry originated from agroforestry. *Cerne* **2016**, *22*, 233–240. [[CrossRef](#)]
85. dos Santos, R.C.; Carneiro, A.d.C.O.; Vital, B.R.; Castro, R.V.O.; Vidaurre, G.B.; Trugilho, P.F.; Castro, A.F.N.M. Effect of properties chemical and siringil/guaiacil relation wood clones of eucalyptus in the production of charcoal. *Ciênc. Florest.* **2016**, *26*, 657–669.
86. Sturion, J.; Pereira, J.; Chemin, M. Wood quality of Eucalyptus viminalis for energy purposes as a function of spacing and felling age. *Bol. Pesqui. Florest.* **1988**, *16*, 55–59.

87. Resquin, F.; Navarro-Cerrillo, R.M.; Carrasco-Letelier, L.; Casnati, C.R. Influence of contrasting stocking densities on the dynamics of above-ground biomass and wood density of *Eucalyptus benthamii*, *Eucalyptus dunii*, and *Eucalyptus grandis* for bioenergy in Uruguay. *Forest Ecol. Manag.* **2019**, *438*, 63–74. [\[CrossRef\]](#)
88. Demirbaş, A. Fuel characteristics of olive husk and walnut, hazelnut, sunflower, and almond shells. *Energy Sour.* **2002**, *24*, 215–221. [\[CrossRef\]](#)
89. Torreiro, Y.; Pérez, L.; Piñeiro, G.; Pedras, F.; Rodríguez-Abalde, A. The Role of Energy Valuation of Agroforestry Biomass on the Circular Economy. *Energies* **2020**, *13*, 2516. [\[CrossRef\]](#)
90. San José, M.J.; Alvarez, S.; García, I.; Peñas, F.J. A novel conical combustor for thermal exploitation of vineyard pruning wastes. *Fuel* **2013**, *110*, 178–184. [\[CrossRef\]](#)
91. Nunes, L.J.; Loureiro, L.M.; Sá, L.C.; Silva, H.F. Thermochemical Conversion of Olive Oil Industry Waste: Circular Economy through Energy Recovery. *Recycling* **2020**, *5*, 12. [\[CrossRef\]](#)
92. Nunes, L.J.; Godina, R.; Matias, J.C.; Catalão, J.P. Evaluation of the utilization of woodchips as fuel for industrial boilers. *J. Clean. Prod.* **2019**, *223*, 270–277. [\[CrossRef\]](#)
93. Sá, L.C.; Loureiro, L.M.; Nunes, L.J.; Mendes, A.M. Torrefaction as a pretreatment technology for chlorine elimination from biomass: A case study using *Eucalyptus globulus* Labill. *Resources* **2020**, *9*, 54. [\[CrossRef\]](#)
94. Faizal, H.M.; Shamsuddin, H.S.; Heiree, M.H.M.; Hanaffi, M.F.M.A.; Rahman, M.R.A.; Rahman, M.M.; Latiff, Z. Torrefaction of densified mesocarp fibre and palm kernel shell. *Renew. Eng.* **2018**, *122*, 419–428. [\[CrossRef\]](#)
95. Lau, H.S.; Ng, H.K.; Gan, S.; Jourabchi, S.A. Torrefaction of oil palm fronds for co-firing in coal power plants. *Energy Procedia* **2018**, *144*, 75–81. [\[CrossRef\]](#)
96. Conag, A.T.; Villahermosa, J.E.R.; Cabatingan, L.K.; Go, A.W. Energy densification of sugarcane bagasse through torrefaction under minimized oxidative atmosphere. *J. Environ. Chem. Eng.* **2017**, *5*, 5411–5419. [\[CrossRef\]](#)
97. Chiou, B.-S.; Cao, T.; Valenzuela-Medina, D.; Bilbao-Sainz, C.; Avena-Bustillos, R.J.; Milczarek, R.R.; Du, W.-X.; Glenn, G.M.; Orts, W.J. Torrefaction kinetics of almond and walnut shells. *J. Therm. Anal. Calorim.* **2018**, *131*, 3065–3075. [\[CrossRef\]](#)
98. Margaritis, N.; Grammelis, P.; Karampinis, E.; Kanaveli, I.-P. Impact of Torrefaction on Vine Pruning's Fuel Characteristics. *J. Energy Eng.* **2020**, *146*, 04020006. [\[CrossRef\]](#)
99. Volpe, R.; Messineo, A.; Millan, M.; Volpe, M.; Kandiyoti, R. Assessment of olive wastes as energy source: Pyrolysis, torrefaction and the key role of H loss in thermal breakdown. *Energy* **2015**, *82*, 119–127. [\[CrossRef\]](#)
