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Thermochemical evaluation of biochars properties from Portuguese agro-forestry residues for solid fuel applications

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Title:

Thermochemical Evaluation of Biochars Properties from Portuguese Agro-Forestry Residues for Solid Fuel Applications

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Abstract: This study provides a high-quality comparative characterization of biochars derived from regionally significant Portuguese feedstocks: hazelnut shell, pine, pinecone, oak pruning waste, and swine manure. All feedstocks were subjected to pyrolysis at 450 °C to evaluate their potential as solid fuels. The results demonstrate the clear superiority of woody-based biochars for energy applications, with hazelnut shell biochar exhibiting the highest fixed carbon (up to 82.89%) and the highest lower heating value (up to 31.64 MJ/kg). In contrast, swine manure biochar proved unsuitable as a standalone fuel due to its extremely high ash content (48.34%). A notable preliminary finding, based on a single case study, was the significant improvement in carbon content in a slow-cooled hazelnut sample, suggesting that post-pyrolysis conditions are not chemically inert and offer a promising avenue for future research in biochar optimization. This work highlights a hierarchical valorisation model for local biomass, classifying feedstocks for optimal use in premium fuel production, general energy applications, or soil amendment based on their distinct thermochemical properties.

Keywords: Biochar; Pyrolysis; Energy density; Fixed carbon; Heating value; Biomass residues

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1. Introduction

The need for more sustainable energy sources and the urgency of mitigating climate change have intensified research on the thermochemical conversion of biomass [1–4]. Biomass valorisation is aligned with decarbonisation goals, circular economy strategies, and the reduction of waste disposal liabilities [5].

Among the available thermochemical routes, pyrolysis — the thermal decomposition of organic matter under oxygen-limited conditions [3,6] — has attracted particular attention. It yields biochar, a carbon-rich and stable solid material that can be applied both as renewable fuel and as a long-term carbon sequestration agent [7–10]. Biochar consists mainly of aromatic carbon structures [11], and its properties are strongly dependent on feedstock type — whether lignocellulosic (plant cell wall material made of cellulose, hemicellulose and lignin [12]) or nutrient-rich — and on pyrolysis parameters such as temperature, heating rate, and residence time [9,13]. Its capacity of withstanding microbial breakdown results in biochar surviving hundreds of years in soils, turning it into a long-term carbon sequestrating agent as well as an agent of minimizing climate change [9,10].

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Extensive research shows that higher pyrolysis temperatures decrease volatile matter (VM) and increase fixed carbon (FC), leading to denser aromatic structures and improved energy properties [7,11,14–16]. These transformations are also associated with reduced combustion-related emissions [16]. Proximate, ultimate, and calorimetric analyses remain the standard tools for assessing such properties, as they provide data on moisture (M), ash (A), volatile matter, fixed carbon, elemental composition (C, H, N, S, O), and calorific values [10,17–20].
Feedstock type is equally decisive: lignocellulosic residues such as pine cones, or hazelnut shells generally produce low-ash, carbon-rich biochars with high heating values [8,21–26], whereas animal manures tend to yield ash-rich chars with elevated N and S, limiting fuel performance but enhancing agronomic potential [24–26]. In fact, Ippolito et al. [9]

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demonstrate that wood-derived biochars are richer in carbon and poorer in plant-available nutrients compared to manure-derived biochars, which present opposite trends. Tomczyk et al. [27] corroborate these findings, showing ash contents of < 7% for wood biochars versus > 50% for non-wood (e.g., manure) biochars. Additionally, Mukome et al. [28] reveal that feedstock type is a stronger predictor of ash content and C/N ratio than other production variables.

Despite this broad knowledge base, comparative studies under uniform pyrolysis conditions are still scarce. Regionally abundant resources such as hazelnut shells, pine residues, oak pruning waste, and swine manure have seldom been analysed side by side, which makes direct ranking for energy vs. soil applications difficult. Another underexplored aspect is the role of post-pyrolysis cooling, generally assumed to be inert (e.g., 'allowing the reactor/sample to cool to room temperature under N_2') and treated as an independent variable [29–31], although recent advances in process design and thermal control suggests otherwise. Nebyvaev et al. [32] demonstrated that slower post-torrefaction cooling significantly alters biochar's composition, with higher ash, carbon and nitrogen contents, and lower H/C and O/C ratios, indicating enhanced fuel properties. However, similar effects have not yet been systematically investigated for biochar produced through conventional pyrolysis, especially for feedstocks like hazelnut shells or manure — a gap that this study aims to address.

Finally, calorific correlations (e.g., Channiwala–Parikh) are widely applied to predict higher heating value (HHV) from elemental composition [33–35], but deviations are reported for lignin-rich or highly aromatic chars, stressing the need for experimental validation. Furthermore, current solid biofuel standards (ISO 17225-2) are designed for wood pellets, not biochars, which exposes a regulatory gap and complicates market uptake [36].

Despite the abundance of general literature on biochar, the unique compositional variability and high annual volume of Portugal's agro-forestry residues—specifically pinecone, hazelnut shell, and local swine manure—necessitates a dedicated, rigorous study. This work provides the local and regional industrial data required by Portuguese circular economy policies (e.g., the National Action Plan for Sustainable Bioeconomy [37]),

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making the findings directly relevant for regional waste valorisation strategies, a crucial aspect not addressed by generic international studies. This study addresses these gaps by providing a comparative thermochemical characterisation of five representative feedstocks from northern Portugal (hazelnut shells, pine, pinecones, oak pruning residues, and swine manure). By analysing proximate, ultimate, and calorimetric properties under identical pyrolysis conditions, and by contrasting fast- and slow-cooling regimes, this work clarifies how feedstock and post-treatment affect biochar suitability for energy and agronomic applications. In addition, empirical HHV predictions are validated against calorimetric data, and results are benchmarked against ISO 17225-2 standards to discuss the commercial implications of biochar valorisation. Specifically, biochars, even those with superior calorific values, often diverge from the premium standard's strict ash and nitrogen limits. This misalignment necessitates experimental validation and benchmarking against the standard to clearly define the market potential and regulatory barriers for biochar valorisation. Crucially, the comparative results under uniform conditions allow for a direct, unbiased ranking of intrinsic feedstock properties, while the preliminary analysis of the slow-cooling sample establishes a novel working hypothesis: that post-pyrolysis thermal history is a non-inert, optimisable process lever for enhancing biochar quality.

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2. Methods and Materials

2.1. Feedstock and biochar production

The northern region of Portugal generates significant and quantified volumes of agricultural and forestry waste, making the selection of feedstocks strategically critical for regional waste management. The study's focus on these five materials is robustly justified by their high annual availability in the NUTS II Norte region, a crucial factor for industrial upscaling and circular economy goals. Official statistics for the NUTS II Norte region confirm that the volume of pine and pine cone residues exceeds 168,547 tonnes/year and oak residues total 65,376 tonnes/year [38]. Furthermore, the selected agricultural wastes are high-volume: Dried manure is estimated at 38,456 tonnes/year [39,40], and the significant availability of almond and hazelnut shells (totalling over 52,245 tonnes/year based on FAO/IPB data [41,42]) reinforces the strategic focus on regional shell residues.

