

Biomass fuel quality from Eucalyptus species in short rotation systems

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Abstract

Using biomass of forest origin to obtain solid, liquid, and gaseous fuels has demonstrated its potential both at an experimental level and in commercial situations. Where the composition of the biomass used affects the quality of the fuel produced, for example, in thermochemical processes; therefore, it is relevant to know the properties of the different biomass fractions of forest energy crops derived from the different species of *Eucalyptus*. This framework evaluated the energetic parameters of *Eucalyptus benthamii*, *Eucalyptus dunzii*, and *Eucalyptus grandis* planted at densities of 2220, 3330, 4440, and 6660 trees per hectare and evaluated 56 months after planting. In the wood of the stump, the essential density of the wood, the heating value, and the ash content were determined, with which the fuel value index was calculated. The wood, bark, and leaves and their elemental chemical composition and heating value were evaluated. These results were contrasted by analyzing the variance between species and plantation densities. In addition, models were developed and evaluated to estimate the heating value based on each biomass type's chemical composition. The results showed similarities between the biomass of different *Eucalyptus* species, the absence of effects due to planting density, and that the carbon, oxygen, and ash contents are essential for more excellent calorific value. The biomass of all species have an interesting potential for pyrolysis and gasification processes, however *E. grandis* is the species that combines the best results. The prediction models for the heating value of the different biomass fractions have an attractive precision based on the elements above.

Introduction

In the context of reducing greenhouse gas emissions, it is always interesting to explore the potential of different types of biomass of agricultural or forestry origin. Forest biomass presents an almost neutral CO₂ balance, uses marginal or unsuitable soils for agriculture, and produces high yields (wood and logging residues) per unit of time and surface. In forest biomass, it is known that the growth rates and heating content of the different types of forest biomass determine the energy yield per unit of area and time. However, it has yet to be well-known how the quality of biomass affects the yields in thermomechanical conversion processes (e.g., gasification, pyrolysis, and torrefaction) of lignocellulosic materials [1]. Technologies that present energy conversion efficiencies are higher than biological conversions due to their high destructive capacity of organic compounds, short conversion times, and exothermic reaction stages [2]. Furthermore, some pyrolysis products can be easily stored and transported to their final destination compared to fermentation processes [3]. Both biological and thermochemical conversions attempt to transform low-energy carbonaceous materials into different fuels. Biological processes have yet to show relevant efficiencies in converting lignocellulosic materials from *Eucalyptus* crops. Therefore, thermochemical conversions are proposed as the most promising to synthesize fuels from *Eucalyptus* wood [4]. For energy conversion processes, variables such as density, heating value (dependent on moisture content), fixed carbon/volatile ratio, ash content, and hydrogen/oxygen content are of interest [5, 6]. Lignocellulosic biomass has relatively high carbon, volatile, and fixed carbon values at the same time as low oxygen and hydrogen contents compared to other materials of plant origin [7]. The carbon content has a positive relationship with the heating content of the biomass, and the oxygen and hydrogen contents have a negative relationship with the heating content since the energy contained in the carbon-hydrogen and carbon-oxygen bonds are lower than the carbon-carbon bond [2]. These authors defined that hydrogen and oxygen content relationships with carbon in lignocellulosic biomass have medium and high reactivity levels in thermal conversion processes. In these thermal processes, the volatile fraction released in pyrolysis (biomass is subjected to high temperature in the absence of air) is composed of different gases (CH₄, CO, H₂, CO₂, and H₂O). If the gaseous fraction of pyrolysis is high, ignition is facilitated by improving the combustion process, and the energy released is fed back to the pyrolysis process [8, 9]. In turn, the content of this fraction is positively and negatively correlated with the H/C and O/C ratios, respectively. A low remaining carbon fraction - after the release of volatile gases - (excluding moisture and ash) indicates high reactivity, greater ease of ignition, and shorter residence time to complete combustion. The remaining carbon fraction comprises the source material and carbonaceous residues formed during pyrolysis [6]. For *Eucalyptus* biomass these values are in ranges of 80–86% and 14–19%, respectively [10, 11]. These fractions indicate biomass's ease of igniting, gasifying, or oxidizing, depending on the process used [5]. The waste from the thermal processes for obtaining energy corresponds to the ash fraction and, depending on its content, can determine a reduction in the available energy content. The energy content of biomass - expressed in gigajoules (GJ) per hectare - depends on productivity since the density of wood and heating value slightly vary with silvicultural aspects such as species and plantation density [12]. Foekel [13] indicated that the contents of lignin, fixed carbon, and fatty extractives would hierarchically give the most significant effects on the heating value of biomass. Furthermore, this author indicates that lignin presents around 60% elemental carbon, with a lower heating value of 24 to 26 MJ.kg⁻¹. A variable considered by some authors to analyze the usefulness of biomass as a raw material for energy by estimating the fuel value index that considers density, heating value, and ash content [14–16]. However, for some domestic uses, the ease of ignition and the capacity to produce embers are the most critical aspects, downplaying the importance of ashes [17].

