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VALORIZATION OF Cistus ladanifer AND Erica arborea SHRUBS FOR FUEL: WOOD AND BARK THERMAL CHARACTERIZATION

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ABSTRACT

As a form of upgraded biomass characterized by its high energy density, low production costs, and low process energy requirements, wood pellets are an environmentally friendly fuel allowing for carbon neutral heating with high energy efficiency. In this work, the suitability of a valorization of the woods from the two most representative shrub species from the Iberian Peninsula (namely *Cistus ladanifer* and *Erica arborea*) for heating has been assessed. Whereas *Erica arborea* met the requirements of ISO 17225-2:2014 for EN*plus*-B class (the calorific content for both wood and bark was high and not significantly different, and the ash content was permissible for specimens with branch diameter \geq 2,8 cm), *Cistus ladanifer* was in the limit of the normative and only met the requirements in terms of acceptable ash percentage (1,9%) and heating value (19 kJ·g⁻¹) for old specimens with branch diameters \geq 3,4 cm. Consequently, while the harvest of *E. arborea* for its use as fuel does not need to be selective, that of *C. ladanifer* should be limited to the most robust specimens and foliage should be avoided.

Keywords: Ash content, biomass resources, gum rockrose, heating values, tree heath.

INTRODUCTION

A significant proportion of Mediterranean forest vegetation consists of evergreen small diameter hardwood shrubs, such as *Cistus ladanifer* (gum rockrose) and *Erica arborea* (tree heath), which have been traditionally used as fuelwood for domestic heating purposes. In the geographic area under study (Castilla y León, Spain) both species are so abundant that their utilization as a biomass resource for energy purposes has aroused significant interest: In fact, since 2012, field studies aimed at this valorization, funded by the European Union through the LIFE+ and Joule programs, have been conducted in several municipalities in the province of Zamora (Spain). The ultimate goal would be to collect tree heath and gum rockrose for their combustion in district heating facilities (municipal boilers) in Fabero (Soria, Spain) and Las Navas del Marqués (Ávila, Spain), as well as for the electricity production plant located in Garray (Soria, Spain). Of the two bushes into consideration, the most potentially profitable would be *E. arborea*, whose heating value was recently reported to be the highest of all evergreen Mediterranean hardwood species (Barboutis and Lykidis 2014).

The use of biomass as an energy source provides substantial socio-economic and environmental benefits. However, bio-fuels have low bulk densities which limit their use to areas around their origin, being this drawback a restrictive factor for their energy use. Nevertheless, densification by pelleting minimizes this disadvantage. Global pellet production has considerably increased in the last years (from 7 to 19 million tons between 2006 and 2012 (Duca *et al.* 2014)), mainly in Europe and North America, and the growth in pellet consumption has resulted in more diversity. Consequently, the industry has

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started looking for products such as wastes obtained from forestry and scrubland wood. The doubtful quality of these materials originated the development of quality standards in some countries, so as to guarantee the right use of the different types of pellets in combustion equipment.

Due to differences in chemical structure, bark and wood from *C. ladanifer* and *E. arborea* should show different properties, and –in particular– those related to their applicability as fuels. This differentiation is important because the bark of all evergreen hardwood species usually presents significantly higher ash content than wood and, in agreement with the international standard ISO 17225-2:2014 (International Organization for Standardization 2014) –which has recently superseded the European Standard EN 14961-2 for the quality characteristics of pellets (European Pellet Council 2011)–, the threshold ash content value is 2%. In this normative, the required net calorific value (NCV) or lower calorific value (LHV) is \geq 16,56 kJ·g⁻¹ and the higher heating value (HHV) is \geq 18,82 kJ·g⁻¹.

The aims of the study presented herein have been: (i) to correlate the results of our analytical determinations and related calculations on HHV and ash content (AC) for bark and wood from *C. ladanifer* and *E. arborea* with those from other direct and indirect methods used in the literature; and (ii) to explore which bark diameters would meet the ISO 17225-2:2014 (International Organization for Standardization 2014)/ENplus (ENplus 2015) requirements for HHV and AC with a view to the valorization of these two shrub species as fuels. This is in line with the work by other authors on woods from other species (Duca et al. 2014, Miranda et al. 2017).

