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Production of Biochar from Vine Pruning: Waste Recovery in the Wine Industry

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Abstract: The production of residual biomass, such as vine pruning, presents environmental problems since its elimination is usually carried out through the uncontrolled burning of the remaining materials and with the emission of greenhouse gases without any counterpart. The use of these residues to produce biochar presents several advantages. In addition to the more common energy recovery, other conversion ways allowing new uses, such as soil amendment and carbon sequestration, can be analyzed as options as well. In the present study, vine pruning biomasses are characterized to evaluate the behavior of the different constituents. Then, the different possible applications are discussed. It is concluded that materials resulting from the pruning of vineyards have excellent characteristics for energy recovery, with an increment of more than 50% in the heating value and almost 60% in the carbon content when carbonized. This recovery procedure contributes to creating new value chains for residual materials to promote sustainable practices in the wine sector.

Keywords: biochar; vine pruning; biomass waste; circular economy; sustainability

1. Introduction

The use of biomass as a form of energy acquired a recent interest, despite being the oldest form of energy, accompanying developing mankind since the discovery of fire [1,2]. Obviously, in modern times, there are many innovations in improving fuels, but mainly concerning converting and valuing this form of energy [3,4]. While the use of biomass may have been limited to the direct combustion of branches and trunks in the early days of mankind, today, conversion includes improving fuels through thermochemical conversion technologies, such as torrefaction, pyrolysis and gasification, which are later more efficiently used in combustion recovery processes [5,6].

This recovery process may allow incorporating a set of materials that are not commonly used, mainly due to several unfavorable characteristics, such as high moisture content, excess of inert materials, low-density, and lower calorific value. These properties contributed to the exclusive use of materials presenting characteristics classified as good [7]. This segregation, besides the preference for some species, also includes the preference for specific parts, such as trunks, neglecting less favorable parts, such as branches, leaves, bark, or roots [8].

One of the sectors where the use and reincorporation of waste materials into supply chains can be presented as a necessity is the agro-industrial sector, now following sustainability and circular economy [9–11]. Within this so diverse sector, the wine industry emerges as an excellent field for developing this trend. First, due to the diversity of residual forms available, such as bagasse, stalks, or pruning materials, but also due to the quantities cyclically produced, which may cause environmental problems, such as CO_2 emissions during uncontrolled waste burning, its disposal in landfills, or simple abandonment in piles [12–14].

The use of vine pruning materials in pyrolysis processes is a possibility that allows the resolution of several environmental problems, namely those related to managing the large volumes generated annually, but also adding some value to the materials, since its elimination results mostly in costs [15–17]. In this way, recovering these materials creates new value chains and introduces a circular economy perspective, contributing to the sector's sustainability [18–20]. Biochar production converts the waste into materials with higher added value, higher energy density, which are not perishable by biological agents, hydrophobic, and even can be used to replace coal, serving as a mitigating agent for climate changes [21,22]. This biochar can also be used in soil amendment functions, taking advantage of its adsorption capacity to capture polluting elements or to fix nutrients, and serves as a sink, sequestering carbon in the soil, and thereby contribute once again to mitigate climate changes [13,23].

This study aims to characterize vine pruning material, analyze its chemical composition, and understand the behavior of the materials when submitted to a pyrolysis process. Possibilities for use are also discussed, with a perspective of adding value to the materials and introducing circular economy processes in the wine industry by implementing new practices. We discuss how introducing these circular economy practices can lead to the sustainability of the sector, namely through the resolution of environmental problems and creating new value chains for waste materials.

2. Materials and Methods

2.1. Sampling and Material Preparation

The biomass of vine pruning was collected during December 2020 in vineyards located in the Ponte de Lima region (North Portugal). The material was subsequently cut into portions with dimensions close to 3 cm, as shown in Figure 1, to facilitate drying and grinding.

For biochar production, we used a BARRACHA (model K-3) high-temperature furnace, which uses electrical resistances for generating heat. This furnace also presents a built-in thermal controller that enables programming four temperature stages with respective residence times. The preparation of the samples was made with the aid of conventional aluminum paper used to wrap the material into a cylindrical shape. Because the aluminum paper has two distinct sides, it should be noted that the opaque part of the sheet must be directed towards the outside so that during the carbonization process, the heat is not reflected.

The definition of temperature stages and a scheme of the programmable stages are presented in Table 1. Temperatures were chosen based on the definition presented by Nunes (2020) [24], while the residence times were selected based on the studies by Ribeiro et al. (2018), Sá et al. (2020) and Nunes et al. (2021) [20,25,26]. Figure 2 shows the material wrapped in the aluminum foil and the material after the biochar production phase.

Figure 1. Samples collected for the characterization and biochar production tests.

Table 1. Scheme of the programmable stages according to the temperature and residence time.

Stages	Carbonization Steps	Temperature (°C)	Residence Time (min)	Heating Rate (°C.min^{-1})
1	Initial heating/pre-drying	T_{room}–180	30	5
2	Post-drying and intermediate heating	180–3400	60	3.7
3	Carbonization	400	90	-
4	Cooling	400–50 °C	Until can safely open the furnace	-

(a)   **(b)**

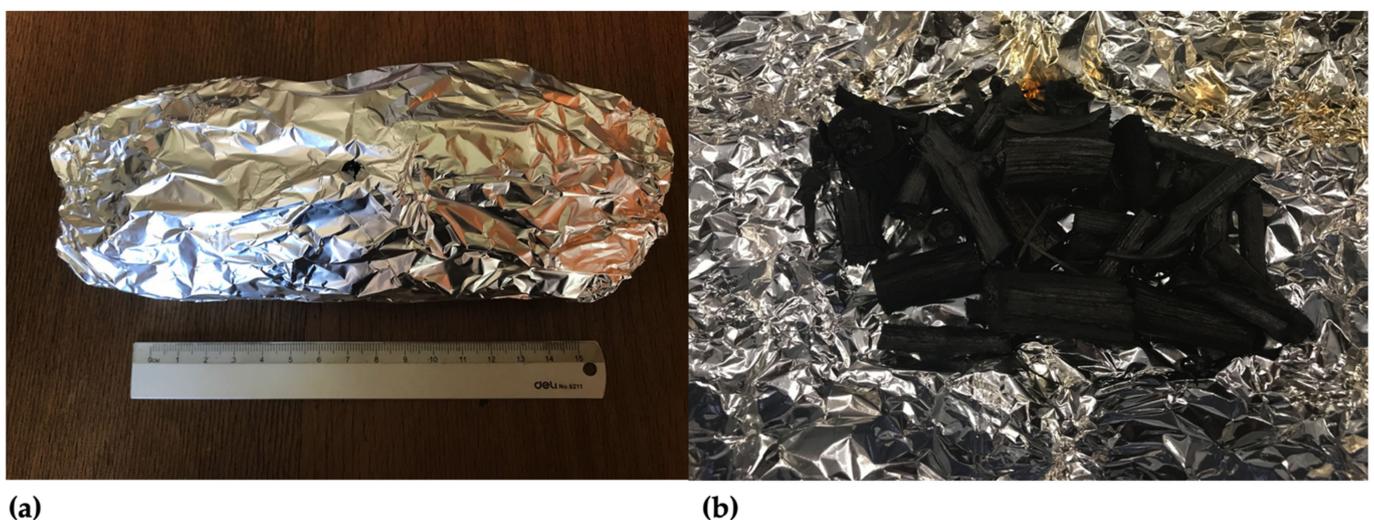**Figure 2.** (**a**) Material wrapped in the aluminum foil; (**b**) produced biochar.