Biomass with high hydrogen and oxygen content have a low energy content [6]. In the biomass of *Eucalyptus* and pine trees, the carbon, oxygen, and hydrogen contents are in the order of 42–50%, 38–52%, and 6–8%, respectively, and the concentrations of nitrogen and sulfur

are very low [7, 10, 18]. The oxidation of biomass by complete combustion transforms carbon, hydrogen, and oxygen into CO₂, H₂O, and heat energy [19]. When the carbon contents are high, gasification is favored, and a greater volume of fuel gases and an increase in the process temperature are obtained [20]. Pérez et al. [21] evaluated the gasification efficiency of different forest species and found that it increases by increasing the carbon/oxygen ratio due to a lower reaction temperature, which favors the formation of CH₄. Bhatti and Chouhan [22] evaluated the gasification efficiency of different forest species and found that it increases by increasing the carbon/oxygen ratio due to a lower reaction temperature, which favors the formation of CH₄. Callén et al. [23] agrees with these results by indicating that biomass with a high content of volatiles, carbon, fixed carbon, and hydrogen favor the formation of CO, and with high contents of ash and sulfur, they would form C₂H₄.

Heating value is evaluated in a standard way using a bomb calorimeter, although it can be estimated with models or indirect techniques (e.g., NIR spectroscopy) if it is complemented with an ultimate analysis of the biomass [24]. These authors developed models based on ultimate analysis of fuels, although some authors highlight the convenience of using the proximate analysis parameters to estimate the heating value of biomass [25–27]. Although there are models for estimating heating power based on various chemical characteristics of different types of biomass, models have been reported [28]. These equations could obtain imprecise results if they are extrapolated [29].

Based on the above, this work analyzed the hypotheses: i) The species and planting densities of *Eucalyptus* differ in the composition and structure of their biomass fractions, altering their combustion properties. Changes in species and density of *Eucalyptus* plantations modify the composition and structure of their wood and biomass fractions, altering their combustion properties; ii) the calorific value of the biomass fractions of these plantations can be estimated with a high degree of precision with a model based on the chemical composition of each biomass.

The general objective of this study was to evaluate the energy potential of *Eucalyptus* species with high planting densities. The specific objectives were: i) analyze the thermochemical parameters of the biomass in terms of the fuel properties of different combinations of species and planting densities ii) fitting equations for estimating the higher heating value of different biomass fractions based on the ultimate and proximate analysis.

Methodology

Study Area

In the spring of 2010 (October and November), two tests were installed in CONEAT soil groups 7 and 9 [30] in the northern and coastal areas of Uruguay, respectively. The sites studied are located at 32°13'30" S, 55° 54'40" W and 32°24'05" S and 57°31'02" W. The soils used were ochric Luvisols/Acrisols and Planasols in Tacuarembó and Ochric District Argisols from Paysandú, respectively [31] (Table S1, Supplementary material). The climate of this area corresponds to Cfa according to the Köppen-Geiger classification [32] with an average monthly temperature of 17 and 19 °C [33] and annual rainfall of 1430 and 1297 mm during the site evaluation period of Tacuarembó and Paysandú, respectively.

Experimental design

E. benthamii, *E. dunnii* and *E. grandis* were the *Eucalyptus* species evaluated, whose origins are APS Pinhão (Paraná State, Brazil), Undera (Moleton West Coffs Harbour, Australia) and INIA seed orchard (Uruguay), respectively. Each species was planted at four different initial densities: 2220, 3330, 4440, and 6660 trees ha⁻¹ with a distance between plants of 0.5, 0.75, 1, and 1.5 m. A distance between rows of 3 m was used in all cases. Each plot was composed of 6 rows of 25 plants, each with an average surface area of 706, 468, 350, and 234 m².