MATERIAL AND METHODS

The quantity known as higher heating value (also referred to as gross energy, upper heating value, gross calorific value (GCV) or higher calorific value (HCV)) is determined by bringing all the products of combustion back to the original pre-combustion temperature and, in particular, condensing any vapor produced. This is the same as the thermodynamic heat of combustion, since the enthalpy change for the reaction assumes a common temperature of the compounds before and after combustion, in which case the water produced by combustion is condensed to a liquid, hence yielding its latent heat of vaporization.

Calculations for the estimation of biomass and heating values may be obtained either by direct or by indirect methods. Direct methods involve the destruction of heavy biomass, whereas in indirect methods equations are used to estimate heating values from measurements of other variables, making the process easier (Bombelli *et al.* 2009).

In the first part of this study, heating values were determined by a destructive method, which comprised the selection, felling and extraction of biomass of each of the species and its subsequent combustion. *C. ladanifer* samples had a height of 115,3±32,4 cm and a crown width of 28,68±15,25 cm while *E. arborea* samples had a height of 158,2±49,0 cm and a crown width of 103,7±60,0 cm.

The aerial part was separated from the roots using a saw and then, following an analogous procedure to that described by Ruiz-Peinado *et al.* (2012), root systems were excavated by using a tractor with a shovel and then spades to complete the job. For each plant, soil was excavated down in a circular area of twice the mean crown diameter. In addition to the main body of the roots, those remaining in the hole were also collected. Samples were transported to the laboratory (ETSIIAA facilities, Universidad de Valladolid, Spain), where they were separated into different fractions and weighed (fresh weight). In the case of *C. ladanifer*, they were classified into leaves, xerochastic capsules, branches (thin: 3-7 mm in diameter; thick: 7-17 mm in diameter) and roots. On the other hand, for *E. arborea*—given its morphology and the impracticality of leaves separation—they were divided into four fractions: leaves with flowers and fruits, fine material (<1 cm), thick material (<5 cm) and roots, in agreement with Mello *et al.* (2012).

In addition to aforementioned information, the stem diameter (2R), bark thickness (f) and wood and bark percentages were characterized for both species. The proportion of bark was calculated as the

ratio of bark area in a transverse section to the total stem area of this section, according to equation (Barmpoutis *et al.* 2015):

$$Z = 100 \left[f \frac{\left(2R - f\right)}{R^2} \right] \quad (1)$$

where Z=bark percentage (%), R=barked stem radius (cm) and f=bark thickness (cm).

For the determination of the bark percentage, the transverse surfaces were assumed to be circular. Consequently, bark and wood were separated and the materials were ground by means of a portable chipper. The resulting data is summarized in Table 1.

Table 1. Stem diameter and bark thickness of the shrub species under study. Values are given as an average of 10 repetitions, followed by the minimum and maximum values in brackets.

Species	Stem diameter, 2R (cm)	Bark thickness, $f(cm)$	Bark, <i>Z</i> (%)	Wood (%)
C. ladanifer	1,9 (1,8-2,3)	0,15 (0,07-0,20)	29	71
C, ladanifer (old specimens)	3,4 (2,3-4,2)	0,20 (0,11-0,40)	22,5	77,5
E. arborea	2,8 (2,6-3,6)	0,18 (0,10-0,30)	25	75

It should be noted that for the study of C. ladanifer two sets of individuals were selected: ones with average stem diameter (1,9 cm trunk diameter) and also robust old specimens (older than 12 years, according to the equation $y = 1,5496 \text{ x} + 1,5342 \text{ } R^2$ (Valares Masa et al. 2016)), with diameters above the average, provided that this second group was more likely to meet the EN standard. Ten repetitions were carried out for each group.

Calorific values, expressed as HHV, for *C. ladanifer* and *E. arborea* fractions were calculated from elemental analysis data in agreement with the US Institute of Gas Technology (IGT) (Talwalkar *et al.* 1981): HHV = 0,341(%C) + 1,322(%H) - 0,12(%O+%N), where %C, %H, %O, %N are the mass fractions in wt% of dry material and HHV the heating value for dry material in MJ/kg. Although originally derived from data on coal, this formula has been shown to give acceptable results for a wide range of carbonaceous materials including biomass (CHPQA 2008).

Alternatively, HHV values were also calculated from holocellulose and lignine+extractives percentages, following the guidelines of Aseeva *et al.* (2005) and Kienzle *et al.* (2001) and applying a factor of 17,5 for holocellulose and of 25,5 for the lignine+extractives mixture.