2.2. Laboratory Characterization Tests

To carry out the laboratory characterization tests, the procedures described in the following reference standards were used:

- ISO 17225-1: 2014—Solid biofuels—Fuel specifications and classes—Part 1: General requirements.
- ISO 16948: 2015—Solid biofuels—Determination of total content of carbon, hydrogen and nitrogen.
- ISO 16967: 2015—Solid biofuels—Determination of major elements—Al, Ca, Fe, Mg, P, K, Si, Na and Ti.
- ISO 16968: 2015—Solid biofuels—Determination of minor elements—Ar, Cd, Cobalt, Cr, Copper, Hg, Mn, Mo, Ni, Pb, Sb, V and Zn.
- ISO 16994: 2016—Solid biofuels—Determination of total content of sulfur and chlorine.
- ISO 18125: 2017—Solid biofuels—Determination of calorific value.
- ISO 21404: 2020(en)—Solid biofuels—Determination of ash melting behavior.
- ASTM E870—82(2019)—Standard Test Methods for Analysis of Wood Fuels (with reference documents: ASTM D1102—84(2021)—Standard Test Method for Ash in Wood; ASTM E871—82(2019)—Standard Test Method for Moisture Analysis of Particulate Wood Fuels; ASTM E871—82(2019)—Standard Test Method for Moisture Analysis of Particulate Wood Fuels)—Determination of proximate analysis by thermogravimetry.

3. Results and Discussion

The materials resulting from vine pruning are normally used as firewood for heating and as fuel in bakery and restaurant ovens [27]. In Portugal, for example, traditionally, it is the preferred fuel for piglet roasters restaurants in the Bairrada region [28]. However, given the considerable volumes of biomass produced annually throughout the country, it is very difficult to collect and use it, given the dispersion of wine production throughout the territory, which is usually abandoned, or else eliminated by burning the leftovers [29,30]. Despite the recognized properties as a fuel, previously reported in several works, such as those by Duca et al. (2016), Torreiro et al. (2020), Nunes et al. (2020) or Atelge et al. (2020), where several characterizations of materials and different forms of energy recovery, such as anaerobic digestion, pyrolysis or gasification, are presented, still exists a deep lack of knowledge concerning creating value chains using these materials and about the best options to manage the amounts yearly generated [31–34].

The results obtained in the thermogravimetric analysis for vine pruning samples, dry and carbonized material, are presented in Table 2.

Table 2. TGA results.

	Moisture (%)		Volatiles (%)		Ashes (%)		Fixed Carbon (%)	
	Dry	**Biochar**	**Dry**	**Biochar**	**Dry**	**Biochar**	**Dry**	**Biochar**
Sample 1	3.74	1.35	77.83	33.33	1.42	7.30	19.51	59.36
Sample 2	3.77	1.37	77.84	34.51	1.41	7.33	19.46	58.16
Sample 3	3.51	1.30	77.72	33.85	1.42	7.22	19.78	58.94
Average	3.67	1.34	77.80	33.90	1.42	7.28	19.58	58.82
Standard deviation	0.14	0.03	0.07	0.59	0.01	0.06	0.17	0.61
Confidence	0.16	0.04	0.08	0.67	0.01	0.07	0.20	0.69

After drying in a laboratory oven for 12 h at 90 °C, the sample material showed an average value of 3.67 ± 0.16%. The volatile content showed an average value of 77.80 ± 0.08%. The ash content showed an average value of 1.42 ± 0.01%. The fixed carbon content showed an average value of 19.58 ± 0.20%. The moisture content after carbonization of the samples showed an average value of 1.34 ± 0.04%. The volatile content showed an average value of 33.90 ± 0.67%. The ash content showed an average value of 7.28 ± 0.07%. The fixed carbon content showed an average value of 58.82 ± 0.69%.

The thermogravimetric analysis (Figure 3) demonstrated that the moisture content changes to residual values, reaching a minimum value of 1.34%, in line with the results obtained by Ren et al. (2013), with values below 2.00% for temperatures of 300 °C, or in work by Barzegar et al. (2020), which obtained 1.90% moistures for the same conditions [35,36]. As expected, the volatile content had a significant reduction, going from the initial 77.80% to a value of 33.90%. This result is justified by the loss of mass verified since this occurs mainly due to the volatilization of hemicellulose, which is the compound responsible for forming most of the volatile organic compounds and structural water [37–40]. As the ash consists essentially of nonvolatilizable metal oxides, the increase observed in its content is justified with the verified mass loss since it is proportional [41,42]. With the release of oxygenated compounds, the fixed carbon content increased from 19.58% to 58.82%. This increase in the fixed carbon content is one of the advantages of the thermochemical conversion process since it allows the obtention of a material with higher carbon content and greater viability for energy recovery, but also because of the possibility that it opens for other uses, namely in soil amendment, due to the adsorbent capacity that biochar presents, and which has been widely studied [43–45].
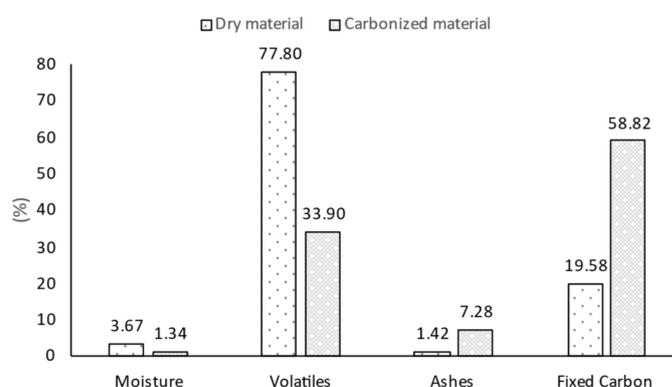
Figure 3. Evolution of moisture, volatiles, ashes and fixed carbon contents after carbonization of vine pruning.

The results obtained for CHNO analysis are presented in Table 3.

Table 3. CHNO results.

	C (%)		H (%)		N (%)		O (%)	
	Dry	**Biochar**	**Dry**	**Biochar**	**Dry**	**Biochar**	**Dry**	**Biochar**
Sample 1	47.12	73.55	6.36	4.69	0.71	1.209	45.79	20.53
Sample 2	46.48	73.62	6.42	4.60	0.62	1.213	46.47	20.55
Sample 3	45.23	73.40	6.05	4.62	0.28	1.175	48.42	20.78
Average	46.28	73.53	6.28	4.64	0.54	1.20	46.89	20.62
Standard deviation	0.96	0.11	0.20	0.05	0.23	0.02	1.37	0.14
Confidence	1.09	0.13	0.22	0.05	0.26	0.02	1.55	0.16

The C content for the dry samples showed an average value of 46.28 ± 1.09. The H content showed an average value of 6.28 ± 0.22. The N content showed an average value of 0.54 ± 0.26%. The O content showed an average value of 46.89 ± 1.55. The C content for the biochar samples showed an average value of 73.53 ± 0.13%. The H content showed an average value of 4.64 ± 0.05%. The N content showed an average value of 1.200 ± 0.02%. The O content showed an average value of 20.62 ± 0.16.