The layout of the plots in the field was divided plots. The main plot corresponds to the species, and the secondary plot corresponds to the planting density in a complete randomized block design, with three repetitions, totaling 36 plots. The tillage prior to planting was carried out using a subsoiler at a depth of approximately 40 cm, plus two eccentric tillages. Planting was manual with a single dose of different fertilizers depending on the study area: 150 kg ha⁻¹ of 18/46/0 (N, P, K) in Tacuarembó and 180 kg ha⁻¹ of 14/ 12/30 (N, P, K) in Paysandú; plus 6% S, 0.2% B, and 0.3% Zn.

Biomass sampling

At 56 months (2015), an inventory of all the trees in each trial was carried out to establish diameter classes and identify three trees with low, medium, and high diameter values at breast height in each plot. After felling these trees, samples of wood disks with bark at the base, 50% and 75% of the commercial height, and samples of ~ 200 g of leaves from the middle part of the crown were extracted. The wood was separated from the bark in each disc, dried at 60°C, and ground in a processor (RETSCH mill, model SR 200, Haan, Germany) to a particle

size less than mesh number 40–60 (between 0.25 and 0.4 mm). The same procedure was applied to the leaf samples. Drying was carried out in an open circulation oven with forced ventilation (Thermo Scientific Waltham, Massachusetts, USA) a 60 °C until a constant weight was reached, and the dry matter content of each fraction was estimated, preventing nitrogen volatilization. The moisture content on a wet basis (H, %) of the three fractions after drying was 9–10%. The sampling procedure was part of a set of evaluations to determine other variables of interest. [34].

Laboratory determinations

Higher heating value of biomass fractions

With the result of the grinding of each of the fractions of each tree, the dry basis higher heating value (*HHV*, MJ Kg⁻¹) of each fraction was measured according to the PEC.FORES.017 procedure based on the DIN 519001: 2000 [35] and 51900 standards. 2: 2003 [36]. For this determination, a composite sample obtained from each disc was made, considering the relative surface of each one. The average of each plot was estimated with the values of each tree's biomass fraction.

Ultimate and Proximate Analysis of biomass fractions

The ultimate analysis (*UA*, %) of the different fractions of each tree was expressed as a percentage of carbon (*C*), hydrogen (*H*), oxygen (*O*), nitrogen (*N*), and sulfur (*S*). In addition, the proximate analysis (*PA*, %) was estimated, composed of fixed carbon (*FC*), volatile material (*VM*), and ashes (*A*). The wood fraction considered the relative area of each studied tree disc. The mean values of the plot's biomass fractions were calculated from each tree's values. *C*, *H*, *N*, and *S* values were determined with the Thermo flash 2000 equipment, and *O* was determined as the remaining difference at 100%. The proximate analysis (*PA*) components were determined according to the NBR 8112 standard.

Basic apparent density of wood

Once the bark-free wood discs were extracted, they were immediately stored in closed nylon bags to maintain moisture saturation and measure the green volume by water displacement. The determination of each disc's basic apparent density (*Wd*, g cm⁻³) was based on this volume and the dry weight value. The dry weight was determined after the samples were dried in an oven a 100 °C ± 3 until a constant weight was obtained. The density value of each tree was determined as follow [37]:

$$Wdt = \frac{(AB \times Wdb + AB50 \times Wdb50 + AB75 \times Wdb75)}{(AB + A50 + A75)}$$

Where *Wdt* is the wood density of the tree, *Wdb*, *Wd50*, and *Wd75* are the densities of each disk, and *AB*, *A50*, and *A75* are the areas of each disk at heights 0, 50, and 75% of the commercial height, respectively. The average weighted basic density (*Wdw*) value of the plot was obtained from the individual values of each tree.

Fuel value index of the wood

With the *HHV* value, the lower calorific value (*LHV*, KJ Kg⁻¹) was calculated based on the standard (UNE Normalización Española 2018) [38] as follow:

$$LHV = HHV - 212.2 \times H - 0.8 \times (O + N) \times (1 - 0.01 \times H) - 24.43 \times H$$

The *LHV*, *Wdw* and *A* values of each wood sample were used to calculate the Fuel Value Index (*FVI*) of a composite sample of each tree, considering the relative area of each disc. This index allows biofuels (in this case wood) to be ranked so that the parameters that have positive effects are divided by those that have negative effects on it as follow:

$$FVI = \frac{LHV}{1000} \times \frac{Wdw}{A}$$

The average *FVI* value of the plot was obtained from the individual values of each tree.