100. Dyjakon, A.; García-Galindo, D. Implementing agricultural pruning to energy in europe: Technical, economic and implementation potentials. *Energies* **2019**, *12*, 1513. [\[CrossRef\]](#)
101. Boumanchar, I.; Charafeddine, K.; Chhiti, Y.; Alaoui, F.E.M.H.; Sahibed-dine, A.; Bentiss, F.; Jama, C.; Bensitel, M. Biomass higher heating value prediction from ultimate analysis using multiple regression and genetic programming. *Biomass Convers. Biorefinery* **2019**, *9*, 499–509. [\[CrossRef\]](#)
102. Ren, C.; Guo, D.; Liu, X.; Li, R.; Zhang, Z. Performance of the emerging biochar on the stabilization of potentially toxic metals in smelter-and mining-contaminated soils. *Environ. Sci. Pollut. Res.* **2020**, *27*, 1–11. [\[CrossRef\]](#)
103. Verslype, N.I.; de Souza Caldas, R.M.; Machado, J.; Martins, F.M.G.; Fernandez, H.M.; Rodrigues, J.I. Sustainable agriculture in temporary and permanent crops in Portugal| Agricultura sustentável em culturas temporárias e permanentes em Portugal. *Rev. Geama* **2016**, *2*, 211–219.
104. Pagels, J.; Strand, M.; Rissler, J.; Szpila, A.; Gudmundsson, A.; Bohgard, M.; Lillieblad, L.; Sanati, M.; Swietlicki, E. Characteristics of aerosol particles formed during grate combustion of moist forest residue. *J. Aerosol Sci.* **2003**, *34*, 1043–1059. [\[CrossRef\]](#)
105. Zhao, P.; Shen, Y.; Ge, S.; Chen, Z.; Yoshikawa, K. Clean solid biofuel production from high moisture content waste biomass employing hydrothermal treatment. *Appl. Energy* **2014**, *131*, 345–367. [\[CrossRef\]](#)
106. Demirbas, A. Combustion systems for biomass fuel. *Energy Sour. Part A* **2007**, *29*, 303–312. [\[CrossRef\]](#)
107. Deboni, T.L.; Simioni, F.J.; Brand, M.A.; Lopes, G.P. Evolution of the quality of forest biomass for energy generation in a cogeneration plant. *Renew. Energy* **2019**, *135*, 1291–1302. [\[CrossRef\]](#)
108. Samadi, S.H.; Ghobadian, B.; Nosrati, M. Prediction and estimation of biomass energy from agricultural residues using air gasification technology in Iran. *Renew. Eng.* **2020**, *149*, 1077–1091. [\[CrossRef\]](#)
109. Williams, A.; Jones, J.; Ma, L.; Pourkashanian, M. Pollutants from the combustion of solid biomass fuels. *Prog. Energy Combust. Sci.* **2012**, *38*, 113–137. [\[CrossRef\]](#)

110. Shen, G.; Xue, M.; Wei, S.; Chen, Y.; Zhao, Q.; Li, B.; Wu, H.; Tao, S. Influence of fuel moisture, charge size, feeding rate and air ventilation conditions on the emissions of PM, OC, EC, parent PAHs, and their derivatives from residential wood combustion. *J. Environ. Sci.* **2013**, *25*, 1808–1816. [\[CrossRef\]](#)
111. De Lucena Tavares, S.R.; dos Santos, T.E. Uso de diferentes fontes de biomassa vegetal para a produção de biocombustíveis sólidos. *Holos* **2013**, *5*, 19–27. [\[CrossRef\]](#)
112. Strzalka, R.; Erhart, T.G.; Eicker, U. Analysis and optimization of a cogeneration system based on biomass combustion. *Appl. Therm. Engineer.* **2013**, *50*, 1418–1426. [\[CrossRef\]](#)
113. Bazargan, A.; Gebreegziabher, T.; Hui, C.-W.; McKay, G. The effect of alkali treatment on rice husk moisture content and drying kinetics. *Biomass Bioenergy* **2014**, *70*, 468–475. [\[CrossRef\]](#)
114. Manzone, M.; Gioelli, F.; Balsari, P. Effects of Different Storage Techniques on Round-Baled Orchard-Pruning Residues. *Energies* **2019**, *12*, 1044. [\[CrossRef\]](#)