The trend of evolution of the CHNO contents after the carbonization of the material (Figure 4) demonstrated consistency with previous studies, and the consonance with the behavior revealed by other forms of biomass, with the values of the C content showing a significant increase, from 46.28% to 73.53%, while, in the opposite direction, the O content

drops from the initial 46.89% to 20.62%, after the carbonization process. These results are in line with the recognized elimination of oxygenated products resulting from the degradation of hemicellulose [13,46–48]. The N content showed a slight increase, from 0.54% to 1.20%, associated with its concentration, justified by the average weight loss of $78.31 \pm 1.00\%$ observed, while the H content showed a slight decrease, from the initial 6.28% to 4.64%, associated with its contribution to forming volatile organic compounds [49]. In addition, the analysis of the H/C and O/C ratios, which show a sharp decrease, indicates increased calorific value, since after being projected in a van Krevelen diagram, biochar will present a position closer to the origin of the graphic when compared to the projection of the ratios obtained with the CHO contents for the dry samples of vine pruning.
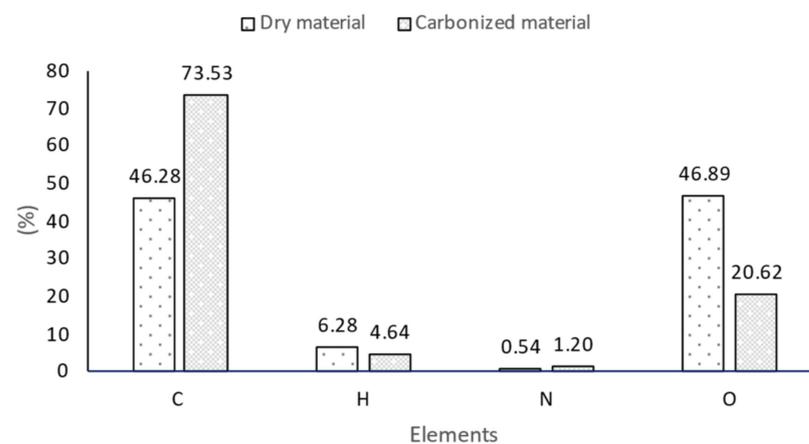
Figure 4. Evolution of CHNO contents after carbonization of vine pruning.

The oxygen content of a fuel is a determining factor for the efficiency of its conversion during combustion. The availability of oxygen in the fuel increases the combination with hydrogen to produce water, which subsequently lowers the temperature of the flame. As shown in Figure 5, pyrolysis causes a reduction in the oxygen content and increases the carbon content without, however, significantly altering the hydrogen content. As saw earlier, the pyrolysis process, like what happens with the biomass torrefaction process, leads to the volatilization of one of the constituent compounds of biomass, which is hemicellulose, mainly in the temperature range between 220 °C and 320 °C, as described by Nunes et al. (2020) [24]. When this temperature is exceeded, accelerated cellulose decomposition begins. However, the procedure is similar and continues to lean towards the elimination of oxygen [50,51].

This reduction in the oxygen content significantly improves the combustibility of the biochar, but this may not even be the greatest advantage and the best way to enhance this material since, as recent studies indicate, its use as a soil amendment to take advantage of its adsorbent properties for the removal of polluting elements, or even the fixation of nutrients, can be an advantage with a more positive impact than energy recovery [52,53]. Another possibility that emerges from incorporating biochar in soils is related to the carbon sequestration capacity, contributing to the mitigation of climate changes since it is a negative emission technology [54,55].
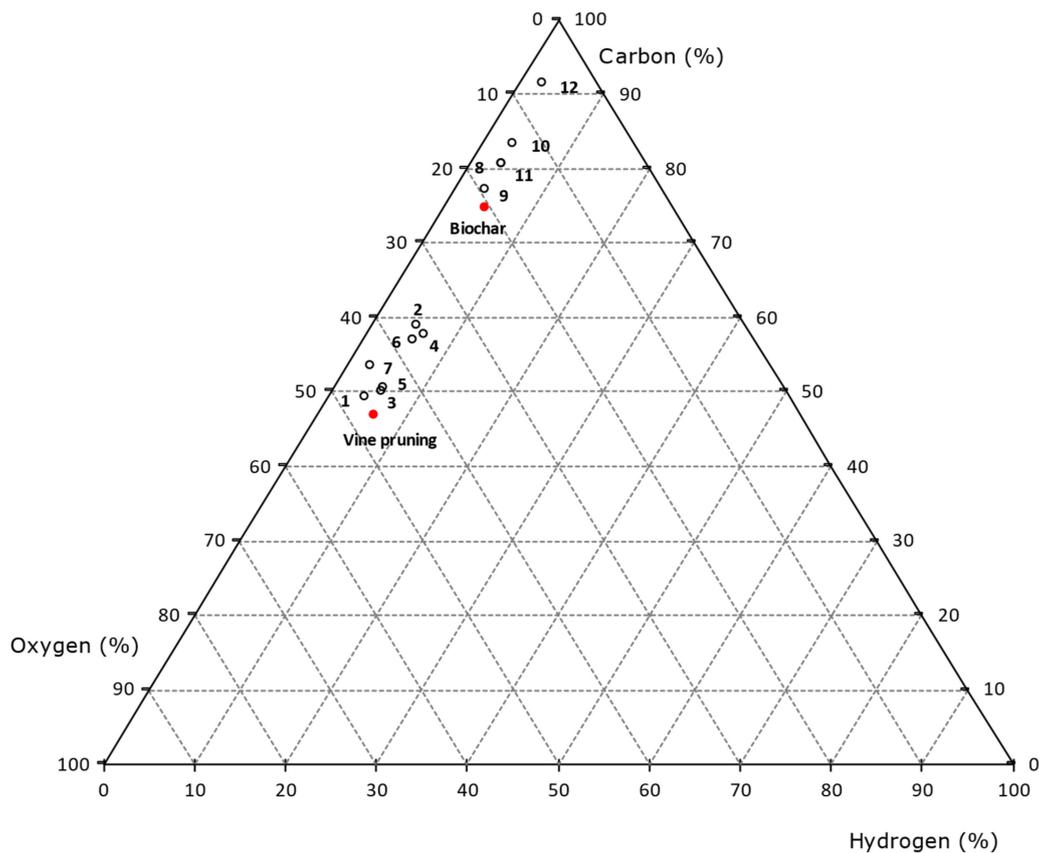
Figure 5. Triangular diagram representing CHO contents. As can be seen, the content of CHO for vine pruning is similar to those found by Nunes et al. (2020) and Sá et al. (2020), both for dry and carbonized samples [26,33]. Vine pruning and biochar are the samples analyzed in the present work; samples 1 to 6 and samples 7 to 12 are, respectively, dry samples and carbonized samples from previous referred studies, as follows: 1 and 7—rice husks; 2 and 8—almond shells; 3 and 9—kiwi pruning; 4 and 10—olive pomace; 5 and 11—*Pinus pinaster*; and 6 and 12—*Eucalyptus globulus*.