This study presents a detailed thermochemical characterization of biochars produced from diverse biomass feedstocks subjected to controlled pyrolysis conditions. The feedstocks used in this study were collected from two primary sources. Woody samples, including hazelnut shells, pine, pinecones, and oak pruning residues, were sourced from the Botanical Garden of the University of Trás-os-Montes e Alto Douro (UTAD). The swine manure was collected from UTAD's agricultural facilities.

2.1.1. Pyrolysis Conditions

All feedstocks were subjected to pyrolysis in a fixed-bed reactor at a final temperature of 450ºC. The heating conditions were standardized for all runs to ensure direct comparability: a heating rate of 10ºC/min was applied until the peak temperature of 450ºC was reached, followed by a holding time of 60 min at the peak temperature. The 450ºC final temperature was selected as the standardized condition for this comparative study, as this range is optimal for maximizing the fixed carbon content necessary for solid fuel applications [5,7].

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Crucially, the pyrolysis was conducted under ambient atmospheric air (without external inert gas supply). The reactor was not purged, meaning only the initial ambient air remained trapped inside the sealed vessel before heating, establishing an oxygen-limited environment during the process. This methodology, deviating from strict inert-gas pyrolysis, was deliberately chosen to reflect simplified, non-purged industrial process designs, focusing on ease of operation. While the temperature (450ºC) places the process firmly in the pyrolysis regime, the presence of air introduces a controlled partial oxidation effect (similar to an intensified torrefaction or mild oxidative pyrolysis). While this partial oxidation may slightly reduce the final biochar yield compared to inert pyrolysis (due to enhanced carbon combustion), it promotes a more aromatic, stable carbon structure and a faster removal of oxygenated components, which enhances the final fuel quality and is often desirable for solid fuel applications [43,44].

2.1.2. Post-Pyrolysis Cooling Procedures

Following the 60 min holding time, two distinct cooling procedures were employed to manage the highly reactive state of the hot biochar:

a) Standard Rapid Cooling

This procedure was applied to the five primary biochars (pine, pinecone, oak, swine manure, and the standard hazelnut shell biochar). Upon completion of the holding time, the reactor was immediately removed from the furnace and tightly sealed to prevent fresh air ingress. The sealed reactor was then rapidly cooled to near ambient temperature in a circulating water bath. This immediate sealing and rapid cooling procedure is critical because the biochar, still at 450ºC upon removal, would otherwise rapidly undergo uncontrolled auto-oxidation or combustion if exposed to a continuous supply of atmospheric air, consuming carbon and altering the final product properties. This procedure ensures the measured properties represent the end-state of the 450ºC pyrolysis stage.

b) Case Study: Slow Cooling

This procedure was performed as a single comparative experiment solely using a hazelnut shell sample. Upon completion of the holding time, the reactor containing the biochar was immediately sealed. The sealed reactor was then left to cool passively inside the furnace until ambient temperature was reached (approximately 48 hours). The sealing of the reactor was the critical step to prevent fresh air ingress during the long cooling period.

The data for the slow-cooled hazelnut shell sample is included as a preliminary finding based on a single experimental run, intended solely to explore the potential impact of protracted post-pyrolysis conditions and establish a novel working hypothesis. Further systematic experimentation across all feedstocks is required to conclusively validate this effect.

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2.2. Proximate Analysis

The proximate analysis determines the moisture, volatile matter, ash, and fixed carbon contents of the samples, with all results expressed as weight percentages.

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Each biochar sample was placed in a Protherm PLF 100/6 furnace (Protherm, Ankara, Turkey) at 105 °C until a constant weight was achieved, indicating complete moisture removal in accordance to ISO 18134-3 standard [45]. The moisture content (%) was then determined from the difference between the sample weight before and after drying.

From the dried samples obtained in the moisture analysis, a subsample was weighed and placed in a sealed crucible. It was then heated at 900 °C until its mass remained constant, indicating that all volatile organic components had been released ISO 18123 [46] standard. The percentage of volatile matter was calculated based on the mass loss during this stage. Following the volatilisation step, the remaining residue was subjected to ashing in a muffle furnace at 550 °C in accordance to ISO 18122 [47]. The process continued until the sample reached a stable weight, confirming the complete oxidation of the organic fraction. The ash content (%) was subsequently determined from the weight difference before and after ashing.

The fixed carbon content was then determined by subtracting the percentages of moisture, volatile matter, and ash from the total mass (100%) (Equation (1)).

$$FC = 100\% - M\% - VM\% - A\% \qquad (1)$$

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Each biochar sample was analyzed in triplicate, and the results are expressed as the mean ± standard deviation to ensure analytical consistency.

2.3. Ultimate Analysis

Ultimate analysis was conducted to determine the elemental composition of the biochar samples, specifically C, H, N, and S, in accordance with the ISO 16948 [48] standard. Samples were analysed using a ThermoScientific FlashSmart CHNS/O elemental analyser (Waltham, MA, USA). The analyser quantified C, H, N, and S contents directly, while O content was calculated by subtracting the C, H, N, S, and ash contents from 100% (Equation (2)).

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Each biochar sample was analyzed in triplicate, and the results are expressed as the mean ± standard deviation to ensure analytical consistency.

$$\%O = 100\% - \%C - \%H - \%N - \%S - \%A \quad (2)$$

2.4. Calorimetric Analysis

The HHV and lower heating value (LHV) on an air-dry basis were determined using an isoperibolic calorimeter (Model 6300, Parr Instruments, Moline, IL,USA), in accordance with the procedures outlined in ISO 18125 [49]. Prior to analysis, the calorimeter was calibrated with a certified benzoic acid standard (Parr Benzoic Acid No. 3415, Moline, IL,USA) to verify and maintain the accuracy of the measurements.

Each biochar sample was analyzed in triplicate, and the results are expressed as the mean ± standard deviation to ensure analytical consistency.

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2.5. Calculation of HHV

Besides the calorimetric measurements, HHV of the biochars was also estimated with the correlation developed by Channiwala and Parikh [33]. This approach uses the ultimate analysis to predict HHV and allows a direct comparison with the experimental results. The correlation is given by Equation (3).

$$\text{HHV (MJ/kg)} = 0.3491C + 1.1783H + 0.1034S - 0.1034O - 0.0151N - 0.0211A \quad (3)$$

where *C, H, S, O, N* and *A* represent the mass fractions (wt.%, dry basis) of carbon, hydrogen, sulphur, oxygen, nitrogen and ash, respectively.

