



Article

Energy Recovery from Invasive Species: Creation of Value Chains to Promote Control and Eradication

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Abstract: The use of biomass as an energy source presents itself as a viable alternative, especially at a time when the mitigation of climate change requires that all possibilities of replacing fossil fuels be used and implemented. The use of residual biomass also appears as a way to include in the renewable energy production system products that came out of it, while allowing the resolution of environmental problems, such as large volumes available, which are not used, but also by the elimination of fuel load that only contributes to the increased risk of rural fires occurrence. Invasive species contribute to a significant part of this fuel load, and its control and eradication require strong investments, so the valorization of these materials can allow the sustainability of the control and eradication processes. However, the chemical composition of some of these species, namely *Acacia dealbata*, *Acacia melanoxylon*, *Eucalyptus globulus*, *Robinia pseudoacacia* and *Hakea sericea*, presents some problems, mainly due to the nitrogen, chlorine and ash contents found, which preclude exclusive use for the production of certified wood pellets. In the case of *Eucalyptus globulus*, the values obtained in the characterization allow the use in mixtures with *Pinus pinaster*, but for the other species, this mixture is not possible. From a perspective of local valorization, the use of materials for domestic applications remains a possibility, creating a circular economy process that guarantees the sustainability of operations to control and eradicate invasive species.

Keywords: invasive forest species; wood pellets; circular economy; sustainability; value chain



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1. Introduction

The use of biomass as an energy source is increasingly presented as a current alternative, in the permanent search for more sustainable forms of energy, which can somehow replace traditional sources of fossil origin, such as oil and coal [1]. However, the use of biomass as an energy source is not a recent application, since this is the oldest energy source that man learned to use, from the moment that they discovered how to control fire for their own benefit, passing this on to be part of daily life situations [2]. Since time immemorial, human populations have started to have in their routine the acquisition of biomass fuels, through their collection and storage, thus being available to supply needs such as space heating, cooking, lighting, and even protection by keeping wild animals away [3].

Currently, biomass remains the most widespread source of energy among the most remote populations, essentially due to its availability and ease of use, giving it the epithet “energy of the poor”, since they are usually the most disadvantaged populations, mainly in Africa, Southeast Asia and some regions of Latin America, which this more rudimentary use continues to occur [4]. However, in the more developed countries there is also an increase in the use of biomass as a source of primary energy because of, in addition to the traditional consumption associated with the heating of residential spaces in the form of firewood consumption, the consumption of fuels derived from biomass, such as wood pellets and briquettes, both for heating, but also for more industrial applications, such as the production of industrial steam, and even the production of electric energy [5].

These more industrial uses, however, have led to an increasing standardization of fuel quality criteria in order to optimize their use, defining a set of characteristics, namely its heating value, but also the maximum limits of certain chemical constituents, such as the content of sulfur, chlorine and alkali metals, due to their behavior during combustion, and contribution to the occurrence of corrosive, fouling and slagging phenomena [6,7]. For this reason, the use of biomass is currently very limited to selected types which meet a set of quality requirements, leaving a set of forms of biomass considered to be residual in the supply chains, as are the materials resulting from operations forest management and agricultural activity [8,9].

Within this huge group of residual biomasses resulting from forest management operations, there are numerous tree and shrub species, which, since they have no commercial and/or industrial application, are abandoned on forest land, even after cutting, contributing to the increase in fuel load and consequent increase in the risk of rural fires [10]. Some of these species, in turn, are even exotic species, with invasive behavior, which due to their aggressiveness and competitiveness vis-à-vis native species, are conquering space and replacing native flora, making it possible to identify these situations all over the world [11]. This substitution of native species by invasive species has very negative effects that go far beyond the loss of biodiversity and changes in ecosystems, since they also hinder the development of productive forests by competing directly with the installed species [12].

In Portugal, the phenomenon of the expansion of invasive species has acquired very worrying proportions, mainly with a group of species of the genus *Acacia*, from which the *Acacia dealbata* and the *Acacia melanoxylon* stand out, but also with other species, namely the *Eucalyptus globulus*, the *Robinia pseudoacacia* and *Hakea sericea* [13]. This group of species has progressed almost exponentially, already covering extensive areas. However, the problem is not limited to these species, there are also problematic situations with *Acacia longifolia*, *Cortaderia selloana*, *Arundo donax* and *Ailanthus altissima*, among others, with which different means have been employed in order to try to eradicate, or at least control, the progression of these species [14]. The most serious situation in Portugal is that of the uncontrolled expansion of *Acacia dealbata*. This species has grown in area by more than 400% since the 70s of the 20th century, being currently the invasive species that occupies the largest area in the national territory (Figure 1). However, other species exhibit similar behaviors, making the situation even more serious.

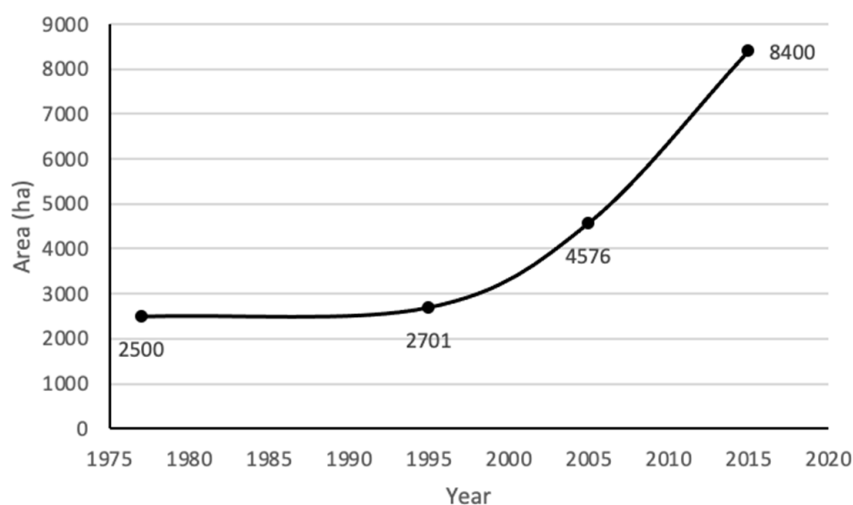


Figure 1. Evolution of the area occupied by *Acacia dealbata* (adapted from [14–16]).

The creation of value chains, with the objective of promoting the use of these species, presents itself as a possibility that allows the balance of the costs generated with the operations of control of the invaders [17]. These value chains, which already exist today, encourage the forwarding of these residual materials to biomass thermoelectric plants, which give them a low financial value, often scarcely enough to pay for the different tasks of forest management, such as cutting, filling and transport, and giving no value to the combustible material, claiming its low density, high moisture content and, mainly, due to the low energy properties that some species have [18]. However, there are some species that may have a good potential for energy recovery, and that, even if they are not used as the sole source of raw material for the production of fuels derived from biomass, can be incorporated with traditional species, namely the *Pinus pinaster*, or other resinous species [19].