The results obtained in the determination of S and Cl are shown in Table 4.

Table 4. S and Cl results.

	S (ppm)		Cl (ppm)	
	Dry	**Biochar**	**Dry**	**Biochar**
Sample 1	181	186	92.7	1.3
Sample 2	184	179	13.8	6.5
Sample 3	190	183	16.4	7.7
Average	185	183	41.0	5.2
Standard deviation	5	3.5	44.8	3.4
Confidence	5	4	50.7	3.9

For dried samples, the S content showed an average value of 185 ± 5 ppm. The Cl content showed an average value of 41.0 ± 50.7 ppm. For carbonized samples, the S content showed an average value of 183 ± 4 ppm. The Cl content showed an average value of 5.2 ± 3.9 ppm.

It is very common for different forms of biomass to have low sulfur contents, as is evidenced in several studies, such as those by Arias et al. (2008) and Simonic et al. (2020) [56,57]. The result obtained proves this trend since the value obtained is low, being in line with the values allowed, for example, by the ENplus® standard, which is 0.04% [58]. Chlorine, on the other hand, can appear in abundant quantities, being one of the agents responsible for the corrosion of combustion equipment that most contributes to damage

and maintenance stops [59,60]. However, a recent study by Sá et al. (2020) proved that chlorine could be eliminated from the final product through thermochemical conversion processes, as seen in the results obtained, in which from the initial 0.0041%, it changed to 0.0005%, that is, to a practically null value, as is presented in Figure 6 [26].
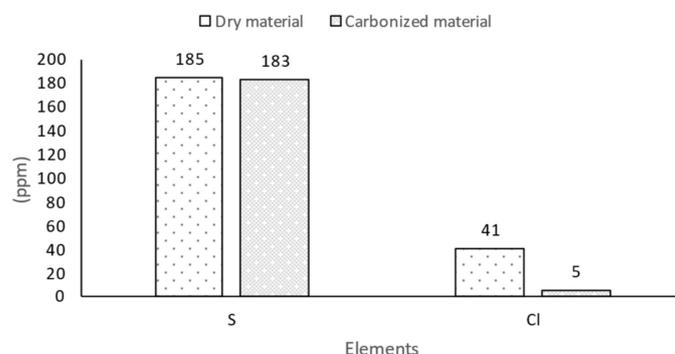
Figure 6. Evolution of S and Cl contents after carbonization of vine pruning.

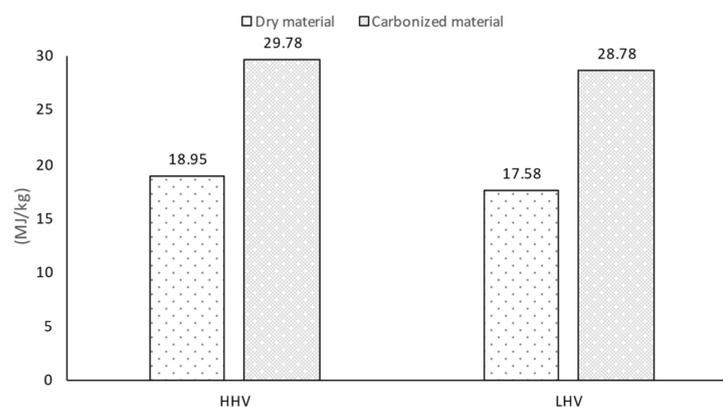The results obtained for HHV and LHV are shown in Table 5.

Table 5. HHV and LHV results.

	HHV (MJ/kg)		LHV (MJ/kg)	
	Dry	**Biochar**	**Dry**	**Biochar**
Sample 1	18.95	29.84	17.58	28.84
Sample 2	18.95	29.71	17.58	28.72
Sample 3	18.95	29.78	17.58	28.78
Average	18.95	29.78	17.58	28.78
Standard deviation	0.002	0.006	0.002	0.006
Confidence	0.002	0.007	0.002	0.007

The HHV of the dry samples showed an average value of 18.95 ± 0.002 MJ/kg. LHV showed an average value of 17.58 ± 0.002 MJ/kg. The HHV of carbonized samples presented an average value of 29.78 ± 0.007 MJ/kg. The LHV presented an average value of 28.78 ± 0.007 MJ/kg.

In previous works, such as those carried out by San José et al. (2013), where developing a novel conical combustor for thermal exploitation of vineyard pruning wastes is presented, the results obtained to follow the values obtained in the present work [61]. Also, in the work of Bilandzija (2012), who assesses the energy potential of several fruits pruned biomass in Croatia, including vine pruning, the average values of HHV and LHV for dry materials are confirmed [62]. The use of biowastes is a topic with growing and current interest, namely due to introducing the concepts of circular economy and sustainability in the wine industry and the agrarian environment in general. Several recent studies address the theme and present results on characterizing materials, even comparing variations between the different vine varieties used, as is the case of the works by Sun et al. (2020), Acquadro et al. (2020), Bisaglia & Romano (2018) or Loupit et al. (2020) [63–65], but also in the perspective of new valuation methodologies, as is the case presented by Allesina et al. (2018), which addresses using vine pruning as fuel in small-scale gasifiers [66], or the case presented by Margaritis et al. (2020), which deals with the impact of torrefaction on the characteristics of vine pruning fuel [67]. Regarding the pyrolysis or carbonization process, there are also several works already in existence, such as those by Tag et al. (2016), Azuara et al. (2017), Dunnigan et al. (2018), Hoffmann et al. (2019) and Sun et al. (2020), and that validate the results obtained here [23,63,68–70]. As can be seen in Figure 7, the heating value for carbonized materials increases by more than 50%. This demonstrates the advantages of using a thermochemical conversion process such as pyrolysis to valorize

these residual materials, both for the potential energy generated and associated logistical advantages. Such logisticl advantages include reduction of volume, energy densification and ease of storage, since the materials, being hydrophobic, can be stored outside, and because they do not rot or are subject to biological activity, as demonstrated in the work of Nunes et al. (2021) [20].

Figure 7. Evolution of HHV and LHV after carbonization of vine pruning.

The results obtained concerning the mass loss for the carbonized samples of vine pruning are shown in Table 6.

Table 6. Determination of mass loss of carbonized samples of vine pruning.

	Initial Mass (g)	Final Mass (g)	Mass Loss (%)
Sample 1	229.18	47.11	79.44
Sample 2	261.70	60.01	77.07
Sample 3	257.04	55.49	78.41
Average	249.31	54.20	78.31
Standard deviation	17.59	6.55	1.00
Confidence	19.90	7.41	1.00

The mass loss presented an average value of 78.31 ± 1.00%. The values verified in the mass loss are in agreement with the values presented in previous works, such as those by Tag et al. (2016) or Nunes et al. (2020) [23,33]. The values presented in the referred works are included in the range 75–80% for process temperatures of 400 °C and equivalent residence time.

The results for major elements are shown in Table 7.

Table 7. Major elements results for dry samples.