3. Results and Discussion

The properties of the raw feedstocks (Table 1) serve as the baseline for evaluating the upgrading efficiency of the 450ºC pyrolysis process. The lignocellulosic biomasses (pine, pinecone, hazelnut shell, oak) are characterized by high volatile matter (58-75%) and high oxygen content (>45%), typical of native biomass, resulting in relatively low HHV values (17.14-19.34 MJ/kg). In contrast, the pyrolysis process dramatically alters this composition; the fixed carbon content, for instance, increases by a factor of up to 4 in the woody samples (Table 2), directly corresponding to the observed increase in the biochars' HHV (up to 32.20 MJ/kg) (Table 4). This fuel upgrading is directly reflected in the key biochar properties presented in subsequent tables: the substantial increase in Fixed Carbon (Proximate Analysis) and the dramatic reduction in O/C and H/C ratios (Ultimate Analysis) are the primary thermochemical indicators of enhanced Heating Value [50,51].This comparison clearly demonstrates the significant fuel upgrading achieved by the thermal treatment, which is critical for their valorisation as solid fuels.

Table 1. Proximate, Ultimate Analysis, and HHV of Raw Feedstocks

Sample	Moisture $_{ad}$ (wt%)	Volatile Matter$_d$ (wt%)	Ash$_d$ (wt%)	Fixed Carbon$_d$ (wt%)	C$_d$ (wt%)	H$_d$ (wt%)	N$_d$ (wt%)	O$_d$ (wt%)	HHV$_d$ (MJ/kg)
Pine	9.30±0.68	58.00±0.69	0.80±0.03	31.90±0.78	46.25±0.72	4.83±0.15	0.45±0.01	47.67±0.68	18.60±0.66
Pine cone	7.90±0.72	74.85±0.65	0.53±0.01	16.73±0.81	46.81±0.56	7.44±0.09	0.27±0.02	45.43±0.63	19.34±0.38
Hazelnuts shell	9.25±0.13	63.18±0.23	0.77±0.01	26.81±0.13	45.54±0.22	5.33±0.07	0.42±0.02	47.94±0.14	18.41±0.16
Swine manure	8.90±0.14	57.10±0.01	13.40±0.01	20.60±0.18	36.48±0.31	2.45±0.26	5.14±0.12	42.40±0.38	15.89±0.29
Oak prunings	11.20±0.14	62.00±0.03	1.80±0.01	25.00±0.12	46.14±0.44	4.95±0.15	0.82±0.02	46.30±0.23	17.14±0.11

ad – air dried basis; d – dry basis

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When comparing the biochar compositions and properties with international literature, it is important to note the significant impact of geographical and climatic factors on feedstock characteristics. Factors such as soil type, local climate, harvesting practices, and wood species variants (provenance) mean that the initial composition of biomass (e.g., mineral content, moisture, lignin/cellulose ratio) can vary widely, as demonstrated by the comparison with, for example, Nordic feedstocks. Therefore, the use of Percent Difference serves primarily to confirm the fidelity of our thermochemical conversion process against established literature trends and expected compositional variance for different biomes, rather than implying perfect compositional matching with feedstocks from dissimilar biomes.

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3.1. Proximate Analysis

Proximate analysis provides key indicators of fuel quality by quantifying moisture, volatile matter, ash, and fixed carbon. Moisture content is reported on an air-dried (ad) basis, representing the equilibrium moisture of the biochar under typical laboratory storage conditions. Among the samples, the slow-cooled hazelnut shell biochar presented the highest fixed carbon (82.89%) and only 2.05% ash (Table 2), indicating good thermal stability and low inorganic residue [21]. Such composition is typical of lignocellulosic biochars produced at moderate pyrolysis temperatures, reflecting extensive devolatilization and high carbon retention. The high fixed carbon (>70%) and low volatile matter (<25%) contents observed in all woody biochars are attributed to the 450 °C pyrolysis conditions, which cause an almost complete decomposition of hemicellulose and cellulose. The low VM content indicates efficient thermal treatment, resulting in a highly effective devolatilization process that leaves a condensed, aromatic carbon structure (fixed carbon), thereby enhancing the biochar’s storage stability and safety. Conversely, the high ash content in the swine manure biochar (48.34%) is explained by the concentration of inorganic minerals present in the feedstock, which are non-combustible and remain in the solid residue after thermal treatment, effectively reducing the mass fraction of the organic carbon component. The biochar derived from swine manure exhibited the lowest fixed carbon content (36.12%) and the highest ash content (48.34%) among all samples. Compared with the results reported by Zhao et al. [22], for biochar produced at 500 °C (40.2% fixed carbon, 48.4% ash, and 11.0% volatile matter), the fixed carbon content in the present study is approximately 10% lower, whereas the ash content shows a negligible difference of 0.1%.

The hazelnut shell biochar displayed a volatile matter content of 12.10%, an ash content of 2.54%, and a fixed carbon level of 80.43%. When compared to the reference data reported by Bartolucci et al.[3], which reported at 450ºC (20.38% volatile matter, 2.98% ash, and 76.64% fixed carbon) some notable differences were observed. The Percent Difference for volatile matter was 40.66%, indicating a significantly lower devolatilization in the present sample. The ash content was 14.93% lower than the reference, while the fixed carbon was 4.95% higher.

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Differences in pyrolysis conditions, particularly temperature, heating rate and residence time, are probable causes for the observed deviations [22]. Higher pyrolysis temperatures and longer residence times tend to reduce the volatile matter and ash content while increasing the fixed carbon fraction due to enhanced carbonization and aromatization processes [5,23].

Table 2. Biochar Proximate Analysis, Fuel Quality Ratios and Biochar Yield (All samples, except 'Slow-cooling hazelnut', were produced via Standard Rapid Cooling).

Sample	Moisture $_{ad}$ (wt%)	Volatile Matter$_d$ (wt%)	Ash$_d$ (wt%)	Fixed Carbon$_d$ (wt%)	Fuel Ratio (FC/VM)	Biochar Yield (wt%)
Pine	3.77 ± 0.02	20.75 ± 0.30	0.86 ± 0.01	74.61 ± 0.31	3.60	34.81 ± 0.72
Pinecone	6.49 ± 0.10	12.34 ± 0.18	0.96 ± 0.02	80.20 ± 0.21	6.50	36.05 ± 0.95
Hazelnut shell	4.94 ± 0.07	12.10 ± 0.05	2.54 ± 0.01	80.43 ± 0.12	6.65	32.74 ± 0.61
Swine manure	3.49 ± 0.03	12.06 ± 0.18	48.34 ± 0.18	36.12 ± 0.21	2.99	49.56 ± 1.22
Slow-cooling hazelnut shell	5.55 ± 0.09	9.51 ± 0.14	2.05 ± 0.03	82.89 ± 0.20	8.72	32.89 ± 0.58
Oak pruning residues	6.25 ± 0.02	19.49 ± 0.29	22.40 ± 0.35	51.86 ± 0.22	2.66	33.92 ± 0.84

ad – air dried basis; d – dry basis

The Volatile Matter (VM) content was drastically reduced (e.g., from near 60% in woody biomasses to <25% in the biochar), which is a direct consequence of the near-complete devolatilization of hemicellulose and the majority of cellulose into volatile vapors and gases at this temperature.