Experimental HHV values were determined in a Parr 1261 isoperibol bomb calorimeter (Thermo Fisher Scientific, Waltham, MA, USA), according to the method described in BS EN 14918:2009 standard (British Standards Institution 2010). Other experimental values, such as the total enthalpy of combustion, were obtained from differential scanning calorimetry (DSC) curves by numerical integration of the experimental signal on the whole temperature range (30-600 °C). DSC data were obtained on a TA Instruments (New Castle, DE, USA) mod. Q100 v.9.0 DSC equipped with an intracooler cooling unit at -25 °C (with a 1:1 volume mixture of ethylene glycol-water), at a heating rate β =20°C/min and at a N₂:O₂ ratio of 4:1 (20 mL/min). Samples were hermetically sealed in aluminium pans, and an empty pan was used as a reference. TG/DTG analyses were conducted with a Perkin-Elmer (Waltham, MA, USA) STA6000 simultaneous thermal analyser by heating the samples in a slow stream of N₂ (20 mL/min) from room temperature up to 700 °C, with a heating rate of 20 °C/min. Pyris v.11 software was used for data analysis (PerkinElmer 2014). Temperature calibration was performed with high-grade standards, biphenyl (CRM LGC 2610) and indium (Perkin-Elmer, x=99,99%), which was also used for enthalpy calibration.

The elemental analysis and vegetal component percentages data used for above calculations, collected from 25 samples of each species with an average height (Carrión-Prieto et al. 2017), is

summarized in Table 2. For the determination of ash content, the methodology described in ISO 18122:2015 (International Organization for Standardization 2015) was used, using 5 replicates.

Table 2. Overall chemical composition of *C. ladanifer* and *E. arborea* (Carrión-Prieto *et al.* 2017). Values are given as an average of 25 repetitions, followed by the minimum and maximum values in brackets.

	Cistus ladanifer	Erica arborea
Elemental analysis		
C (%)	47,8 (47,5-50,1)	51,0 (49,3-52,8)
H (%)	6,4 (6,0-6,8)	6,2 (6,0-6,4)
N (%)	0,8 (0,3-1,9)	1,0 (0,3-1,1)
O (by diff., %)	~45,0	~41,8
Vegetal components		
Cellulose (%)	55,0 (54,9-55,7)*	40,0 (37,3-41,1)
Lignin (%)	25,3 (24,5-34,2)	39,5 (39,3-40,1)
Hemi-cellulose (%)	10,2 (10,1-10,9)**	11,0 (9,7-13,8)**
Extractive (%)	9,5 (9,4-9,6)	9,5 (5,7-11,0)
<i>Moisture</i> (wt.%)	26,8	26,0

^{*}This cellulose content is higher than that of most woods, which is usually in the 35-50% range.

RESULTS

HHV values calculated from the elemental analysis data

HHV values calculated from elemental analysis data according to the IGT formula are reported in Table 3. HHV values for *Cistus ladanifer*, from the largest to the smallest, were: foliage (20,53 kJ·g⁻¹), thin branches (19,42 kJ·g⁻¹), thick branches (19,16 kJ·g⁻¹) and roots (19,25 kJ·g⁻¹). The result for branches was in close agreement with that reported by Dimitrakopoulos and Panov (2001) (viz. 19,05 kJ·g⁻¹).

HHV values for *Erica arborea*, from the largest to the smallest, were: foliage $(21,29 \text{ kJ} \cdot \text{g}^{-1})$, thick branches $(19,69 \text{ kJ} \cdot \text{g}^{-1})$, thin branches $(20,12 \text{ kJ} \cdot \text{g}^{-1})$, roots $(19,91 \text{ kJ} \cdot \text{g}^{-1})$ and stem wood $(19,8 \text{ kJ} \cdot \text{g}^{-1})$. These results were in reasonably good agreement with those reported by Dimitrakopoulos and Panov (2001) for foliage $(23,59 \text{ kJ} \cdot \text{g}^{-1})$ and branches $(19,34 \text{ kJ} \cdot \text{g}^{-1})$.

Table 3. Carbon (C), hydrogen (H), nitrogen (N) and oxygen (O) percentages for *C. ladanifer* and *E. arborea* fractions and HHV values calculated thereof.