	Al (ppm)	Ca (ppm)	Fe (ppm)	Mg (ppm)	P (ppm)	K (ppm)	Si (ppm)	Na (ppm)	Ti (ppm)
Sample 1	74.54	6972.46	31.15	1303.74	1101.95	8120.49	188.82	407.25	2.71
Sample 2	53.66	7722.37	38.57	1386.39	1077.50	8444.39	137.45	413.72	3.48
Sample 3	53.44	7641.21	32.29	1387.78	1107.98	8168.23	131.67	444.39	2.83
Average	60.55	7445.35	34.00	1359.30	1095.81	8244.37	152.65	421.79	3.01
Standard deviation	12.12	411.54	4.00	48.12	16.14	174.86	31.46	19.84	0.41
Confidence	13.71	465.69	4.52	54.46	18.26	197.87	35.60	22.45	0.47

The Al content showed an average value of 60.55 ± 12.12 ppm. The Ca content showed an average value of 7445.35 ± 465.69 ppm. The Fe content showed an average value of 34.00 ± 4.52 ppm. The Mg content showed an average value of 1359.30 ± 54.46 ppm. The *p* content showed an average value of 1095.81 ± 18.26 ppm. The K content showed

an average value of 8244.37 ± 197.87 ppm. The Si content showed an average value of 152.65 ± 35.60 ppm. The Na content showed an average value of 421.79 ± 22.45 ppm. The Ti content showed an average value of 3.01 ± 0.47 ppm.

The results obtained in determining the content of major elements for the carbonized samples of vine pruning are shown in Table 8.

Table 8. Determination of the content of major elements of carbonized samples.

	Al (ppm)	Ca (ppm)	Fe (ppm)	Mg (ppm)	P (ppm)	K (ppm)	Si (ppm)	Na (ppm)	Ti (ppm)
Sample 1	91.80	14,219.58	60.64	2331.45	2317.61	16,937.31	182.17	422.19	5.15
Sample 2	73.40	14,415.48	50.93	2329.09	2268.36	16,988.84	183.20	412.39	4.52
Sample 3	78.07	13,829.52	52.11	2314.15	2289.80	16,392.79	171.07	429.53	3.68
Average	81.09	14,154.86	54.56	2324.90	2291.92	16,772.98	178.81	421.37	4.45
Standard deviation	9.56	298.29	5.30	9.38	24.69	330.26	6.73	8.60	0.74
Confidence	10.82	337.54	6.00	10.62	27.94	373.72	7.61	9.73	0.83

The Al content showed an average value of 81.09 ± 10.82 ppm. The Ca content showed an average value of 14,154.86 ± 337.54 ppm. The Fe content showed an average value of 54.56 ± 6.00 ppm. The Mg content showed an average value of 2324.90 ± 10.62 ppm. The P content showed an average value of 2291.92 ± 27.94 ppm. The K content showed an average value of 16,772.98 ± 373.72 ppm. The Si content showed an average value of 178.81 ± 7.61 ppm. The Na content showed an average value of 421.37 ± 9.73 ppm. The Ti content showed an average value of 4.45 ± 0.83 ppm.

The results for minor elements are shown in Table 9.

Table 9. Minor elements results for dry samples.

	As (ppm)	Cd (ppm)	Co (ppm)	Cr (ppm)	Cu (ppm)	Mn (ppm)	Ni (ppm)	Pb (ppm)	Zn (ppm)
Sample 1	0.58	0.58	0.40	0.48	23.16	39.64	0.63	0.29	14.51
Sample 2	0.88	0.34	0.20	0.34	26.48	43.44	0.41	0.10	14.53
Sample 3	0.73	0.39	0.32	0.04	25.15	40.95	0.13	0.09	78.40
Average	0.73	0.44	0.31	0.29	24.93	41.34	0.39	0.16	35.81
Standard deviation	0.15	0.13	0.10	0.22	1.67	1.93	0.25	0.11	36.88
Confidence	0.17	0.14	0.11	0.25	1.89	2.18	0.28	0.13	41.73

The As content showed an average value of 0.73 ± 0.17 ppm. The Cd content showed an average value of 0.44 ± 0.14 ppm. The Co content showed an average value of 0.31 ± 0.11 ppm. The Cr content showed an average value of 0.29 ± 0.25 ppm. The Cu content showed an average value of 24.93 ± 1.89 ppm. The Mn content showed an average value of 41.34 ± 2.18 ppm. The Ni content showed an average value of 0.39 ± 0.28 ppm. The Pb content showed an average value of 0.16 ± 0.13 ppm. The Zn content showed an average value of 35.81 ± 41.73 ppm.

The results obtained in determining the content of minor elements for the carbonized samples are shown in Table 10.

Table 10. Determination of the content of minor elements in carbonized samples of vine pruning.

	As (ppm)	Cd (ppm)	Co (ppm)	Cr (ppm)	Cu (ppm)	Mn (ppm)	Ni (ppm)	Pb (ppm)	Zn (ppm)
Sample 1	2.96	0.07	0.11	0.11	45.47	87.53	0.22	0.83	55.52
Sample 2	2.73	0.00	0.00	0.00	46.63	87.58	0.03	0.77	51.59
Sample 3	2.69	0.00	0.00	0.00	45.44	85.70	0.00	0.59	51.55
Average	2.79	0.02	0.04	0,04	45.85	86.94	0.08	0.73	52.89
Standard deviation	0.146	0.040	0.064	0.064	0.679	1.071	0.119	0.125	2.281
Confidence	0.165	0.046	0.072	0.072	0.768	1.212	0.135	0.141	2.581

The As content showed an average value of 2.79 ± 0.165 ppm. The Cd content showed an average value of 0.02 ± 0.046 ppm. The Co content showed an average value of 0.04 ± 0.072 ppm. The Cr content showed an average value of 0.04 ± 0.072 ppm. The Cu content showed an average value of 45.85 ± 0.768 ppm. The Mn content showed an average value of 86.94 ± 1.212 ppm. The Ni content showed an average value of 0.08 ± 0.135 ppm. The Pb content showed an average value of 0.73 ± 0.141 ppm. The Zn content showed an average value of 52.89 ± 2.581 ppm.