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In contrast, the FC content increased significantly across all woody biochars, reaching values >70%. For example, the hazelnut shell (rapid) saw its FC increase from near 27% in the raw biomass to near 82% in the biochar, representing an upgrading factor greater than 3. This increase results directly from the mechanism of carbonization and condensation of the solid residue, forming a more stable and dense aromatic carbon structure.

Ash content remained low (below 2%) in the woody biochars, confirming their high potential as a solid fuel. However, swine manure biochar stands out with an extremely high ash content (48.35%), which, coupled with its relatively high remaining VM (near 38%), confirms its unsuitability for direct energy applications due to the severe dilution of the organic fuel component by non-combustible inorganic minerals.

It is important to note that the ash content reported here represents the ash fraction concentrated in the biochar residue. The increase in ash percentage (wt%) from the feedstock (Table 1) to the biochar (Table 2) is a standard thermochemical observation and a direct consequence of the loss of organic material (volatile matter) during pyrolysis, which concentrates the non-combustible inorganic components in the final solid product.

3.2. Ultimate Analysis

The ultimate analysis evaluates the elemental composition of biochars, namely carbon, hydrogen, nitrogen, sulphur, and oxygen, which are critical parameters for assessing their energetic potential and environmental performance. Swine manure biochar contained the lowest concentrations of carbon and oxygen (37.12% and 10.38%, respectively) and had the highest concentrations of nitrogen and sulphur (2.52% and 0.09%, respectively) among all samples analysed (Table 3). These results reflect the typical composition of biochars derived from animal based residues, which are generally rich in nutrients but have lower carbonization efficiency [8,24]. The low carbon and high heteroatom contents may limit its suitability for energy applications but mechanistically enhance its value in agricultural use: the high ash content corresponds to a high concentration of essential inorganic mineral nutrients (P, K, Ca, Mg) which are concentrated in the solid phase after devolatilization, while the high N content provides a slow-release nitrogen source [25]. Additionally, the high nitrogen content may indicate a greater potential for pollutant emissions such as nitrogen oxides during combustion processes, a factor that must be considered in energy-related applications [26]

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According to the literature, biochars derived from woody biomass such as pine and pinecone are typically rich in carbon [5]. Consistent with this, the biochars produced in this study exhibited high carbon content (80.96% and 82.26%, respectively), along with low nitrogen and oxygen levels. These characteristics suggest a predominantly aromatic and thermally stable carbon structure, favourable for carbon sequestration and energy-dense applications [52–54]. In particular, the hydrogen content was higher in pine (3.04%) than in pinecone (1.78%), potentially reflecting differences in the degradation pathways of lignin and cellulose during pyrolysis [52,55]. When compared to data reported by Handiso, Pääkkönen, & Wilson [56] for pine biochar at 450ºC (82.28% carbon, 3.42% hydrogen, 12.65% oxygen, and 0.08% nitrogen) the results obtained in this study show a good overall agreement. The carbon content of pine differed by only 1.6% (Percent

Difference), while hydrogen content was 11.1% lower, and oxygen showed a 10.5% variation.

A deviation in nitrogen content was observed, with a relative difference of 92.6%, however, the absolute nitrogen levels remained low in both cases, minimizing its impact on performance considerations.

Among all samples analysed, the slow-cooling hazelnut shell biochar exhibited the highest carbon content (82.97%), indicating a high degree of carbonization and structural condensation [53]. In contrast, hazelnut shell biochar removed immediately after pyrolysis showed a slightly lower carbon value (76.88%) and higher oxygen level (17.33%), emphasizing the influence of post-pyrolysis cooling conditions in determining final elemental composition [57]. Compared with the values reported by Bartolucci et al. [3] (80.44% carbon, 2.59% hydrogen, 13.77% oxygen and 0.21% nitrogen) hazelnut shell sample cooled inside the reactor demonstrated strong agreement in carbon content, with a Percent Difference of only 3.1%. The hydrogen content in this study (1.78%) was 31.3% lower, while the oxygen content (12.26%) was 11.0% lower. Nitrogen content (0.94%) showed the largest deviation, with a relative difference of 347.6%. Despite this, the absolute nitrogen levels remained low in both cases.

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Table 3. Ultimate Biochar Analysis

Sample	N_d (wt%)	C_d (wt%)	H_d (wt%)	S_d (wt%)	O_d (wt%)
Pine	1.16 ± 0.02	80.96 ± 0.49	3.04 ± 0.05	n.d.	13.97 ± 0.48
Pinecone	0.97 ± 0.01	82.26 ± 0.96	1.78 ± 0.06	n.d.	14.02 ± 0.91
Hazelnut shell	0.99 ± 0.02	76.88 ± 1.68	2.27 ± 0.07	n.d.	17.33 ± 1.75
Swine manure	2.52 ± 0.04	37.12 ± 0.29	1.54 ± 0.04	0.09 ± 0.01	10.38 ± 0.24
Slow-cooling hazelnut shell	0.94 ± 0.02	82.97 ± 1.67	1.78 ± 0.01	n.d.	12.26 ± 1.65
Oak pruning residues	2.02 ± 0.05	52.39 ± 1.20	1.21 ± 0.05	n.d.	21.99 ± 1.28

d – dry basis; n.d. – Not detected

Woody biomass biochars (pine and pinecone) also showed high carbon content (80.96% and 82.26%, respectively) and low nitrogen and oxygen levels, suggesting a stable, aromatic carbon structure favourable for energy applications.

3.3. The Effect of Cooling Rate: A Promising Preliminary Finding

One of the most notable outcomes of this study is the influence of post-pyrolysis conditions. The slow-cooled hazelnut shell sample showed a considerable increase in fixed carbon content (from 80.43% to 82.89%) and total carbon (from 76.88% to 82.97%).

The observed enhancement in Fixed Carbon and reduction in O/C and H/C (visually confirmed in Figure 1) suggests that the cooling phase is not chemically inert. This is supported by mechanistic understanding: the prolonged residence time of nascent pyrolysis vapors (tars) at elevated temperatures within the sealed reactor promotes their secondary decomposition and condensation (secondary aromatization) onto the solid char surface. This process effectively drives the further removal of residual oxygen and hydrogen, leading to the observed increase in carbonization and fuel quality. While these observations are limited to one feedstock and represent a preliminary finding, it strongly suggests that the cooling phase is not chemically inert and may allow for secondary aromatization reactions. This is likely due to the prolonged residence time of nascent pyrolysis vapors (tars) at elevated temperatures within the sealed reactor, promoting their secondary decomposition and condensation (secondary aromatization) onto the biochar surface. This mechanism effectively increases the yield of fixed carbon and drives the further loss of oxygenated functional groups, as visually confirmed by the shift in the Van Krevelen diagram. This constitutes a promising research avenue for optimizing biochar quality, which should be explored in future work.