This perspective of valorization of residual biomasses, originating from invasive species, can be very helpful in combating, almost always unevenly, the dispersion of these species, contributing to the share of costs with the control and eradication operations [20]. In this way, the creation of these value chains may play a decisive role in the preservation of indigenous biodiversity, while contributing to the reduction in the risk of occurrence of rural fires, since the need to supply valuable raw materials promotes permanent pressure on invasive species, controlling their growth and dispersion, limiting the accumulation of fuel load [21]. In this article, the potential use of these species in the production of wood pellets is discussed, both individually and in mixtures with *Pinus pinaster* wood, in order to justify the creation of value chains that promote pressure on invasive species, ensuring the sustainability of control and eradication operations for these species. The present work has as its main objective the characterization of a set of species, namely, *Acacia dealbata*, *Acacia melanoxylon*, *Robinia pseudoacacia*, *Eucalyptus globulus* and *Hakea sericea*, and their subsequent comparison with the dominant species most used in production of solid fuels derived from biomass, such as wood pellets, which is *Pinus pinaster*.

2. Results

2.1. Thermogravimetric Analysis

The results obtained in the thermogravimetric analysis are shown in Figure 2.

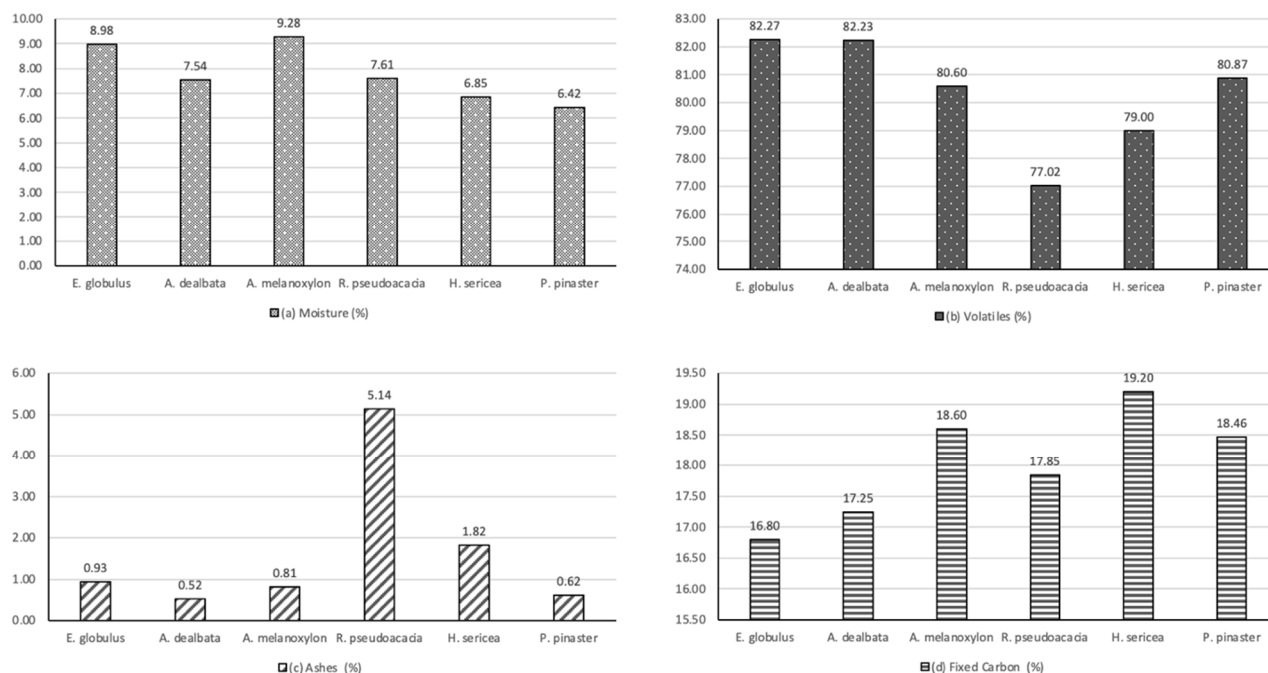


Figure 2. Results of the thermogravimetric analysis.

Moisture is a less important characteristic because it depends directly on the time and type of drying performed. For drying described in Section 2.1. Sampling and preparation, the results varied between 6.42% of *Pinus pinaster* and 9.28% of *Acacia melanoxylon*. The remaining species show very close values, between 6.85% and 8.98%. The volatile content varied between a minimum value of 77.02%, for *Robinia pseudoacacia*, and a maximum value of 82.27%, for *Eucalyptus globulus*. The remaining species varied between 79.00% and 82.23%. The ash content varied between a minimum value of 0.52% for *Acacia dealbata* and a maximum value of 5.14% for *Robinia pseudoacacia*. The remaining species varied between a minimum value of 0.62% and a maximum value of 1.82. The fixed carbon content showed a minimum value of 16.80%, for *Eucalyptus globulus*, and a maximum value of 19.20%, for *Hakea sericea*. The remaining species showed values between 17.25% and 18.60%.

2.2. Elemental Analysis CHNO

The results obtained in the elemental analysis are shown in Figure 3.

The carbon content varied between a minimum value of 47.00% for *Acacia dealbata* and a maximum value of 60.00% for *Hakea sericea*. The remaining species varied between 47.30% and 50.21%. The hydrogen content varied between a minimum value of 5.61%, for *Acacia melanoxylon*, and a maximum value of 6.07%, for *Pinus pinaster*. The remaining species varied between 5.67% and 5.92%. The nitrogen content varied between a minimum value of 0.080%, for *Pinus pinaster*, and a maximum value of 0.711%, for *Hakea sericea*. The remaining species varied between 0.099% and 0.582%. The oxygen content varied between a minimum value of 33.40% for *Hakea sericea* and a maximum value of 47.07% for *Acacia melanoxylon*. The remaining species varied between 43.64% and 46.93%.