Figures 8 and 9 show, respectively, the evolution of major and minor elements present in the analyzed vine pruning biomass. As can be seen, and in line with the average loss of mass observed in the tests, there is a tendency for metallic elements to concentrate since they are not eliminated during the volatilization process that occurs during pyrolysis. The same trend was confirmed by the work of Kraiem et al. (2016) or Picchi et al. (2013) [71,72]. This issue is extremely important, mainly because these elements, which will be found essentially in the form of metal oxides, are the main ones responsible for the phenomena of fouling and slagging that occur in energy recovery systems. Hence, its characterization is particularly important [73].
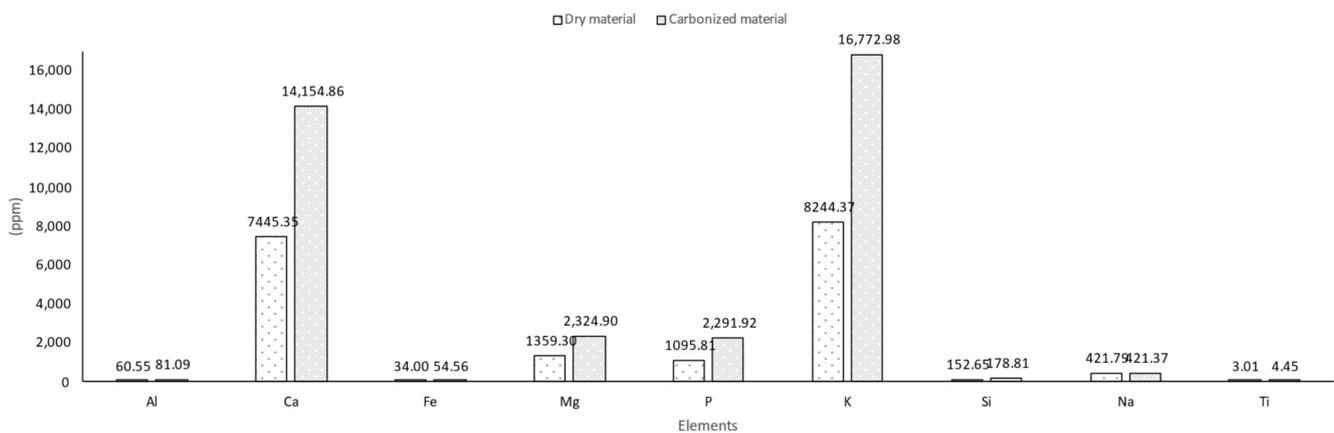

Figure 8. Evolution of the contents of major elements after the carbonization of vine pruning.
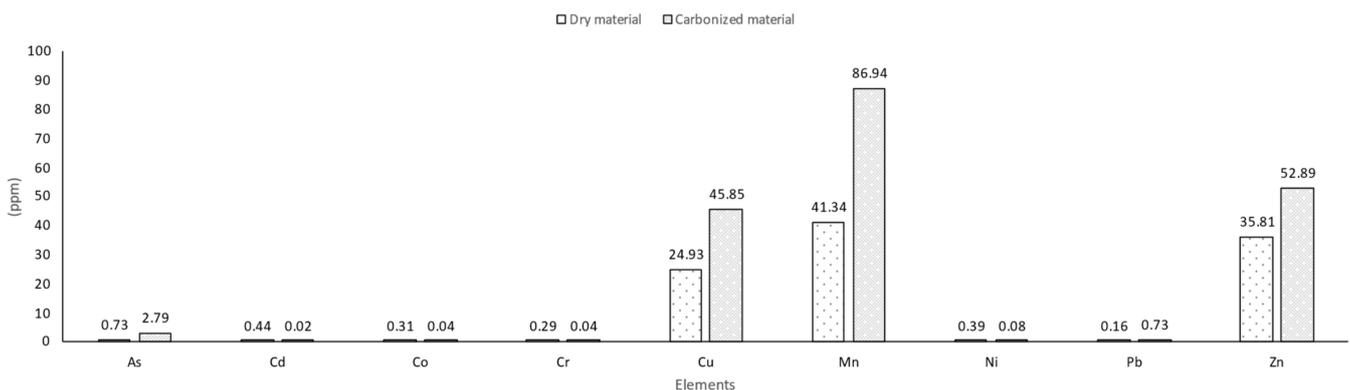

Figure 9. Evolution of minor elements content after carbonization of vine pruning.

4. Conclusions

The wine sector is responsible for generating high volumes of waste, which until the present date, has not been treated in a way to be recovered. The uses of this type of waste are rare, in addition to the traditional ones, essentially as firewood, with the elimination of the remaining volumes carried out using, normally, the uncontrolled burning of these materials, without using the generated energy. In this way, using a process such as pyrolysis to recover residues from vine pruning creates a product with higher added value, allowing its use as fuel, but also in soil amendment, and even for carbon sequestration, contributing

to the mitigation of climate changes. The results obtained confirm the quality of the fuel produced, revealing a significant increase in the heating value and the carbon content. This perspective on the use and recovery of waste resulting from the wine industry fits in with the assumption of policies to introduce processes based on the circular and regenerative economy to implement sustainability principles in the sector.

References

1.   Kennedy, G.E. From the ape's dilemma to the weanling's dilemma: Early weaning and its evolutionary context. *J. Hum. Evol.* **2005**, *48*, 123–145. [CrossRef] [PubMed]
2.   Nunes, L.; Matias, J.C.; Catalao, J.P. Wood pellets as a sustainable energy alternative in Portugal. *Renew. Energy* **2016**, *85*, 1011–1016. [CrossRef]
3.   Isaksson, R.; Johansson, P.; Fischer, K. Detecting supply chain innovation potential for sustainable development. *J. Bus. Ethics* **2010**, *97*, 425–442. [CrossRef]
4.   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]
5.   Guo, M.; Song, W.; Buhain, J. Bioenergy and biofuels: History, status, and perspective. *Renew. Sustain. Energy Rev.* **2015**, *42*, 712–725. [CrossRef]
6.   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]
7.   Nunes, L.J. Torrefied Biomass as an Alternative in Coal-Fueled Power Plants: A Case Study on Grindability of Agroforestry Waste Forms. *Clean Technol.* **2020**, *2*, 270–289. [CrossRef]
8.   Demirbas, A. Potential applications of renewable energy sources, biomass combustion problems in boiler power systems and combustion related environmental issues. *Prog. Energy Combust. Sci.* **2005**, *31*, 171–192. [CrossRef]
9.   Ferreira Gregorio, V.; Pié, L.; Terceño, A. A systematic literature review of bio, green and circular economy trends in publications in the field of economics and business management. *Sustainability* **2018**, *10*, 4232. [CrossRef]
10. Nunes, L.J.R.; Godina, R.; Matias, J.C.d.O. Technological innovation in biomass energy for the sustainable growth of textile industry. *Sustainability* **2019**, *11*, 528. [CrossRef]
11. Nunes, L.; Matias, J.; Catalão, J. Economic evaluation and experimental setup of biomass energy as sustainable alternative for textile industry. In Proceedings of the 2013 48th International Universities' Power Engineering Conference (UPEC), Dublin, Ireland, 2–5 September 2013; pp. 1–6.
12. Santini, C.; Cavicchi, A.; Casini, L. Sustainability in the wine industry: Key questions and research trends[a]. *Agric. Food Econ.* **2013**, *1*, 1–14. [CrossRef]
13. Guo, Z.; Yan, N.; Lapkin, A.A. Towards circular economy: Integration of bio-waste into chemical supply chain. *Curr. Opin. Chem. Eng.* **2019**, *26*, 148–156. [CrossRef]

14. Nunes, L.J.; Loureiro, L.M.; Sá, L.C.; Silva, H.F. Evaluation of the potential for energy recovery from olive oil industry waste: Thermochemical conversion technologies as fuel improvement methods. *Fuel* **2020**, *279*, 118536. [CrossRef]

15. Maniscalco, M.P.; Volpe, M.; Messineo, A. Hydrothermal carbonization as a valuable tool for energy and environmental applications: A review. *Energies* **2020**, *13*, 4098. [CrossRef]

16. Keijer, T.; Bakker, V.; Slootweg, J.C. Circular chemistry to enable a circular economy. *Nat. Chem.* **2019**, *11*, 190–195. [CrossRef]