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3.4. Van Krevelen Diagram and Degree of Carbonization

The Van Krevelen diagram (Figure 1) visually represents the degree of carbonization for each biochar. The woody biomass biochars (pine, pinecone, hazelnut shell) cluster together, characterized by low H/C (<0.5) and O/C (<0.15) ratios, indicating a high degree of coalification [58]. The swine manure biochar is clearly separated, showing a less carbonized nature. Crucially, the slow-cooled hazelnut shell sample is shifted further towards the origin (lower H/C and O/C) compared to its fast-cooled counterpart, visually confirming the enhanced carbonization effect of the slower cooling process.

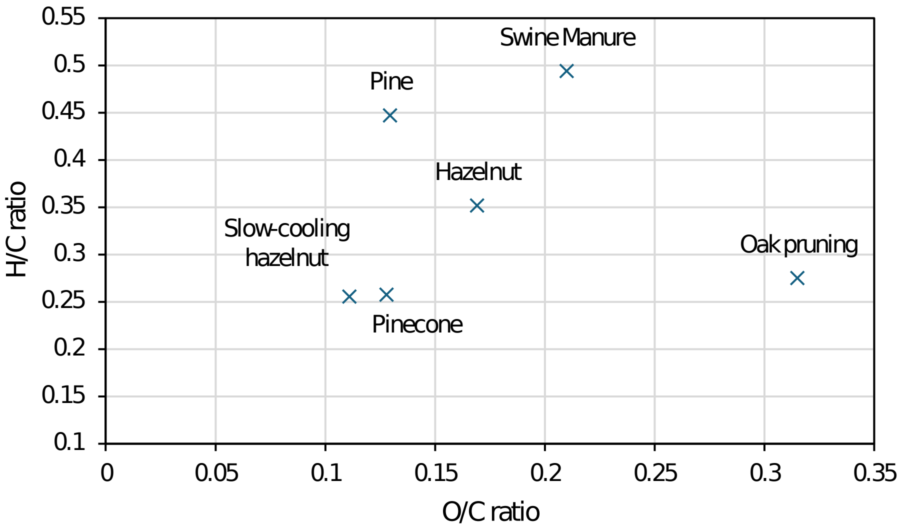

Figure 1. Van Krevelen diagram (H/C vs. O/C atomic ratios) for the produced biochars.

3.5. Calorimetric Properties and Higher Heating Value Validation

Calorimetric analysis determines the higher and lower heating values, providing a direct measure of the energy potential of biochars. Among the tested samples, hazelnut shell biochar exhibited the highest energy content, with a HHV value of 32.20 MJ/kg and a LHV of 31.64 MJ/kg, followed closely by pine and pinecone with LHV of 29.82 MJ/kg and 29.29 MJ/kg, respectively (Table 4). In contrast, the swine manure biochar showed significantly lower values, with a LHV of 12.05 MJ/kg, reflecting its higher ash and lower fixed carbon contents. However, minor discrepancies are observed, particularly for the hazelnut shell biochar, where the measured HHV (32.20 MJ/kg) is significantly higher than the predicted value (27.65 MJ/kg), representing a Percent Difference of 16.46%.

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Compared to literature data, the LHV of hazelnut shell biochar obtained in this study (31.64 MJ/kg) was slightly higher than the 28.73 MJ/kg reported by Bartolucci et al. [3], corresponding to a relative difference of approximately 10.15%. Despite this variation, both results indicate a high energy density, aligning with the elevated carbon content observed in this type of biomass [53]. The pinecone biochar LHV (29.29 MJ/kg) reflects typical woody biomass characteristics, with high carbon and low ash and moisture contents. Wu et al. [59] reported a LHV of 28.92 MJ/kg, the relative difference between both values is approximately 1.29%,

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underscoring the consistency of the results and confirming pinecones as a reliable high-energy feedstock for thermochemical applications.

Table 4. Calorimetric Analysis of biochar

Sample	HHV_{ad} (MJ/kg)	LHV_{ad} (MJ/kg)	Predicted HHV (MJ/kg)
Pine	30.51 ± 0.79	29.82 ± 0.79	30.37
Pinecone	29.78 ± 0.12	29.29 ± 0.12	29.33
Hazelnut shell	32.20 ± 0.26	31.64 ± 0.26	27.65
Swine manure	12.44 ± 0.08	12.05 ± 0.08	12.65
Slow-cooling hazelnut shell	30.17 ± 0.06	29.70 ± 0.06	29.74
Oak pruning residues	18.03 ± 0.09	17.65 ± 0.09	16.94

ad – air dried basis

To validate the consistency of the analytical data, the HHV was predicted using the Channiwala and Parikh empirical [33] equation and compared against the measured values (Table 4). The strong correlation between the predicted and measured values confirms the high quality and reliability of the proximate and ultimate analyses performed.

The comparison between the measured HHV values and those predicted by the Channiwala and Parikh [33] empirical equation (Table 4) demonstrates a strong overall correlation, which validates the accuracy of the proximate and elemental analyses performed. As visually represented in Figure 2, there is a strong linear correlation between the two sets of values, with most data points clustering closely around the ideal 1:1 correlation line. However, minor discrepancies are observed, particularly for the hazelnut shell biochar, where the measured HHV (32.20 MJ/kg) is significantly higher than the predicted value (27.65 MJ/kg).

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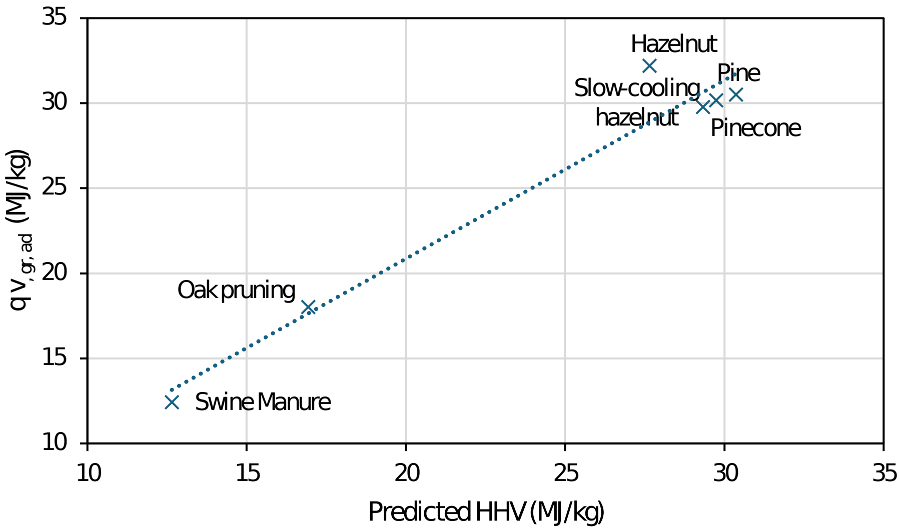

Figure 2. Correlation between the measured HHV of biochar samples and the HHV values predicted by the Channiwala and Parikh empirical equation. The dashed line represents the ideal 1:1 correlation.