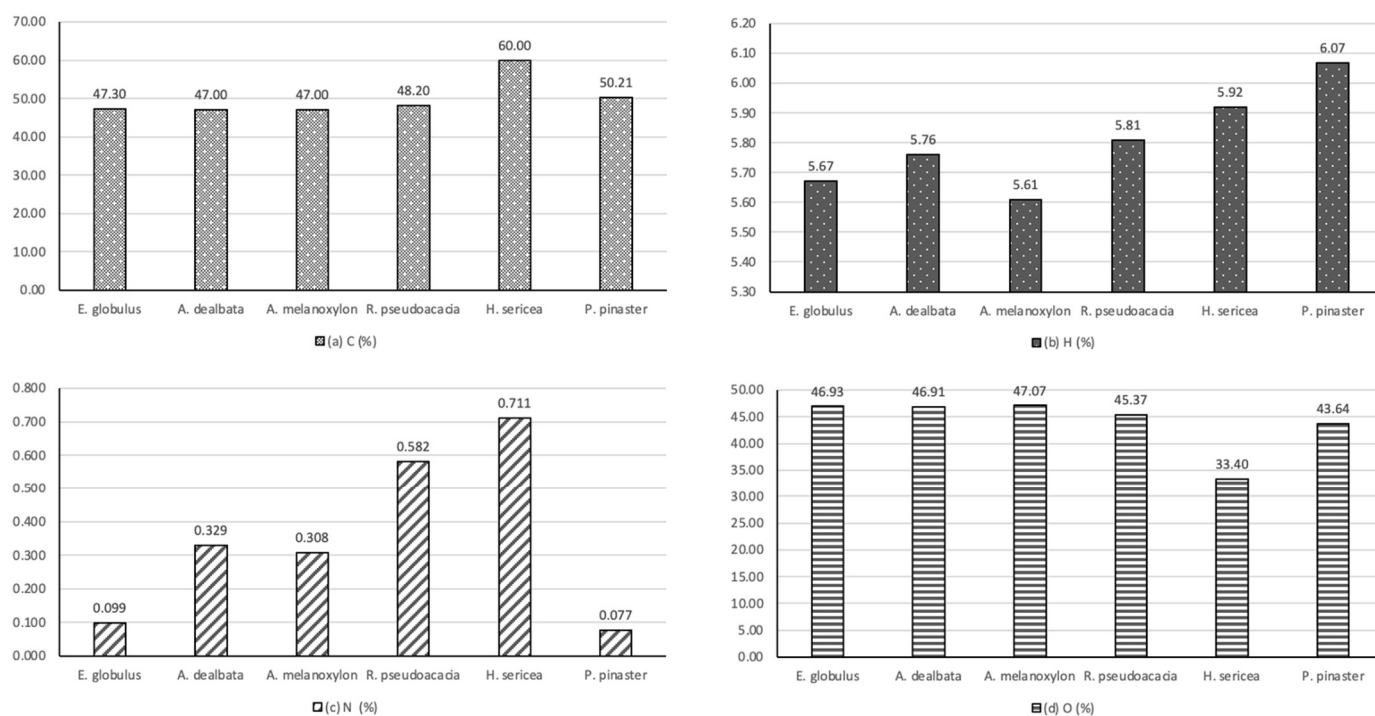


Figure 3. Results of the elemental analysis CHNO.

2.3. Determination of Sulfur and Chlorine Content

The results of the sulphur and chlorine content determination are shown in Figure 4.

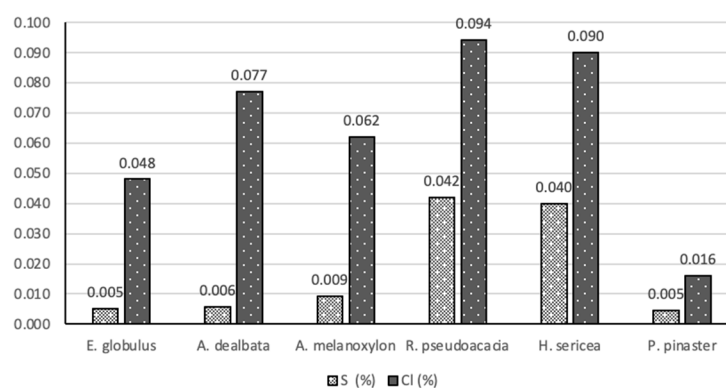


Figure 4. Sulphur and chlorine content.

The sulfur content varied between a minimum value of 0.005%, for *Eucalyptus globulus* and *Pinus pinaster*, and a maximum value of 0.042%, for *Robinia pseudoacacia*. The remaining species varied between 0.006% and 0.040%. The chlorine content varied between a minimum value of 0.016% for *Pinus pinaster* and a maximum value of 0.094% for *Robinia pseudoacacia*. The remaining species varied between 0.048% and 0.090%.

2.4. Determination of the High and Low Heating Value

The results of the heating value determination are shown in Figure 5.

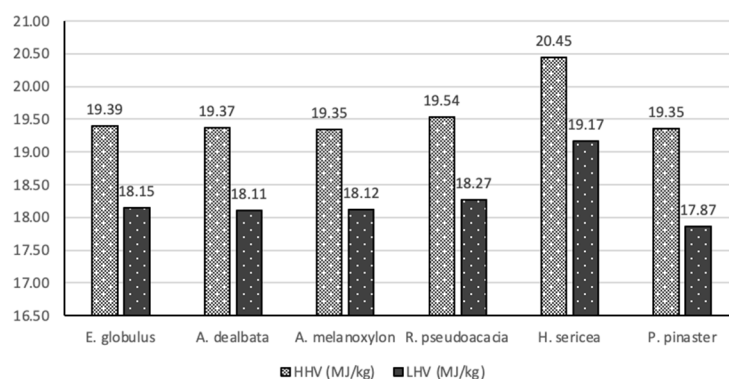


Figure 5. Higher heating value (HHV) and lower heating value (LHV) results.

The high heating value varied from the minimum value of 19.35 MJ/kg, for *Acacia melanoxylon* and for *Pinus pinaster*, to the maximum value of 20.45 MJ/kg, for *Hakea sericea*. The remaining species varied between 19.37 MJ/kg and 19.54 MJ/kg. The low heating value varied from the minimum value of 17.87 MJ/kg, for *Pinus pinaster*, to the maximum value of 19.17 MJ/kg, for *Hakea sericea*. The remaining species varied between 18.11 MJ/kg and 18.27 MJ/kg.

2.5. Determination of the Content of Major Elements

The results of the content of major elements are shown in Figure 6.

The Al content varied between a minimum value of 8.05 mg/kg for *Acacia dealbata* and a maximum value of 307.24 mg/kg for *Pinus pinaster*. The remaining species varied between 19.08 mg/kg and 215.18 mg/kg. The Ca content varied between a minimum value of 1645.15 mg/kg, for *Pinus pinaster*, and a maximum value of 21,917.90 mg/kg, for *Robinia pseudoacacia*. The remaining species ranged from 2214.41 mg/kg to 4830.83 mg/kg. The Fe content varied between a minimum of 21.51 mg/kg for *Acacia dealbata* and a maximum of 268.37 mg/kg for *Pinus pinaster*. The remaining species varied between 38.77 mg/kg and 187.90 mg/kg. The Mg content varied between a minimum of 564.19 mg/kg for *Acacia dealbata* and a maximum of 1474.89 mg/kg for *Robinia pseudoacacia*. The remaining species varied between 645.28 mg/kg and 1120.13 mg/kg. The P content varied from a minimum value of 78.08 mg/kg, for *Pinus pinaster*, up to a maximum value of 480.22 mg/kg. The remaining species varied between 124.93 mg/kg and 312.28 mg/kg. The K content varied from a minimum value of 723.84 mg/kg, for *Pinus pinaster*, up to a maximum value of 3848.58 mg/kg, for *Robinia pseudoacacia*. The remaining species ranged from 1427.42 mg/kg to 3003.84 mg/kg. The Si content varied from a minimum value of 5.13 mg/kg, for *Acacia melanoxylon*, to a maximum value of 993.31 mg/kg, for *Pinus pinaster*. The remaining species varied between 31.47 mg/kg and 856.28 mg/kg. The Na content varied between a minimum value of 436.79 mg/kg, for *Pinus pinaster*, and a maximum value of 1984.70 mg/kg, for *Hakea sericea*. The remaining species varied between 738.66 mg/kg and 1106.17 mg/kg. The Ti content varied between a minimum of 1.22 mg/kg for *Acacia dealbata* and a maximum of 19.22 mg/kg for *Pinus pinaster*. The remaining species ranged from 1.84 mg/kg to 15.68 mg/kg.