	Cistus ladanifer			Erica arborea				
	Leaves	Thin branches	Thick branches	Roots	Leaves	Thin branches	Thick branches	Roots
C (%)	50,07 (0,04)	48,12 (0,03)	47,56 (0,06)	47,76 (0,05)	52,82 (0,02)	49,34 (0,01)	50,26 (0,03)	49,82 (0,12)
11 (0/)	6,4	6,4	6,4	6,4	6,2	6,2	6,2	6,2
H (%)	(0,2)	(0,2)	(0,2)	(0,2)	(0,2)	(0,2)	(0,2)	(0,2)
N (%)	1,89 (0,00)	0,84 (0,00)	0,27 (0,02)	0,36 (0,00)	1,05 (0,00)	0,34 (0,02)	0,38 (0,00)	0,34 (0,02)
O (by diff.%)	41,64	44,60	45,77	45,48	39,93	44,12	43,16	43,64
HHV (kJ·g ⁻¹)	20,53	19,42	19,16	19,25	21,29	19,69	20,12	19,91

^{**}These hemicellulose contents are lower than those of most woods, which usually range from 20% to 30%.

All values for the elemental analysis are given in average \pm standard deviations (in brackets) across five replicates. The value for *C. ladanifer* capsules has been omitted due to its low representativeness and to allow comparison of the components of both species.

HHV values calculated from the component percentages

Using the percentage of biomass distribution in each plant (Table 4), overall HHV for both shrubs was readily calculated.

Component percentage Component Cistus ladanifer Erica arborea Leaves (%) 19 4 Capsules (%) 1 Thin branches (%) 29 20 Thick branches (%) 33 41 Roots (%) 18 35

Table 4. Percentage of biomass distribution in each plant (Carrión-Prieto et al. 2017).

All values are given in average across 25 samples of each species.

Because *C. ladanifer* has 19% of leaves ($\times 20,53 \text{ kJ} \cdot \text{g}^{-1} = 3,87 \text{ kJ} \cdot \text{g}^{-1}$), 29% of thin branches ($\times 19,42 \text{ kJ} \cdot \text{g}^{-1} = 5,655 \text{ kJ} \cdot \text{g}^{-1}$), 33% of thick branches ($\times 19,16 \text{ kJ} \cdot \text{g}^{-1} = 6,346 \text{ kJ} \cdot \text{g}^{-1}$) and 18% of roots ($\times 19,25 \text{ kJ} \cdot \text{g}^{-1} = 3,478 \text{ kJ} \cdot \text{g}^{-1}$), the resultant HHV weighted average was 19,3 kJ·g⁻¹. Likewise, *E. arborea*, with 4% of leaves ($\times 21,29 \text{ kJ} \cdot \text{g}^{-1} = 0,855 \text{ kJ} \cdot \text{g}^{-1}$), 20% of branches ($\times 19,69 \text{ kJ} \cdot \text{g}^{-1} = 3,952 \text{ kJ} \cdot \text{g}^{-1}$), 41% of thick branches ($\times 20,12 \text{ kJ} \cdot \text{g}^{-1} = 8,28 \text{ kJ} \cdot \text{g}^{-1}$) and 35% of roots ($\times 19,91 \text{ kJ} \cdot \text{g}^{-1} = 7,0 \text{ kJ} \cdot \text{g}^{-1}$), yielded a HHV weighted average of 20,0 kJ·g⁻¹.

By applying the weighted average formulas and percentages of bark and wood from Table 1, it was possible to estimate HHV values of 19,5 kJ·g⁻¹ (bark) and 19,3 kJ·g⁻¹ (wood) for random *C. ladanifer* specimens, and of 19,6 kJ·g⁻¹ (bark) and 19,2 kJ·g⁻¹ (wood) for old specimens. As regards *E. arborea*, the bark and wood HHV values were 20,6 kJ·g⁻¹ and 19,9 kJ·g⁻¹, respectively. If, alternatively, the HHV values were calculated from the maximum holocellulose and lignin+extractives percentages (Table 2) using the factors proposed by Aseeva *et al.* (2005) and Kienzle *et al.* (2001) for such fractions, the results obtained were 20,2 kJ·g⁻¹ for *C. ladanifer* and 22,1 kJ·g⁻¹ for *E. arborea*.

HHV experimental values from calorimetry

HHV, determined with an isoperibol bomb calorimeter, according to the method described in the EN 14918:2009 standard, yielded values of 19,7 kJ·g¹ for *C. ladanifer* and 21,0 kJ·g¹ for *E. arborea*.

Results from DSC and TG/DTG curves

DSC curves for *C. ladanifer* and *E. arborea* woods are shown in Figure 1 and their thermal effects (mainly due to holocellulose and lignin combustion) are summarized in Table 5. Overall enthalpy change values obtained from these curves resulted in 18,04 kJ·g⁻¹ and 18,63 kJ·g⁻¹, respectively.