Statistical analysis

The analysis of variance was carried out based on the following model:

$$Y_{ijk} = \mu + \tau_i + \gamma_k + \beta_j + \tau\gamma_{ik} + \varepsilon_{ijk}$$

Where Y_{ijk} is the variable measured in the plot for species i and density k , in block j ; μ is the general average of all observations; τ_i is the effect i of the species; γ_k is the effect k of the density; β_j is the effect j of the block; $\tau\gamma_{ik}$ is the interaction of the species and density (fixed effect); and ϵ_{ijk} is the experimental error associated with each observation, being independent and with a normal distribution of mean 0 and variance σ^2 .

After verification of the assumptions of normality of the residuals and homogeneity of variances (carried out with the Shapiro-Wilk and Brown-Forsythe tests, respectively), the analysis of variances was carried out using the F test of the following variables: *Wdw*, *LHV*, *FVI*, *C*, *H*, *O*, *N*, *S*, *O/C*, *H/C*, *FC*, *A* and *VM*. The effect of the species was contrasted with its interaction with the block effect and the effect of plantation density, and the interaction with the species was contrasted with the mean square of the error. With the variables *LHV*, *Wdw*, and *A*, the partial correlation coefficients with the *FVI* were calculated, and with the components of *UA*, *PA*, *O/C* and *H/C* the simple correlations with the *HHV* were calculated.

Jointly considering the species, plantation densities, and sites, models were fitted with the 144 *UA* and *PA* components observations to estimate the *HHV* of the bark, leaves, and wood fractions. The models with the highest precision were selected using the criteria of $R^2_{adjusted}$, *BIAS*, *RMSE*, *MAE*, and their proportions concerning the mean of the *HHV* measured in each fraction, the distribution of studentized errors, and the distribution of estimated versus measured values (Fig. 4 and Figures S8 to S10, Supplementary material).

Results

Biomass characterization

Energy content

The analysis of the *LHV* values of the bark and leaf fractions showed the highest levels in *E. benthamii* and *E. dunii* in both sites, independent of the plantation density (Table 1). In the wood case, the species did not affect the *Hnv* in both sites and had a lower variability than other evaluated tree fractions.

Table 1

Mean *LHV* values ($\pm$ SE) of the wood, bark, and leaves fractions for the species and planting densities were evaluated at both sites at 56 months age. Different capital letters indicate significant differences between species and different lowercase letters indicate significant differences between planting densities, by means of the Tukey test posteriori of the ANOVA, for each site, with a probability level of 5%.

Site	Species	Planting density (trees ha ⁻¹)	Bark	Leaves	Wood
			-----KJ Kg ⁻¹ -----		
Tacuarembó	<i>E. benthamii</i>	2220	17514 (171) Aa	22558 (177) Ba	18925 (36) Aa
		3330	17455 (179) Aa	22574 (223) Ba	18786 (34) Aa
		4440	17486 (291) Aa	22524 (206) Ba	18709 (92) Aa
		6660	17513 (127) Aa	21953 (246) Ba	18676 (98) Aa
	<i>E. dunnii</i>	2220	16856 (547) Aa	23332 (160) Aa	18699 (104) Aa
		3330	17074 (115) Aa	23383 (192) Aa	18722 (147) Aa
		4440	17026 (176) Aa	23512 (146) Aa	18687 (181) Aa
		6660	17205 (144) Aa	23399 (215) Aa	18671 (110) Aa
	<i>E. grandis</i>	2220	16166 (73) Ba	21374 (134) Ca	18781 (41) Aa
		3330	16184 (145) Ba	21029 (343) Ca	18924 (238) Aa
		4440	16360 (158) Ba	21258 (129) Ca	18853 (55) Aa
		6660	16376 (39) Ba	21249 (272) Ca	18916 (304) Aa
Paysandú	<i>E. benthamii</i>	2220	16863 (149) Aa	22909 (191) Aa	18690 (79) Aa
		3330	17132 (159) Aa	22401 (216) Aa	18644 (41) Aa
		4440	16971 (67) Aa	22314 (396) Aa	18721 (128) Aa
		6660	16881 (129) Aa	22697 (238) Aa	18646 (171) Aa
	<i>E. dunnii</i>	2220	16608 (147) Aa	23115 (662) Aa	18587 (62) Aa
		3330	16766 (73) Aa	22539 (331) Aa	18413 (94) Aa
		4440	16538 (74) Aa	22386 (262) Aa	18505 (79) Aa
		6660	16435 (368) Aa	22584 (566) Aa	18331 (163) Aa
	<i>E. grandis</i>	2220	16103 (60) Ba	21438 (168) Ba	18742(125) Aa
		3330	15980 (36) Ba	21667 (152) Ba	18791 (24) Aa
		4440	16025 (199) Ba	21364 (357) Ba	18755(156) Aa
		6660	16140 (40) Ba	21482 (118) Ba	18859 (211) Aa