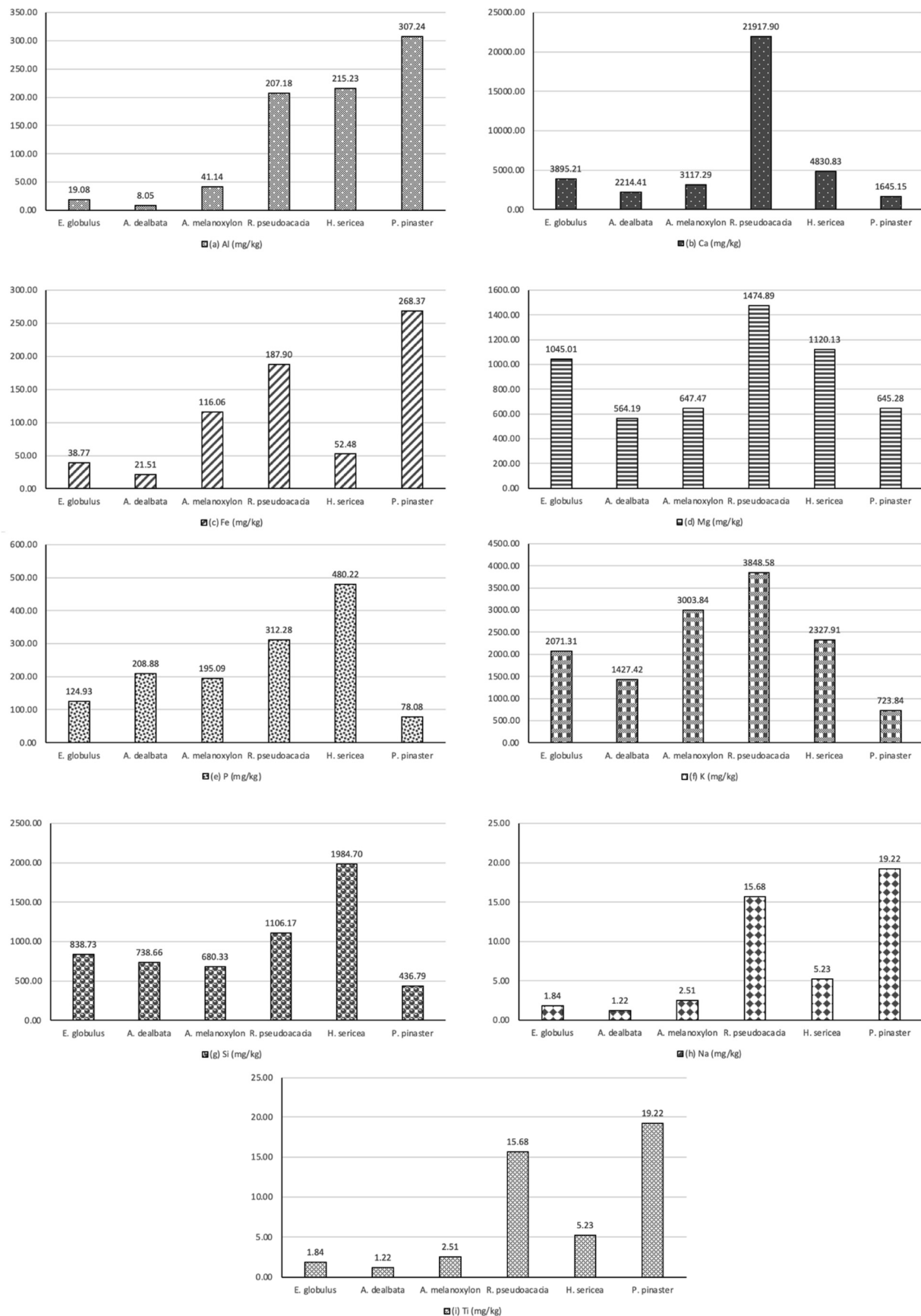


Figure 6. Content of major elements.

2.6. Determination of the Content of Minor Elements

The results of the content of minor elements are shown in Figure 7.