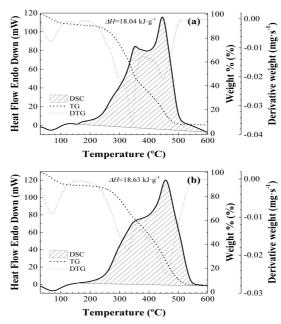


Figure 1. DSC and TG/DTG curves of (a) *C. ladanifer* and (b) *E. arborea* woods.

Table 5. Exothermic effects data for holocellulose and lignin in the DSC thermograms for *C. ladanifer* and *E. arborea* woods.

	Holocellulose (cellulose+hemicellulose)		Lignin		Overall enthalpy change
	T _{peak} (°C)	T _{offset} (°C)	T _{peak} (°C)	T _{offset} (°C)	<i>∆H</i> (kJ.g ⁻¹)
C. ladanifer	365		455	479	18,04
E. arborea	376	392	527	535	18,63

 T_{peak} stands for the temperature at which the maximum mass loss occurred, according to TG/DTG measurements; T_{offset} stands for the temperature at which the maximum value of heat flux occurred, obtained from the DSC thermograms.

The ash content of the various fractions of *C. ladanifer* and *E. arborea* was estimated from the residue after heating at 700 °C (Figures 2, 3, 4 and 5), according to the usual temperature conditions for pyrolysis in oxygen bomb calorimeters (Wang *et al.* 2016). Both the inner and outer parts of the stem and those of the epidermis and cortex of the roots of *C. ladanifer* resulted in percentage values ranging from 0,5% to 0,6% with no significant differences between fractions. Conversely, for *E. arborea*, the percentages for the stem outer part and the root epidermis ranged from 0,6 to 0,9%, while those for the inner parts of the root and the stem were 0,19% and 0,36%, respectively. It is worth noting that all these values were below 2%.

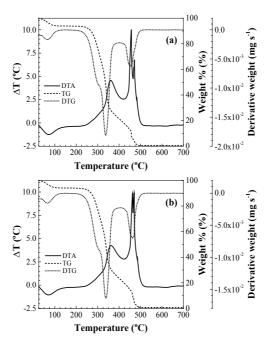


Figure 2. DTA and TG/DTG curves of *C. ladanifer* stems: (a) external fraction and (b) internal fraction.

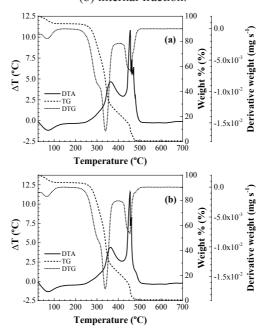


Figure 3. DTA and TG/DTG curves of *C. ladanifer* roots: (a) epidermis and (b) cortex.

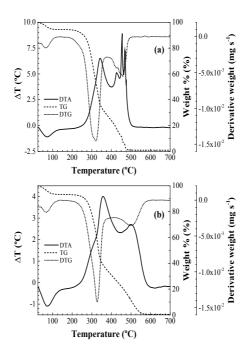


Figure 4. DTA and TG/DTG curves of *E. arborea* stems: (a) external fraction and (b) internal fraction.

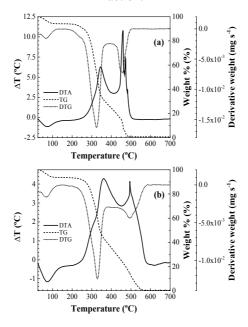


Figure 5. DTA and TG/DTG curves of *E. arborea* roots: (a) epidermis and (b) cortex.

Ash content from UNE-EN ISO 18122:2015 method

Overall experimental ash content values obtained according UNE-EN ISO 18122:2015 norm (International Organization for Standardization 2015) for *C. ladanifer* and *E. arborea* were 1,9% and 1,6% dry weight, respectively. When the ash percentage was broken down for each of the fractions, for *C. ladanifer* it followed the order: foliage (9,0%) > stem bark (7,0-6,5%) > roots (1,4%) > branches (1,1%) > stem wood (0,7-0,6%). Likewise, for *Erica arborea* the AC order followed was: foliage

(5,5%) > stem bark (5,0-4,6%) > roots (1,7%) > branches (1,1%) > stem wood (0,5%). Simplified data for bark and wood fractions is shown in Table 6.