115. Kalembkiewicz, J.; Chmielarz, U. Ashes from co-combustion of coal and biomass: New industrial wastes. *Resour. Conserv. Recycl.* **2012**, *69*, 109–121. [\[CrossRef\]](#)
116. Nunes, L.; Matias, J.; Catalão, J. Biomass combustion systems: A review on the physical and chemical properties of the ashes. *Renew. Sustain. Eng. Rev.* **2016**, *53*, 235–242. [\[CrossRef\]](#)
117. Van der Drift, A.; Van Doorn, J.; Vermeulen, J.W. Ten residual biomass fuels for circulating fluidized-bed gasification. *Biomass Bioenergy* **2001**, *20*, 45–56. [\[CrossRef\]](#)
118. Haykiri-Acma, H.; Yaman, S.; Kucukbayrak, S. Gasification of biomass chars in steam–nitrogen mixture. *Energy Convers. Manag.* **2006**, *47*, 1004–1013. [\[CrossRef\]](#)
119. Rajamma, R.; Ball, R.J.; Tarelho, L.A.; Allen, G.C.; Labrincha, J.A.; Ferreira, V.M. Characterisation and use of biomass fly ash in cement-based materials. *J. Hazard. Mater.* **2009**, *172*, 1049–1060. [\[CrossRef\]](#)
120. Thy, P.; Jenkins, B.; Grundvig, S.; Shiraki, R.; Leshner, C. High temperature elemental losses and mineralogical changes in common biomass ashes. *Fuel* **2006**, *85*, 783–795. [\[CrossRef\]](#)
121. Deng, L.; Zhang, T.; Che, D. Effect of water washing on fuel properties, pyrolysis and combustion characteristics, and ash fusibility of biomass. *Fuel Proc. Technol.* **2013**, *106*, 712–720. [\[CrossRef\]](#)
122. Turn, S.Q.; Kinoshita, C.M.; Ishimura, D.M. Removal of inorganic constituents of biomass feedstocks by mechanical dewatering and leaching. *Biomass Bioenergy* **1997**, *12*, 241–252. [\[CrossRef\]](#)
123. Gao, X.; Wu, H. Combustion of volatiles produced in situ from the fast pyrolysis of woody biomass: Direct evidence on its substantial contribution to submicrometer particle (PM1) emission. *Energy Fuels* **2011**, *25*, 4172–4181. [\[CrossRef\]](#)
124. García, R.; Pizarro, C.; Lavín, A.G.; Bueno, J.L. Characterization of Spanish biomass wastes for energy use. *Bioresour. Technol.* **2012**, *103*, 249–258. [\[CrossRef\]](#)
125. Sun, X.; Shan, R.; Li, X.; Pan, J.; Liu, X.; Deng, R.; Song, J. Characterization of 60 types of Chinese biomass waste and resultant biochars in terms of their candidacy for soil application. *Gcb Bioenergy* **2017**, *9*, 1423–1435. [\[CrossRef\]](#)
126. Singh, K.; Zondlo, J. Characterization of fuel properties for coal and torrefied biomass mixtures. *J. Energy Inst.* **2017**, *90*, 505–512. [\[CrossRef\]](#)
127. Nanou, P.; Carbo, M.C.; Kiel, J.H. Detailed mapping of the mass and energy balance of a continuous biomass torrefaction plant. *Biomass Bioenergy* **2016**, *89*, 67–77. [\[CrossRef\]](#)
128. Dos Santos Viana, H.F.; Martins Rodrigues, A.; Godina, R.; de Oliveira Matias, J.C.; Jorge Ribeiro Nunes, L. Evaluation of the physical, chemical and thermal properties of Portuguese maritime pine biomass. *Sustainability* **2018**, *10*, 2877. [\[CrossRef\]](#)
129. Loureiro, L.M.; Nunes, L.J.; Rodrigues, A.M. Woody biomass torrefaction: Fundamentals and potential for Portugal. *Silva Lusit.* **2017**, *25*, 35–63.
130. Nunes, L.J. A Case Study about Biomass Torrefaction on an Industrial Scale: Solutions to Problems Related to Self-Heating, Difficulties in Pelletizing, and Excessive Wear of Production Equipment. *Appl. Sci.* **2020**, *10*, 2546. [\[CrossRef\]](#)