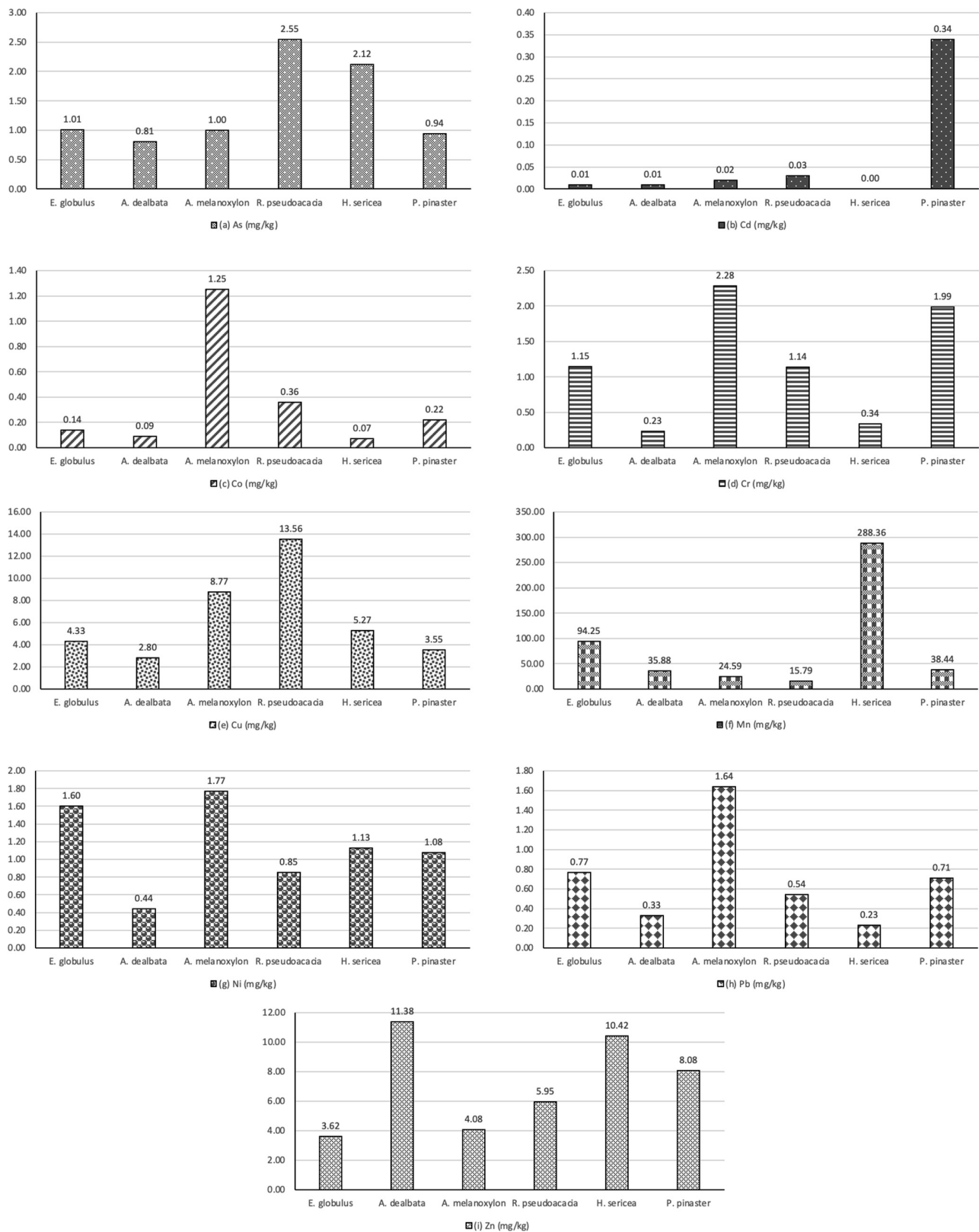


Figure 7. Content of minor elements.

The As content varied between the minimum value of 0.81 mg/kg, for *Acacia dealbata*, and the maximum value of 2.55 mg/kg, for *Robinia pseudoacacia*. The remaining species ranged from 0.94 mg/kg to 2.12 mg/kg. The Cd content varied between the minimum value of 0.00 mg/kg, for *Hakea sericea*, up to a maximum value of 0.34 mg/kg, for *Pinus pinaster*. The remaining species varied between 0.01 mg/kg and 0.03 mg/kg. The Co content varied between the minimum value of 0.07 mg/kg, for *Hakea sericea*, and the maximum value of 1.25 mg/kg, for *Acacia melanoxylon*. The remaining species varied between 0.09 mg/kg and 0.36 mg/kg. The Cr content varied between the minimum value of 0.23 mg/kg, for *Acacia dealbata*, and the maximum value of 2.28 mg/kg, for *Acacia melanoxylon*. The remaining species varied between 0.34 mg/kg and 1.99 mg/kg. The Cu content varied between the minimum value of 2.80 mg/kg, for *Acacia dealbata*, and the maximum value of 13.56 mg/kg, for *Robinia pseudoacacia*. The remaining species varied between 3.55 mg/kg and 8.77 mg/kg. The Mn content varied between the minimum value of 15.79 mg/kg, for *Robinia pseudoacacia*, and the maximum value of 288.36 mg/kg, for *Hakea sericea*. The remaining species varied between 24.59 mg/kg and 94.25 mg/kg. The Ni content varied between the minimum value of 0.44 mg/kg, for *Acacia dealbata*, and the maximum value of 1.77 mg/kg, for *Acacia melanoxylon*. The remaining species varied between 0.85 mg/kg and 1.60 mg/kg. The Pb content varied between the minimum value of 0.23 mg/kg, for *Hakea sericea*, and the maximum value of 1.64 mg/kg, for *Acacia melanoxylon*. The remaining species varied between 0.33 mg/kg and 0.77 mg/kg. The Zn content varied between the minimum value of 3.62 mg/kg, for *Eucalyptus globulus*, and the maximum value of 11.38 mg/kg. The remaining species varied between 4.08 mg/kg and 10.42 mg/kg.

2.7. Ash Fusibility

The results of the ash fusibility temperatures are shown in Figure 8.

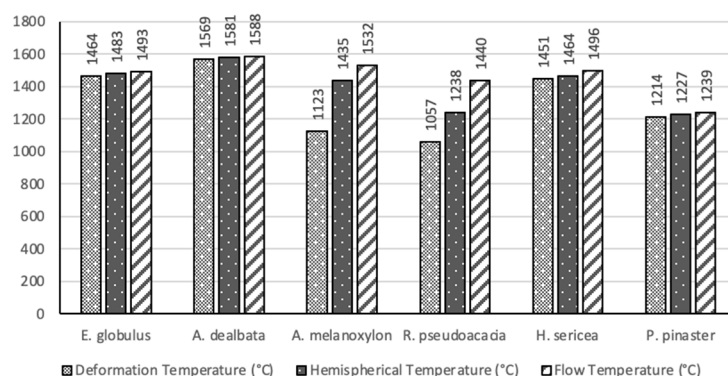


Figure 8. Ash fusibility temperatures.

Deformation temperatures ranged from the minimum value of 1057 °C, for *Robinia pseudoacacia*, and the maximum value of 1569 °C, for *Acacia dealbata*. The remaining species varied between 1123 °C and 1464 °C. Hemispherical temperatures varied between the minimum value of 1227 °C, for *Pinus pinaster*, and the maximum value of 1581 °C, for *Acacia dealbata*. The remaining species varied between 1238 °C and 1483 °C. The flow temperatures varied between the minimum value of 1239 °C, for *Pinus pinaster*, and the maximum value of 1588 °C, for *Acacia dealbata*.

3. Discussion

There are many works available where characterizations of the most diverse types of biomass are presented, in order to assess their combustibility and their physical-chemical properties. An example of this is the review work presented by Cai et al. (2017), where several lignocellulosic biomasses are characterized, including several residual biomasses

of agricultural origin, such as rice husk, rice stalk, cotton stalk, wheat straw or corn stalk, but also residual biomasses of forest origin, like pine or poplar [22]. The objective of this study by Cai et al. (2017) fits that of many others, such as those presented by García et al. (2012), Chiang et al. (2012), Wilson et al. (2011), Fang et al. (2015) or Patel and Gami (2012), always from the perspective that using lignocellulosic biomass-derived biofuels can reduce reliance on fossil fuels and contribute to climate change mitigation [23–27]. Many works are also available regarding the behavior of different forms of biomass when subjected to thermochemical conversion processes, such as torrefaction, pyrolysis or gasification, such as the work of Chen et al. (2014), which addresses the non-oxidative and oxidative torrefaction characterization and SEM observations of fibrous and ligneous biomass [28], or the work of Neves et al. (2011), where biomass pyrolysis is addressed, regarding models, mechanisms, kinetics and some information on product yields and properties [29]. In fact, this perspective of energy recovery through the use of energy densification technologies foresees, at the outset, a need to improve, or in some way, correct, the less positive characteristics, such as low heating value, low density or high content of ashes. However, the most frequent uses presuppose the direct combustion of materials [30–32].