These differences can be attributed to several factors. Firstly, empirical equations like the Channiwala and Parikh model are developed based on a large dataset of various feedstocks, and while they are highly reliable for general applications, they may not perfectly capture the unique chemical structure and complex interactions of specific biomass types [34]. The high lignin content and subsequent aromatic structure of woody biochars, such as that from hazelnut shells, can lead to a higher energy density [35] than predicted by simple elemental correlations.

Secondly, the equation's reliance on elemental composition alone may not fully account for the complex char-forming reactions and post-pyrolysis changes [60]. As demonstrated by our finding on the slow-cooled hazelnut shell sample, the final properties of biochar are not only a function of the peak pyrolysis temperature but also of conditions during the cooling phase. This suggests that the measured HHV reflects a more complete thermochemical profile than can be predicted by a formula based solely on the final elemental percentages.

Despite these minor variations, the strong linear correlation observed across all samples confirms the high quality of our experimental data and supports the use of proximate and elemental analyses as a reliable method for the thermochemical evaluation of biochars.

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3.6. Correlation between Feedstock Composition and Biochar Properties

The superiority of woody-derived biochars (hazelnut shell, pinecone) in terms of fixed carbon (up to 82.89%) and lower heating value (up to 31.64 MJ/kg) is directly attributed to their lignocellulosic composition. Lignin, in particular, is known to produce a more aromatic and thermally stable biochar structure during pyrolysis. This is in contrast with swine manure, which is richer in nutrients and inorganic matter, resulting in a much higher ash content (48.34%). Literature confirms that the high thermal resistance of lignin contributes to greater biochar yield and fixed carbon content compared to cellulose and hemicellulose [12].

3.7. Fuel Ratios and Combustion Behaviour

The Fuel Ratio fixed carbon/Volatile Matter (FC/VM) is a key indicator of combustion quality [61]. As shown in Table 2, the slow-cooled hazelnut shell and pinecone biochars exhibit the highest ratios, indicating a slower, more stable combustion characteristic of high-quality solid fuels [62]. The swine manure biochar has a significantly lower ratio, reinforcing its lower suitability for combustion applications. Although the Oak pruning’s sample exhibited the lowest Fuel Ratio (≈3.0) in the woody set, the most significant functional result remains the swine manure biochar, whose low ratio is compounded by the 48.35% Ash content, making it the overwhelming outlier for fuel applications.

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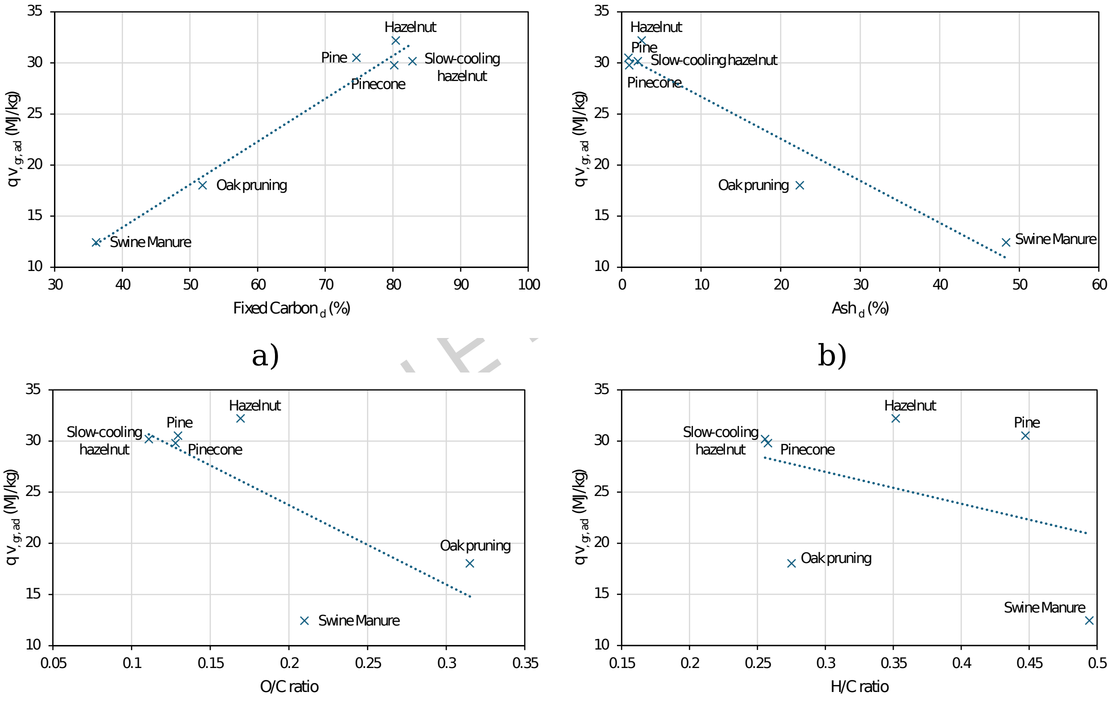
3.8. Graphical Correlation Analysis

To deepen the understanding of the relationships between the biochar properties, several graphical correlations were prepared (Figure 3). Figure 3a reveals a strong positive and linear correlation between the HHV and the fixed carbon content, with a determination coefficient (R2) close to 1. This relationship demonstrates that a higher degree of carbonization directly results in a fuel with greater energy density [63]. In contrast, Figure 3b shows a clear negative correlation between HHV and Ash content, illustrating how the presence of incombustible inorganic matter dilutes the fuel's energy content [64]. The swine manure biochar is an outlier in these graphs, reinforcing its distinct composition.

Figure 3c shows a negative correlation between HHV and the O/C atomic ratio, indicating that the removal of oxygen during pyrolysis is essential for increasing the calorific value [65]. The decrease in the H/C ratio (Figure 3d) reflects the loss of hydrogen and the increase in the aromaticity and stability of the carbon structure [66]. Biochars with low H/C ratios, such as those from pine (H/C = 0.45) and pinecone (H/C = 0.26), and especially the slow-cooled hazelnut shell sample (H/C = 0.26), show the highest HHV values. This phenomenon is aligned with the carbonization process, where the formation of a more condensed and stable carbon matrix (less hydrogen) increases the calorific value [67]. Therefore, this correlation reinforces the robustness of pyrolysis as a process to create high-energy-density solid fuels from biomass [15].



a) b)

c) d)

Figure 3. Correlations between biochar properties. (a) HHV vs. fixed carbon; (b) HHV vs. Ash Content; (c) HHV vs. O/C atomic ratio; (d) HHV vs. H/C atomic ratio.