17. Nunes, L.J.; Loureiro, L.M.; Sá, L.C.; Matias, J.C.; Ferraz, A.I.; Rodrigues, A.C. Energy Recovery of Agricultural Residues: Incorporation of Vine Pruning in the Production of Biomass Pellets with ENplus® Certification. *Recycling* **2021**, *6*, 28. [CrossRef]

18. Winans, K.; Kendall, A.; Deng, H. The history and current applications of the circular economy concept. *Renew. Sustain. Energy Rev.* **2017**, *68*, 825–833. [CrossRef]

19. 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]

20. Nunes, L.J.; Matias, J.C.; Loureiro, L.M.; Sá, L.C.; Silva, H.F.; Rodrigues, A.M.; Causer, T.P.; DeVallance, D.B.; Ciolkosz, D.E. Evaluation of the potential of agricultural waste recovery: Energy densification as a factor for residual biomass logistics optimization. *Appl. Sci.* **2021**, *11*, 20. [CrossRef]

21. Fytili, D.; Zabaniotou, A. Circular economy synergistic opportunities of decentralized thermochemical systems for bioenergy and biochar production fueled with agro-industrial wastes with environmental sustainability and social acceptance: A review. *Curr. Sustain. Renew. Energy Rep.* **2018**, *5*, 150–155. [CrossRef]

22. Nunes, L.J.R.; Meireles, C.I.R.; Gomes, C.J.P.; de Almeida Ribeiro, N.M.C. *Climate Change Impact on Environmental Variability in the Forest*; Springer: Cham, Switzerland, 2020.

23. Tag, A.T.; Duman, G.; Ucar, S.; Yanik, J. Effects of feedstock type and pyrolysis temperature on potential applications of biochar. *J. Anal. Appl. Pyrolysis* **2016**, *120*, 200–206. [CrossRef]

24. 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]

25. 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]

26. 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]

27. Otero, I.; Boada, M.; Tàbara, J.D. Social–ecological heritage and the conservation of Mediterranean landscapes under global change. A case study in Olzinelles (Catalonia). *Land Use Policy* **2013**, *30*, 25–37. [CrossRef]

28. Alves, C.A.; Evtyugina, M.; Cerqueira, M.; Nunes, T.; Duarte, M.; Vicente, E. Volatile organic compounds emitted by the stacks of restaurants. *Air Qual. Atmos. Health* **2015**, *8*, 401–412. [CrossRef]

29. Moreira, M.M.; Barroso, M.F.; Porto, J.V.; Ramalhosa, M.J.; Švarc-Gajić, J.; Estevinho, L.; Morais, S.; Delerue-Matos, C. Potential of Portuguese vine shoot wastes as natural resources of bioactive compounds. *Sci. Total Environ.* **2018**, *634*, 831–842. [CrossRef]

30. Brito, P.S.; Oliveira, A.S.; Rodrigues, L.F. Energy valorization of solid vines pruning by thermal gasification in a pilot plant. *Waste Biomass Valorization* **2014**, *5*, 181–187. [CrossRef]

31. 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]

32. Duca, D.; Toscano, G.; Pizzi, A.; Rossini, G.; Fabrizi, S.; Lucesoli, G.; Servili, A.; Mancini, V.; Romanazzi, G.; Mengarelli, C. Evaluation of the characteristics of vineyard pruning residues for energy applications: Effect of different copper-based treatments. *J. Agric. Eng.* **2016**, *47*, 22–27. [CrossRef]

33. Nunes, L.J.; Loureiro, L.M.; Sá, L.C.; Silva, H.F. Waste recovery through thermochemical conversion technologies: A case study with several Portuguese agroforestry by-products. *Clean Technol.* **2020**, *2*, 377–391. [CrossRef]

34. Atelge, M.; Atabani, A.; Banu, J.R.; Krisa, D.; Kaya, M.; Eskicioglu, C.; Kumar, G.; Lee, C.; Yildiz, Y.; Unalan, S. A critical review of pretreatment technologies to enhance anaerobic digestion and energy recovery. *Fuel* **2020**, *270*, 117494. [CrossRef]

35. Ren, S.; Lei, H.; Wang, L.; Bu, Q.; Chen, S.; Wu, J. Thermal behaviour and kinetic study for woody biomass torrefaction and torrefied biomass pyrolysis by TGA. *Biosyst. Eng.* **2013**, *116*, 420–426. [CrossRef]

36. Barzegar, R.; Yozgatligil, A.; Olgun, H.; Atimtay, A.T. TGA and kinetic study of different torrefaction conditions of wood biomass under air and oxy-fuel combustion atmospheres. *J. Energy Inst.* **2020**, *93*, 889–898. [CrossRef]

37. Martínez, M.G.; Dupont, C.; Thiéry, S.; Meyer, X.-M.; Gourdon, C. Impact of biomass diversity on torrefaction: Study of solid conversion and volatile species formation through an innovative TGA-GC/MS apparatus. *Biomass Bioenergy* **2018**, *119*, 43–53. [CrossRef]

38. Bates, R.B.; Ghoniem, A.F. Biomass torrefaction: Modeling of volatile and solid product evolution kinetics. *Bioresour. Technol.* **2012**, *124*, 460–469. [CrossRef]

39. Chen, W.-H.; Peng, J.; Bi, X.T. A state-of-the-art review of biomass torrefaction, densification and applications. *Renew. Sustain. Energy Rev.* **2015**, *44*, 847–866. [CrossRef]

40. Zhang, Z.; Duan, H.; Zhang, Y.; Guo, X.; Yu, X.; Zhang, X.; Rahman, M.M.; Cai, J. Investigation of kinetic compensation effect in lignocellulosic biomass torrefaction: Kinetic and thermodynamic analyses. *Energy* **2020**, *207*, 118290. [CrossRef]

41. Lu, K.-M.; Lee, W.-J.; Chen, W.-H.; Lin, T.-C. Thermogravimetric analysis and kinetics of co-pyrolysis of raw/torrefied wood and coal blends. *Appl. Energy* **2013**, *105*, 57–65. [CrossRef]

42. Lu, J.-J.; Chen, W.-H. Investigation on the ignition and burnout temperatures of bamboo and sugarcane bagasse by thermogravimetric analysis. *Appl. Energy* **2015**, *160*, 49–57. [CrossRef]

43. Yao, Y.; Gao, B.; Zhang, M.; Inyang, M.; Zimmerman, A.R. Effect of biochar amendment on sorption and leaching of nitrate, ammonium, and phosphate in a sandy soil. *Chemosphere* **2012**, *89*, 1467–1471. [CrossRef]

44. Uchimiya, M.; Lima, I.M.; Klasson, K.T.; Wartelle, L.H. Contaminant immobilization and nutrient release by biochar soil amendment: Roles of natural organic matter. *Chemosphere* **2010**, *80*, 935–940. [CrossRef]

45. Jiang, T.-Y.; Jiang, J.; Xu, R.-K.; Li, Z. Adsorption of Pb (II) on variable charge soils amended with rice-straw derived biochar. *Chemosphere* **2012**, *89*, 249–256. [CrossRef]