The comparative analysis of forms of residual biomass and their potential framing with premium raw materials, certified by the international standards in force, as is the case of ENplus[®], has also been addressed by extensive literature. For example, the work presented by Agar et al. (2018) addresses the production of pellets from agricultural and forest biomass [33], while de Souza et al. (2020) addressed the possibility of producing pellets from eucalyptus biomass and coffee growing wastes residues with acceptable properties for commercialization standards, which includes the ENplus[®] standard [34]. In other words, the possibility of integrating different forms of biomass has been a necessity for a long time, since it would allow, in case of success and compliance with the quality criteria, the reduction in the cost of the acquisition of raw materials at the same time, which presents a solution for the disposal/reuse of a set of waste, which until now has not been subject to any type of recovery [13].

Thus, the classification of the properties of any residual raw material, as is the case of the species selected in the present study, with the parameters defined with one of the standards used internationally for the certification of fuels derived from biomass, as is the case of ENplus[®] standard, allows, in a simple and accessible way, the validation or exclusion of the use of a certain material (species), or at least, it allows indicating whether it is possible to incorporate a certain percentage of these materials in any way [35]. Table 1 shows the values allowed for the main parameters indicated for the raw materials used in the production of wood pellets by the ENplus[®] standard. This standard divides products into three categories according to the origin of the raw materials, with categories A2 and B destined to products resulting from the processing of waste materials, which include the species used in the present study [36]. However, in the case of incorporating percentages of residual biomass with premium raw materials, and if the parameters defined in the standard are met, the final products can be included in category A1, which has the highest added value [37].

The results obtained by the characterization of these biomass species, which are summarized in Table 2, present a relatively different framework. In the table, the values marked in italics represent the values that meet the requirements of categories A2 or B, and in bold, the values that do not fit into any of the categories. The remaining values are within the limits imposed by the ENplus[®] A1 standard. As expected, *Pinus pinaster* fully complies with all the requirements presented by the ENplus[®] standard, while none of the other species fully comply with all parameters. However, some of the species present values very close to the permitted limits, so that their incorporation with, for example, *Pinus pinaster*, appears as possible, and thus meet the requirements defined by the standard ENplus[®].

Table 1. Limit values for properties defined by the ENplus[®] standard.

		ENplus [®]		
		A1	A2	B
Moisture	%		≤10	
Ash	%	≤0.7	≤1.2	≤2
LHV	MJ/kg		≥16.50	
N	%	≤0.3	≤0.5	≤1.0
S	%		≤0.04	≤0.05
Cl	%		≤0.02	≤0.03
Deformation Temp.	°C	≥1200		≥1100
As	mg/kg		≤1	
Cd	mg/kg		≤0.5	
Cr	mg/kg		≤10	
Cu	mg/kg		≤10	
Pb	mg/kg		≤10	
Hg	mg/kg		≤0.1	
Ni	mg/kg		≤10	
Zn	mg/kg		≤100	

Table 2. Comparative analysis of the results obtained with the parameters defined by the ENplus[®] standard.

		<i>P.p.</i>	<i>E.g.</i>	<i>A.d.</i>	<i>A.m.</i>	<i>R.p.</i>	<i>H.s.</i>
Moisture	%	6.42	8.98	7.54	9.28	7.61	6.85
Ash	%	0.62	0.93	0.52	0.81	5.14	1.82
LHV	MJ/kg	17.87	18.15	18.11	18.12	18.27	19.17
N	%	0.08	0.099	0.329	0.308	0.582	0.711
S	%	0.0045	0.005	0.006	0.009	0.042	0.040
Cl	%	0.016	0.05	0.08	0.06	0.09	0.09
Deformation Temp.	°C	1214	1464	1569	1123	1057	1451
As	mg/kg	0.94	1.01	0.81	1.00	2.55	2.12
Cd	mg/kg	0.34	0.00	0.00	0.00	0.03	0.00
Cr	mg/kg	1.99	1.15	0.23	2.28	1.14	0.34
Cu	mg/kg	3.55	4.33	2.80	8.77	13.56	5.27
Pb	mg/kg	0.71	0.77	0.33	1.64	0.00	0.23
Hg	mg/kg	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
Ni	mg/kg	1.08	1.60	0.44	1.77	0.85	1.13
Zn	mg/kg	8.08	3.62	11.38	4.08	5.95	10.42

As can be seen in the results presented in Table 2, the incorporation of these materials in the production of certifiable wood pellets, only seems possible for the biomass of *Eucalyptus globulus*, which would easily dilute the values above the requirements defined in the standard, allowing the incorporation of a percentage of 25%, which allows the production of wood pellets of category A1. An incorporation of 50% of *Eucalyptus globulus* biomass would only allow for category B certification, since the chlorine content would always be close to the upper limit of 0.03% indicated in the standard for this category. The remaining species present values that are too high in some parameters, namely in nitrogen content, with values ranging between 0.308% and 0.711%, mainly for *Hakea sericea* and *Robinia pseudoacacia*, but also due to the accumulation of other parameters outside the limits defined, as for the ash content, with *Robinia pseudoacacia* reaching 5.14%, and in the chlorine content, where it reaches 0.09%, together with *Hakea sericea*. However, the use of these residual biomasses remains possible, especially if the objective is not to produce certified materials, but rather to be used less domestically, and to support the local biomass recovery.

The local valorization of residual biomasses, as those analyzed in the present study, as well as others with similar properties, can always be a solution. Usually, given the lower

requirement of the proximity markets, where the most evaluated requirement is the fuel cost, in detriment to the quality and combustibility requirements, such products can be used. The possibility of using these residual biomasses in thermochemical conversion processes, namely in the production of biochar, not as an energy product, but rather as a soil amendment product and as a carbon sequestration methodology, must be evaluated, with regard to the creation of value chains for residual biomass. This perspective of creating value chains, which aim to promote the maintenance of actions to control and eradicate invasive species, contributes systematically to the revitalization of ecosystems. This positive condition is effective when the pressure caused on the populations of invasive species decrease their strength, allowing native species to develop and return to occupy their space.

4. Materials and Methods

4.1. Sampling and Material Preparation

The species were selected for their availability and abundance and were collected in areas where their proliferation has been noted for the speed of propagation and occupation of space. Thus, the samples were collected in the locations shown in Table 3. Thus, samples of five invasive species were collected, namely, *Acacia dealbata*, *Acacia melanoxylon*, *Eucalyptus globulus*, *Robinia pseudoacacia* and *Hakea sericea*. Samples of *Pinus pinaster* were also collected to serve as a point of comparison. All samples were collected in the form of adult tree trunks, and in the case of invasive species, the all-in method was chosen. That is, none of the constituent parts, such as branches or leaves, have been discarded.

Table 3. Location of sample collection points used in the present study.