These correlations not only validate the analytical data but also provide a comprehensive view of the thermochemical conversion mechanisms of biomass and the interrelationships between the biochar properties. Figure 3d further supports the trends observed in the previous correlations by illustrating a clear, strong negative relationship between the HHV and the H/C atomic ratio. This correlation is a direct consequence of the pyrolysis process itself. As biomass is heated, deoxygenation and

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dehydrogenation reactions occur, progressively breaking down the original lignocellulosic structure [12]. This process leads to the loss of hydrogen and oxygen in the form of water, methane, and other gases, leaving behind a more condensed and stable carbon matrix [67]. Consequently, a lower H/C ratio signifies a higher degree of carbonization and aromaticity, which are the primary drivers of increased energy density [68]. This is evident as the highest HHV values, for instance, the slow-cooled hazelnut shell sample, correspond to the lowest H/C ratios. The positioning of the swine manure biochar as an outlier on this graph, with a significantly higher H/C ratio than the woody biochars, reinforces its distinct chemical composition and the lack of extensive carbonization during pyrolysis due to its high inorganic content [27]. This finding directly complements the insights gained from the Van Krevelen diagram (Figure 1), where the biochar samples migrate towards the origin as they become more carbonized. Both graphical representations collectively validate the effectiveness of pyrolysis as a tool for increasing the energy density of biomass and confirm that the final properties of the biochar are directly linked to its degree of aromatization and condensation.

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In conclusion, while the strong linear correlations observed between and compositional parameters (fixed carbon, H/C, O/C ratios) align with established literature for biochar production at (even under partial oxidation conditions), the utility of this analysis lies in highlighting the novel deviations observed in the dataset. Firstly, the swine manure biochar acts as a distinct outlier, significantly lowering the overall correlation and demonstrating its fundamental unsuitability as a standalone solid fuel due to high ash content, regardless of the fixed carbon value. Secondly, and crucially, the Slow-Cooled hazelnut shell sample exhibits a distinct displacement relative to the main rapid-cooled group. Specifically, when plotted on the Van Krevelen diagram or against fixed carbon, this sample demonstrates the lowest H/C and O/C ratios and highest fixed carbon content for the given pyrolysis temperature. This superior fuel quality, achieved solely by modifying the post-pyrolysis cooling rate (i.e., time under sealed conditions), provides concrete graphical evidence that the thermal history after the peak temperature is a critical, chemically active process, strongly supporting the major outcome claimed in this study. The strong correlations observed in Figure 3, while confirming established biochar trends, serve two crucial functions for this comparative study. Firstly, they validate the analytical quality and the fidelity of the conversion process across five diverse feedstocks. Secondly, the linear relationship between HHV and Fixed Carbon ($R^2 \approx 1$) provides the quantitative basis for the proposed Hierarchical Valorisation Model, visually confirming that the degree of carbonization is the primary intrinsic driver of the fuel's energy potential hierarchy for these feedstocks.

3.9. Stoichiometric Air Requirement

The stoichiometric (theoretical) air required for complete combustion is a fundamental parameter for boiler design [69]. Fuels with a higher degree of carbonization, such as the slow-cooled hazelnut shell, require more air per kg of fuel (Table 5). Conversely, fuels with high oxygen content, like the oak pruning residue biochar, require less external air for combustion. Given the significant differences in ash content, a detailed analysis of the mineral composition is essential for evaluating combustion risks. While specific XRF data are reserved for future work, the nature of the feedstocks allows for predictive inferences. The high ash content in swine manure is anticipated to be rich in alkaline earth metals (Ca, Mg) and nutrients (P, K), increasing the risk of slagging and fouling at typical combustion temperatures. Conversely, the woody biochars are expected to have ash predominantly composed of Ca and K, which contributes less to severe slagging but influences ash melting behaviour.

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Table 5. Calculated Stoichiometric Air Requirement

Sample	$O_{2,stoi}$ (kg O_2 / kg fuel)	Stoichiometric Air (kg air / kg fuel)
Pine	2.26	9.75
Pinecone	2.20	9.47
Hazelnut shell	2.06	8.87
Swine manure	1.01	4.36
Slow-cooling hazelnut shell	2.23	9.62
Oak pruning residues	1.27	5.49

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3.10. Cooling Kinetics as a Lever for Energy-Efficient Biochar Optimization

While numerous studies correlate biochar properties with peak pyrolysis temperature, our work introduces a novel dimension by investigating post-pyrolysis thermal history. The finding that the slow-cooled hazelnut shell sample exhibits the lowest O/C and highest HHV (for the 450ºC group) demonstrates that the cooling phase is not chemically inert. This suggests that extended thermal exposure post-pyrolysis promotes greater C and H condensation and removal of residual oxygenated compounds, offering a new lever for process optimization that minimizes energy consumption associated with excessively high peak temperatures. This observation opens the door for further process modelling to integrate cooling dynamics into biochar quality prediction frameworks.

4. Strategic Implications and Future Outlook

This study provided an in-depth thermochemical characterization of biochars from locally sourced biomass in northern Portugal. Woody biomass-derived biochars consistently showed superior fuel properties compared to swine manure biochar. Beyond laboratory-scale characterization, these findings carry practical relevance for regional biomass management.

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4.1. A Hierarchical Valorisation Model for the Region

Based on the comprehensive thermochemical characterization of the biochars, a hierarchical waste management model is proposed for Northern Portugal. This model aims to maximize the value and impact of each feedstock, classifying biochars into three distinct application levels, each justified by the experimental data obtained.

Level 1: High-Quality Energy Valorisation (Premium Biochars)

This level includes biochars from hazelnut shell and pinecone. Their classification is due to their exceptional fuel properties: low ash content (2.54% and 0.96%, respectively), high fixed carbon (>80%), and a very high LHV, reaching 31.64 MJ/kg for hazelnut shell and 29.29 MJ/kg for pinecone. These values far exceed the ISO 17225-2 standard for premium wood pellets (≥ 16.5 MJ/kg) [36]. These biochars are ideal for replacing

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fossil fuels in industrial systems and for producing high-energy-density pellets [70]. The slow-cooled hazelnut shell sample, in particular, with an LHV of 29.70 MJ/kg and the highest fixed carbon content (82.89%), represents an even higher niche product.

Level 2: General Energy Valorisation or Blending

Biochars from pine and oak pruning residues fall into this category. Although they show good energy potential, their ash contents are higher (0.86% for pine and 22.40% for oak pruning residues) than those of premium biochars. The oak pruning biochar, in particular, has an ash content that makes it unsuitable for standard combustion systems, but it still maintains a LHV of 17.65 MJ/kg. These materials are more suitable for combustion systems with a higher tolerance for ash, or they can be used in blends (co-combustion) to improve the energy quality of other lower-value solid fuels, such as the swine manure biochar itself or raw biomass residues [71].