46. Chen, D.; Gao, A.; Cen, K.; Zhang, J.; Cao, X.; Ma, Z. Investigation of biomass torrefaction based on three major components: Hemicellulose, cellulose, and lignin. *Energy Convers. Manag.* **2018**, *169*, 228–237. [CrossRef]

47. Zhang, Z.; Zhao, Y.; Wang, T. Spirulina hydrothermal carbonization: Effect on hydrochar properties and sulfur transformation. *Bioresour. Technol.* **2020**, *306*, 123148. [CrossRef]

48. Wang, T.; Zhai, Y.; Zhu, Y.; Li, C.; Zeng, G. A review of the hydrothermal carbonization of biomass waste for hydrochar formation: Process conditions, fundamentals, and physicochemical properties. *Renew. Sustain. Energy Rev.* **2018**, *90*, 223–247. [CrossRef]

49. Chen, Y.-C.; Chen, W.-H.; Lin, B.-J.; Chang, J.-S.; Ong, H.C. Fuel property variation of biomass undergoing torrefaction. *Energy Procedia* **2017**, *105*, 108–112. [CrossRef]

50. Piskorz, J.; Radlein, D.; Scott, D.S. On the mechanism of the rapid pyrolysis of cellulose. *J. Anal. Appl. Pyrolysis* **1986**, *9*, 121–137. [CrossRef]

51. Antal, M.J.J.; Varhegyi, G. Cellulose pyrolysis kinetics: The current state of knowledge. *Ind. Eng. Chem. Res.* **1995**, *34*, 703–717. [CrossRef]

52. Chan, K.Y.; Van Zwieten, L.; Meszaros, I.; Downie, A.; Joseph, S. Agronomic values of greenwaste biochar as a soil amendment. *Soil Res.* **2008**, *45*, 629–634. [CrossRef]

53. Singh, B.; Singh, B.P.; Cowie, A.L. Characterisation and evaluation of biochars for their application as a soil amendment. *Soil Res.* **2010**, *48*, 516–525. [CrossRef]

54. Woolf, D.; Amonette, J.E.; Street-Perrott, F.A.; Lehmann, J.; Joseph, S. Sustainable biochar to mitigate global climate change. *Nat. Commun.* **2010**, *1*, 1–9. [CrossRef] [PubMed]

55. Glaser, B.; Parr, M.; Braun, C.; Kopolo, G. Biochar is carbon negative. *Nat. Geosci.* **2009**, *2*, 2. [CrossRef]

56. Arias, B.; Pevida, C.; Fermoso, J.; Plaza, M.; Rubiera, F.; Pis, J. Influence of torrefaction on the grindability and reactivity of woody biomass. *Fuel Process. Technol.* **2008**, *89*, 169–175. [CrossRef]

57. Simonic, M.; Goricanec, D.; Urbancl, D. Impact of torrefaction on biomass properties depending on temperature and operation time. *Sci. Total Environ.* **2020**, *740*, 140086. [CrossRef]

58. Monedero, E.; Portero, H.; Lapuerta, M. Pellet blends of poplar and pine sawdust: Effects of material composition, additive, moisture content and compression die on pellet quality. *Fuel Process. Technol.* **2015**, *132*, 15–23. [CrossRef]

59. Nielsen, H.P.; Frandsen, F.; Dam-Johansen, K.; Baxter, L. The implications of chlorine-associated corrosion on the operation of biomass-fired boilers. *Prog. Energy Combust. Sci.* **2000**, *26*, 283–298. [CrossRef]

60. Lith, S.C.v.; Frandsen, F.J.; Montgomery, M.; Vilhelmsen, T.; Jensen, S.A. Lab-scale investigation of deposit-induced chlorine corrosion of superheater materials under simulated biomass-firing conditions. Part 1: Exposure at 560 °C. *Energy Fuels* **2009**, *23*, 3457–3468. [CrossRef]

61. 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]

62. Bilandzija, N. Energy potential of fruit tree pruned biomass in Croatia. *Span. J. Agric. Res.* **2012**, 292–298.

63. Sun, X.; Wei, X.; Zhang, J.; Ge, Q.; Liang, Y.; Ju, Y.; Zhang, A.; Ma, T.; Fang, Y. Biomass estimation and physicochemical characterization of winter vine prunings in the Chinese and global grape and wine industries. *Waste Manag.* **2020**, *104*, 119–129. [CrossRef]

64. Acquadro, S.; Appleton, S.; Marengo, A.; Bicchi, C.; Sgorbini, B.; Mandrone, M.; Gai, F.; Peiretti, P.G.; Cagliero, C.; Rubiolo, P. Grapevine green pruning residues as a promising and sustainable source of bioactive phenolic compounds. *Molecules* **2020**, *25*, 464. [CrossRef]

65. Loupit, G.; Prigent, S.; Franc, C.; De Revel, G.; Richard, T.; Cookson, S.J.; Fonayet, J.V. Polyphenol profiles of just pruned grapevine canes from wild Vitis accessions and Vitis vinifera cultivars. *J. Agric. Food Chem.* **2020**, *68*, 13397–13407. [CrossRef]

66. Allesina, G.; Pedrazzi, S.; Puglia, M.; Morselli, N.; Allegretti, F.; Tartarini, P. Gasification and wine industry: Report on the use vine pruning as fuel in small-scale gasifiers. In Proceedings of the European Biomass Conference and Exhibition, Copenhagen, Denmark, 14–18 May 2018; pp. 722–725.

67. 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]

68. Azuara, M.; Sáiz, E.; Manso, J.A.; García-Ramos, F.J.; Manyà, J.J. Study on the effects of using a carbon dioxide atmosphere on the properties of vine shoots-derived biochar. *J. Anal. Appl. Pyrolysis* **2017**, *124*, 719–725. [CrossRef]

69. Dunnigan, L.; Morton, B.J.; Ashman, P.J.; Zhang, X.; Kwong, C.W. Emission characteristics of a pyrolysis-combustion system for the co-production of biochar and bioenergy from agricultural wastes. *Waste Manag.* **2018**, *77*, 59–66. [CrossRef]

70. Hoffmann, V.; Jung, D.; Zimmermann, J.; Rodriguez Correa, C.; Elleuch, A.; Halouani, K.; Kruse, A. Conductive carbon materials from the hydrothermal carbonization of vineyard residues for the application in electrochemical double-layer capacitors (EDLCs) and direct carbon fuel cells (DCFCs). *Materials* **2019**, *12*, 1703. [CrossRef]

71. Kraiem, N.; Lajili, M.; Limousy, L.; Said, R.; Jeguirim, M. Energy recovery from Tunisian agri-food wastes: Evaluation of combustion performance and emissions characteristics of green pellets prepared from tomato residues and grape marc. *Energy* **2016**, *107*, 409–418. [CrossRef]

72. Picchi, G.; Silvestri, S.; Cristoforetti, A. Vineyard residues as a fuel for domestic boilers in Trento Province (Italy): Comparison to wood chips and means of polluting emissions control. *Fuel* **2013**, *113*, 43–49. [CrossRef]

73. García, R.; Pizarro, C.; Álvarez, A.; Lavín, A.G.; Bueno, J.L. Study of biomass combustion wastes. *Fuel* **2015**, *148*, 152–159. [CrossRef]