Species	Location
<i>Acacia dealbata</i>	Casal do Rei (Seia—Portugal)
<i>Acacia melanoxylon</i>	Loureiro (Oliveira de Azeméis—Portugal)
<i>Eucalyptus globulus</i>	Loureiro (Oliveira de Azeméis—Portugal)
<i>Robinia pseudoacacia</i>	Albernoa (Aljustrel—Portugal)
<i>Hakea sericea</i>	Casal do Rei (Seia—Portugal)
<i>Pinus pinaster</i>	Vale de Cambra (Portugal)

In the sample preparation procedure, the sequence used in a wood pellet production unit was followed, using exclusively *Pinus pinaster* as a raw material, so the *Pinus pinaster* wood was previously debarked before proceeding with the drying. The rest of the wood was not debarked, since the industrial debarking process used is optimized to operate only with *Pinus pinaster* logs, and if the other mentioned species were included in the process, this operation would not be carried out efficiently. Then, the size of the collected samples was reduced to a granulometry equivalent to that normally used in the industrial process, that is, to a G30 size woodchips, which was subjected to drying in a laboratory oven at 100 °C for a period of 12 h. After drying, the material of all samples was ground again, until the dimension normally used in the industrial process of wood pellet production was reached, with a d_{50} within the range [1.13–3.86]. Subsequently, the laboratory characterization of the samples followed with the thermogravimetric analysis, the elemental analysis, the calorimetric analysis, the chemical analysis and the analysis of the fusibility of the ashes. All samples were collected and analyzed in triplicate and the results presented are the average values for each species.

4.2. Thermogravimetric Analysis (TGA)

The thermogravimetric analyzer used was an ELTRA THERMOSTEP model. One gram of each sample was introduced into crucibles and placed inside an oven, along with an empty reference crucible. As temperature increased, crucibles were weighted on a precision scale. Moisture, volatiles, and fixed carbon content were determined in this order throughout the heating process. Lastly, the final residue represents the ash content.

4.3. Elemental Analysis (CHNO)

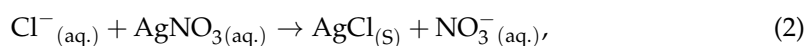
Elemental analysis was performed in a LECO CHN628. The operational principle consists of weighing a sample in tin foil that is later placed in the autoloader. The sample is then introduced into the primary furnace containing only pure oxygen, which results in fast and complete combustion. Carbon, hydrogen, and nitrogen present in the sample are oxidized to CO₂, H₂O, and NO_x, respectively, and are swept by the oxygen carrier gas through a secondary furnace for further oxidation and particulate removal. Detection of H₂O and CO₂ occurs through separate, optimized, non-dispersive infrared cells, while the NO_x gases are reduced to N. Lastly, N₂ is detected when the gas passes through a thermal conductivity cell. After the analysis is complete, moisture content obtained through thermogravimetric analysis is introduced into the software and the CHN contents are automatically calculated. Following that, it is possible to estimate the oxygen content on a dry basis (w_{O,db}) from Equation (1), as follows:

$$w_{O,db} (\%) = 100 - w_{C,db} - w_{H,db} - w_{N,db} - w_{S,db} - w_{Cl,db}, \quad (1)$$

where w_{C,db} is the carbon content on a dry basis (%), w_{H,db} is the hydrogen content on a dry basis (%), w_{N,db} is the nitrogen content on a dry basis (%), w_{S,db} is the sulfur content on a dry basis (%), and w_{Cl,db} is the chlorine content on a dry basis (%).

4.4. Determination of Chlorine Content

Chloride titration was the method chosen to determine the chlorine content, and the equipment used was a TITROLINE 7000 titrator from SI Analytics. For this procedure, sample preparation involves previous digestion of the sample, performed in a SINEO MDS-6G microwave, since titration requires a liquid sample. Chlorine content determination is achieved by potentiometric titration. This method consists of measuring the potential difference while the titrant, in this case, AgNO₃, is added. Equation (2), as follows, presents the redox reaction that occurs:



As next step, a software creates a spreadsheet with the potential difference and titrant volume variation over time. First derivative can then be calculated through Equation (3), as follows, and the equivalence point can be determined as the volume corresponding to the maximum of the first derivative:

$$f'(x) = \frac{\Delta U}{\Delta V} = \frac{U_i - U_{i-1}}{V_i - V_{i-1}} f'(x) = \frac{\Delta U}{\Delta V} = \frac{U_i - U_{i-1}}{V_i - V_{i-1}}, \quad (3)$$

where ΔU is the potential difference variation (mV) and ΔV is the volume variation (mL).

Chlorine content on a dry basis (w_{Cl,db}) is then determined by Equation (4), in compliance with the European standard EN15289:

$$w_{Cl,db} (\%) = \frac{(C - C_0) \times V}{m} \times 100 \times \frac{100}{100 - M_{ad}} w_{Cl,db} (\%) = \frac{(C - C_0) \times V}{m} \times d \times \frac{100}{100 - M_{ad}}, \quad (4)$$

where C is the concentration of chloride in the solution (mg/L), C₀ is the concentration of chloride in the blank solution (mg/L), V is the volume of the solution (l), m is the mass of the test portion used in the digestion (mg), and M_{ad} is the moisture content in the analysis test sample (%).

4.5. Heating Value

Heating value, also known as the heating value, defines the energy content of biomass fuel [38]. This parameter can be described in two ways: higher heating value (HHV), or gross heating value, refers to the heat released from fuel combustion along with the vaporization energy from water. On the other hand, lower heating value (LHV) or net heating value is based on steam as the product, which means its vaporization energy is

not considered heat [39]. The heating value of biomass, both higher and lower, can be determined experimentally by employing an adiabatic bomb calorimeter. The model used in this project was the 6400 Automatic Isoperibol Calorimeter by PARR INSTRUMENT. After each procedure, the equipment provides the corrected temperature increase that is later used for the determination of the heating value. Due to the nitrogen and oxygen-rich atmosphere inside the calorimeter, nitric acid and sulphuric acid are formed, respectively, and the heat of formation of both acids must be disregarded. For HNO_3 , the wash water for the pump was titrated with NaOH (0.1 M), and Equation (5) was applied, while for H_2SO_4 , knowing the sulfur content Equation (6) can be applied:

$$Q_{N,S} = 1.43 \times V_{\text{NaOH}}, \quad (5)$$

where $Q_{N,S}$ is the heat contribution relative to nitric acid formation (cal) and V_{NaOH} is the volume of NaOH used in the titration of the wash water of the pump (ml).

$$Q_{S,\text{add}} = 13.61 \times w_{S,\text{db}}, \quad (6)$$

where $Q_{S,\text{add}}$ is the additional contribution relative to sulfur dioxide formation and $w_{S,\text{db}}$ is the sulfur content on a dry basis (%).

With this information, Equation (7) can be applied to obtain the gross heating value, or high heating value, at a constant volume, $q_{V,\text{gr}}$ (J/g), as follows:

$$q_{V,\text{gr}} = \left(\frac{\varepsilon \times \theta - Q_{\text{thread}} - Q_{N,S} - Q_{S,\text{add}}}{m} \right) \times 4.1868, \quad (7)$$

where ε is the heating capacity of the calorimeter (previously determined) (cal/°C), θ is the corrected temperature increase (°C), Q_{thread} is the heat contribution relative to the thread combustion (cal), $Q_{N,S}$ is the heat contribution relative to nitric acid formation (cal), $Q_{S,\text{add}}$ is the additional contribution relative to sulfur dioxide formation (cal), and m is the mass of the sample (g).