Table 6. Experimental values for ash content (AC) from bark and wood fractions.

	Overall AC (%)	Bark AC (%)	Wood AC (%)
C. ladanifer	2,45	7,0	0,7
C. ladanifer (old specimens)	1,9	6,5	0,6
E. arborea	1,6	5,0	0,5

Values are given in average across 5 repetitions.

DISCUSSION

The experimental and calculated HHV values for *C. ladanifer* specimens of indiscriminate age were in the 19,0-19,4 range, as compared to 19,2-20,2 kJ·g⁻¹ for old specimens. These results were slightly higher than those reported (according to the superseded EN 14775 norm) by García Rosa (2013) (17,8 kJ·g⁻¹) and Martínez *et al.* (2000) (17,9 kJ·g⁻¹), and slightly lower than those reported by Marques *et al.* (2011) (21,4 kJ·g⁻¹). Analogous results for *E. arborea* were in the 19,9-22,1 kJ·g⁻¹ range, in excellent agreement with those reported by Zabaniotou *et al.* (2000) (20,58 kJ·g⁻¹) and Tihay *et al.* (2009) (21,4 kJ·g⁻¹) and somewhat higher than those reported by Barmpoutis *et al.* (2015) (19,95 kJ·g⁻¹).

Whole enthalpy change values from thermal analysis were around 18,04 kJ·g⁻¹ and 18,63 kJ·g⁻¹ for *C. ladanifer* and *E. arborea*, respectively. These values can be assigned to low heating values (LHV), provided that they would be in good agreement with those expected from the holocellulose and lignin net calorific values (ca. 17 kJ·g⁻¹ and ca. 21 kJ·g⁻¹, respectively (Energy research Centre of the Netherlands 2012)) and the percentages reported in Table 2. In fact, the value reported in the literature for the LHV of *C. ladanifer* is 17,9 kJ·g⁻¹ (Martínez *et al.* 2000), very close to the one reported herein.

The ash values obtained for randomly-chosen specimens of *C. ladanifer* according to UNE-EN ISO 18122:2015 (International Organization for Standardization 2015) testing standard were lower than those referred by Ferro *et al.* (2015) (3,0-3,2%) and Marques *et al.* (2011) (whole plant 3,1%; wood 0,8%), determined according to earlier EN norms, and were in agreement with those informed by Martínez *et al.* (2000) (2,3%). For *E. arborea*, results presented in this study were lower than those reported by Dimitrakopoulos and Panov (2001) (2,5% for leaves and 1,6% branches), Doat *et al.* (1981) (2,4%) and Boubaker *et al.* (2004) (3,5%).

Regarding the ash content broken down for each of the fractions, the highest value was obtained for stem bark (around 6,0%), thus identifying this fraction as the one which compromises the use of these shrubs as fuelwood.

In terms of the requirements of ISO 17225-2:2014 (International Organization for Standardization 2014) for ash content of pellets (EN*plus*-B class) and in view of Table 7, *C. ladanifer* stems with a diameter of 1,9 cm would be non-compliant, while those with diameters over 3,4 cm would be acceptable. Consequently, we propose this minimum barked diameter to produce pellets of EN*plus*-B class. The barked diameter value proposed for *E. arborea* is entirely coincident with that suggested by Barboutis and Lykidis (2014) following the EN 14961-2 norm.

Table 7. Minimum barked diameter to meet the requirements of ISO 17225-2:2014 norm (International Organization for Standardization 2014) for ash content of pellets and associated HHV values.

	Diameter (cm)	Ash (%)	EN class	HHV (kJ·g ⁻¹)
C. ladanifer	3,40	1,9	EN <i>plus</i> B	19,2
E. arborea	2,80	1,5	ENplus B	19,9

CONCLUSIONS

One of the requirements of current European standards concerning biofuels in the form of pellets for their use in rural district heating is the ash percentage maximum, limited to 2%. Ash content is significantly influenced by the bark and foliage percentages of the plants to be used as fuel. Both shrub species under study, *C. ladanifer* and *E. arborea*, yielded HHV values that met the requirements established in the regulations for their use as fuel. However, only the ash contents for *E. arborea* were compliant without ambiguity. In the case of *C. ladanifer*, biomass ash percentage was in the upper limit of the normative and this would be a problem for its acceptance as fuelwood. To ensure its adequacy, only old specimens (with stem diameters ranging from 2 to 4,8 cm) should be harvested, avoid foliage.

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