Level 3: Nutrient Recycling and Soil Improvement

The swine manure biochar is classified at this valorisation level. Its unsuitability as a standalone fuel is evident from its LHV of 12.05 MJ/kg and, crucially, its extremely high ash content of 48.34%. However, this energetic "disadvantage" is its greatest agricultural advantage, as the ash is rich in essential minerals such as phosphorus and potassium, and the biochar itself has a significant nitrogen content (2.52%) [72]. This makes it an excellent soil amendment and slow-release fertilizer, contributing to sustainable agriculture and the circular economy of the region. Its application to the soil not only recycles nutrients but also acts as a carbon sequestration agent, demonstrating its superior environmental value [73].

In conclusion, the proposed hierarchical valorisation model offers a strategic framework for managing Northern Portugal's diverse agro-forestry residues. This approach moves beyond a 'one-size-fits-all' view of biochar by recognizing that its optimal use depends fundamentally on the feedstock's inherent properties. By scientifically classifying these biochars, this model not only promotes the most efficient use of each resource (from premium fuel production to nutrient-rich soil amendment) but also maximizes both the economic value and the environmental benefits of

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biomass valorisation. This tiered strategy provides a clear and actionable pathway for regional stakeholders to contribute to a more sustainable, circular economy, reducing waste while generating valuable products and mitigating climate change [74].

4.2. Carbon Sequestration Potential

The low H/C (<0.5) and O/C (<0.15) atomic ratios for the woody biochars indicate a high degree of carbonization and increased aromaticity. Aromatic structures are significantly more resistant to microbial decomposition, ensuring that the sequestered carbon remains stable in soil for hundreds of years, unlike the original biomass [75]. This quantifies the long-term climate benefit of converting these residues into biochar, creating a stable carbon reservoir [73].

4.3. Comparison with ISO 17225-2 Solid Biofuel Standards

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From a commercial perspective, comparing the best-performing biochars to the ISO 17225-2 standard for premium wood pellets (Class A1) provides a useful benchmark (Table 6) [36]. The outstanding calorific values of hazelnut shell (31.64 MJ/kg) and pinecone biochars (29.29 MJ/kg) place them well above the minimum threshold of 16.5 MJ/kg, confirming their competitiveness as high-energy solid fuels. However, other parameters such as ash (2.54% for hazelnut shell) and nitrogen content (~1% for both woody biochars) exceed the strict limits set for premium-grade pellets.

Table 6. Comparison of Top Biochars with ISO 17225-2 (Class A1) Standard [36]

Parameter	Hazelnut shell Biochar	Pinecone Biochar	ISO 17225-2 (Class A1 - Premium Wood Pellets)
LHV (MJ/kg, ad)	31.64	29.29	≥ 16.5
Ash Content (%, d)	2.54	0.96	≤ 0.7
Nitrogen Content (%, d)	0.99	0.97	≤ 0.3
Sulphur Content (%, d)	n.d.	n.d.	≤ 0.04

n.d. – Not detected

This divergence highlights that while the biochars significantly exceed the calorific value requirements, their ash (for hazelnut shell) and nitrogen contents are higher than the premium class standard. This leads to a rich discussion: biochar is a fantastic fuel, but to be commercialized as a high-

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quality standard product, it might require post-treatment, blending with other materials, or the development of new, biochar-specific standards to account for its unique properties. The data highlights a critical gap between existing solid biofuel standards and the characteristics of high-quality biochars, suggesting a need for industry-specific guidelines.

4.4. Operational Implications of Ash and Nitrogen Content

The high ash contents in swine manure (48.34%) and oak pruning waste (22.40%) are strong indicators of potential operational problems in boilers, such as slagging and fouling [76]. Manure-derived ash is typically rich in potassium (K), phosphorus (P), and silicon (Si) [77]. These elements are known to lower the ash melting point, leading to slag formation and deposition on heat exchange surfaces [78]. This increases maintenance costs and reduces thermal efficiency, providing a strong argument against using these feedstocks as pure fuels [76]. This is supported by studies noting the high concentration of problematic ash-forming elements in manure-derived biochar [23].

5. Conclusions

In summary, this study provides a high-quality comparative thermochemical characterization of regionally significant Portuguese agro-forestry residues, establishing the woody biochars (pine, hazelnut shell, pinecones) as highly efficient solid fuels with HHV values exceeding 30 MJ/kg. The most notable finding of this comparative analysis is the unsuitability of swine manure for energy valorisation due to its extremely high ash and nitrogen content. Furthermore, the preliminary results from the slow-cooled hazelnut shell sample showed a considerable increase in fixed carbon content (from 80.43% to 82.89%) and total carbon (from 76.88% to 82.97%). The observed enhancement in fuel quality via slow-cooling suggests a promising avenue for biochar optimization. However, it must be acknowledged that extending the processing time carries an implicit energetic penalty. For this optimization to be industrially viable, the thermal energy retained in the reactor during the prolonged cooling phase must be effectively recovered or integrated into the overall process heat balance, particularly in large-scale pyrolysis units. A dedicated techno-

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economic or LCA study would be necessary to quantify the net energy gain and carbon emissions impact of implementing slow-cooling commercially.

Woody biomass-derived biochars, such as hazelnut shell and pinecone, exhibited uniformly low volatile matter, high fixed carbon, and high calorific values profiles agreeing with the literature. In contrast, swine manure-derived biochar displayed higher ash content, lower fixed carbon, and significantly reduced calorific value, corroborating the prior publications on animal waste residues, which often yield biochars with lower energy density and higher inorganic content.

The anticipated pattern of lower volatile content and higher fixed carbon levels in more carbonized biochars was clearly observed. These shifts are critical for biochar's utility as a renewable solid fuel: higher fixed carbon and lower ash result in greater heat release upon combustion, reduced environmental emissions, and improved thermal stability, making woody biochars more suitable for energy generation.

By combining these experimental observations with literature benchmarks, this work identifies hazelnut shell and pine-derived biochars as the most promising feedstocks for solid fuel applications in the regional context. Meanwhile, manure-derived biochar shows greater value as a nutrient source or soil amendment, though with limited energy potential.

Considering all results, the study supports the dual role of biochar, as both a tool for carbon sequestration and a viable solid biofuel alternative, especially when produced from agroforestry residues. It highlights the importance of feedstock selection and pyrolysis conditions in optimizing biochar quality. These findings contribute to sustainable biomass management strategies in Portugal and offer guidance for integrating biochar into renewable energy systems and carbon mitigation pathways.

While the results underscore the promise of lignocellulosic residues for energy applications, future work should explore the impact of process scale-up and the integration of catalytic or post-treatment strategies to further enhance biochar performance. Crucially, the full assessment of biochar as a solid fuel requires detailed combustion and emission analysis (e.g., thermal efficiency, NOx, and SOx emissions), which is the primary limitation of the current study and a critical next step. Moreover, future

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work will focus on Level 2 mechanistic analysis, including spectroscopic characterization and thermodynamic process modeling.

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Data Availability Statement: The raw data supporting the conclusions of this article will be made available by the authors on request.

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