Equation (8) was used to calculate the gross heating value at constant volume on a dry basis, $q_{V,\text{gr},\text{db}}$ (J/g), as follows:

$$q_{V,\text{gr},\text{db}} = q_{V,\text{gr}} \times \frac{100}{100 - M_{\text{ad}}} = q_{V,\text{gr}} \times \frac{100}{100 - M_{\text{ad}}}, \quad (8)$$

where $q_{V,\text{gr},\text{db}}$ is the gross heating value at constant volume (J/g) and M_{ad} is the moisture content in the analysis test sample (%). Lastly, the net heating value at constant pressure on a dry basis, $q_{p,\text{net},\text{db}}$ (J/g), can be calculated through Equation (9), as follows:

$$q_{p,\text{net},\text{db}} = q_{V,\text{gr},\text{db}} - 212.2 \times w_{H,\text{db}} - 0.8 \times (w_{O,\text{db}} + w_{N,\text{db}}), \quad (9)$$

where $q_{V,\text{gr},\text{db}}$ is the gross heating value at constant volume on a dry basis (J/g), $w_{H,\text{db}}$ is the hydrogen content on a dry basis (%), $w_{O,\text{db}}$ is the oxygen content on a dry basis (%), and $w_{N,\text{db}}$ is the nitrogen content on a dry basis (%). According to the European standard EN14918, $(w_{O,\text{db}} + w_{N,\text{db}})$ is obtained from Equation (10), as follows:

$$(w_{O,\text{db}} + w_{N,\text{db}}) = 100 - w_{A,\text{db}} - w_{C,\text{db}} - w_{H,\text{db}} - w_{S,\text{db}} \quad (10)$$

where $w_{A,\text{db}}$ is the ash content on a dry basis (%), $w_{C,\text{db}}$ is the carbon content on a dry basis (%), $w_{H,\text{db}}$ is the hydrogen content on a dry basis (%), and $w_{S,\text{db}}$ is the sulfur content on a dry basis (%).

4.6. Chemical Analysis by ICP-OES

Inductively coupled plasma atomic emission spectroscopy (ICP-AES), also known as inductively coupled plasma optical emission spectrometry (ICP-OES), is an analytical

technique, which produces excited atoms and ions that emit electromagnetic radiation at different wavelengths and is used for the determination of trace elements. The main advantages are its multi-element capability, broad dynamic range, and effective background correction [40]. For the preparation of the samples, microwave digestion was once again necessary to ensure that the capillaries did not get obstructed. The model used for the analysis was a THERMO SCIENTIFIC (iCAP 6000 series). A peristaltic pump delivered the digested samples to an analytical nebulizer and introduced them into the plasma flame that breaks down the samples into charged ions, releasing radiation with specific wavelengths. In the end, a software generates a spreadsheet with the results. Equations (11) and (12) were used, as follows, to calculate the content of each element in the sample on a dry basis ($w_{i,db}$), in compliance with standards EN15289, EN15290 and EN15297:

$$w_{i,db} = \left(\frac{\text{mg}}{\text{kg}} \right) = \frac{(C - C_{i,0}) \times V}{m} \times \frac{100}{100 - M_{ad}} \quad (11)$$

where C_i is the concentration of the element in the diluted sample digest (mg/L), $C_{i,0}$ is the concentration of the element in the solution of the blank experiment (mg/L), V is the volume of the diluted sample digest solution (mL), m is the mass of the test portion used (g), and M_{ad} is the moisture content in the analysis test sample (%).

$$w_{S,db} (\%) = \frac{(C - C_0) \times V}{m} \times 0.3338 \times 100 \times \frac{100}{100 - M_{ad}} \quad (12)$$

where C_i is the concentration of sulfate in the solution (mg/L), $C_{i,0}$ is the concentration of sulfate in the solution of the blank experiment (mg/L), V is the volume of the diluted sample digest solution (mL), m is the mass of the test portion used (g), 0.3338 is the stoichiometric ratio of the relative molar masses of sulfur and sulfate, and M_{ad} is the moisture content in the analysis test sample (%).

4.7. Fusibility of the Ashes

This determination makes it possible to estimate the behavior of biomass ash when combustion is carried out, for example, in boilers or burners. During the combustion process, ashes may occur, such as slagging and fouling. Slagging is the deposit of ash in the bottom and walls of the furnaces, while fouling is the deposit of ash in the air flow zones (which can cause clogging of pipes). The formation of slagging and fouling depends on the ash content of a biomass, as well as on the elemental composition of the ash. The determination of ash fusibility consists of monitoring the behavior of ash melting along a temperature ramp. Thus, this test allows to predict the formation of slagging and fouling in thermal conversion processes. These data must be related to the ash content (determined using the TGA) and the content of the different ash components (determined by ICP/OES). The fusibility test can be carried out with an oxidizing atmosphere (air) or reducing atmosphere (60% CO + 40% CO₂). The choice of atmosphere must be related to the combustion conditions of the boiler or burner. If the boiler operates in atmospheres rich in fuel (with oxygen deficit), its atmosphere will be mostly reducing, with incomplete combustion and CO formation. As a general rule, reducing atmospheres cause ash to melt at lower temperatures, thus causing greater slagging and fouling problems. Therefore, the fuse test must reflect these characteristics and adapt to the customer's combustion process. During the fusibility test, the ash melting behavior is monitored and the following characteristic temperatures are determined:

- Initial temperature: temperature at which the test starts up to 550 °C;
- Shrinking temperature: shrinkage to 95% of the area recorded at 550 °C;
- Deformation temperature: temperature at which the first rounding of the vertices of the cylinders occurs;
- Hemisphere temperature: temperature at which the height of the cylinder is equal to half the width;

- Fluid temperature: temperature at which the height is equal to half the height recorded at the hemisphere temperature.

In the present study, the samples, converted to ashes, were subsequently placed in a plastic dish, where two drops of ethyl alcohol are added, and using a spatula they are homogenized until a uniform paste is obtained. Then this paste is transferred to the mold, where the cylinder is compacted. After being removed from the mold, the cylinders are placed on the zirconia lamella. The samples are then placed inside the chamber of the ash fusibility furnace, which in this specific case was a SYLAB IF 2000-G device.

5. Conclusions

The use of residual biomass in the production of wood pellets is an opportunity for the circularization of the local economy associated with forest management operations. It also presents itself as an opportunity for the sustainability of operations to control invasive species, as it contributes to the creation of value chains for residual products that until now had no added value. The incorporation of these materials in the production of certified wood pellets presents some difficulties, since these materials do not meet the chemical requirements imposed by the standards that regulate the quality of the final products. However, the recovery of residual biomass from actions to control and eradicate invasive species can be a reality, especially for uses that do not imply product certification, and especially when the recovery of materials in industrial environments is not involved, where adverse effects, such as corrosion, fouling or slagging, can result in serious damage and unforeseen maintenance to combustion equipment.

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