Ultimate and Proximate Analysis

The results of the proximate analysis of the different biomass fractions in the Tacuarembó trial show that plantation density has practically no effect on any of the components (Table 2). In the wood fraction (probably the one with the most significant potential for use), only *E. grandis* is detected as having the lowest *A* content values, although with very similar levels between the three species. The leaves fraction shows the lack of effect of the species in all the components, while the bark fraction shows the greatest variability in the different components. In this case, *E. grandis* has the highest values of *A* and volatiles, while *E. benthamii* registers the highest values of fixed carbon. At the Paysandú site, a similar behavior was observed in that the plantation density does not affect the proximate analysis of the wood and leaf fractions. In that case, *E. dunnii*, higher *A* content values were reached in the mentioned fractions. However, in the bark fraction, a significant interaction was detected between the factors species and plantation density in the contents of volatiles and fixed carbon, but no defined pattern of this interaction was found.

Regarding the proximate analysis, a similar result is obtained in the Tacuarembó trial since the contents of the analyzed elements are not affected by the plantation density (Tables 3a and 3b). *E. grandis* has a higher *O* content in the bark and leaf fractions, while *E. benthamii* and *E. dunnii* have higher *C*, *H*, and *N* contents. On the other hand, the wood of these species has lower *C* contents and very high values. Similar in the rest of the elements analyzed. The *O/C* atomic ratios indicate that *E. dunnii* and *E. grandis* have the highest proportion of *C* in the wood fraction but comparatively the lowest in the bark and leaf fractions (Table 4). The *H/C* atomic ratios are equal between species in the wood and leaf fractions, with *E. benthamii* with the lowest values in the leaf fraction.

Table 2

Mean values ($\pm$ SE) of the *PA* of the bark, leaf, and wood fractions for the species and planting densities evaluated in the two sites at the age of 56 months. Different capital letters indicate significant differences between species, and different lowercase letters indicate significant differences between planting densities using the Tukey posterior test of the ANOVA for each site, with a probability level of 5%.

Sites	Species	Planting density (trees ha ⁻¹)	Bark			Leaves			Wood		
			VM	FC	A	VM	FC	A	VM	CF	A
			-----%-----								
Tacuarembó	<i>E. benthamii</i>	2220	80.8 (0.6) Ba	13.2 (1.1) Aa	6.0 (0.6) Ba	84.1 (0.5) Aa	12.2 (0.5) Aa	3.6 (0.1) Ab	89.1 (0.7) Aa	10.4 (0.7) Aa	0.5 (0.1) ABa
		3330	81.4 (1.1) Ba	12.8 (1.0) Aa	5.7 (0.2) Ba	85.3 (0.3) Aa	10.8 (0.4) Aa	3.8 (0.1) Aab	89.3 (0.2) Aa	10.3 (0.2) Aa	0.5 (0.04) ABa
		4440	81.4 (1.8) Ba	12.3 (1.8) Aa	6.3 (0.1) Ba	84.4 (0.9) Aa	11.3 (0.7) Aa	4.4 (0.2) Aa	88.6 (1.1) Aa	10.9 (1.1) Aa	0.5 (0.1) ABa
		6660	79.7 (0.5) Ba	14.5 (0.4) Aa	5.8 (0.3) Ba	84.2 (1.2) Aa	11.1 (1.3) Aa	4.7 (0.2) Aa	89.4 (0.1) Aa	10.1 (0.1) Aa	0.4 (0.1) ABa
	<i>E. dun nii</i>	2220	84.0 (1.0) Aa	9.5 (0.9) Ba	6.5 (0.7) ABa	83.6 (0.5) Aa	11.7 (0.5) Aa	4.7 (0.3) Ab	89.9 (0.6) Aa	9.5 (0.6) Aa	0.7 (0.04) Aa
		3330	84.5 (0.4) Aa	8.2 (0.2) Ba	7.3 (0.4) ABa	83.9 (0.4) Aa	10.9 (0.3) Aa	5.2 (0.6) Aab	89.5 (0.1) Aa	9.8 (0.1) Aa	0.8 (0.1) Aa
		4440	84.1 (0.7) Aa	9.4 (0.3) Ba	6.5 (0.4) ABa	84.6 (1.5) Aa	10.3 (1.4) Aa	5.1 (0.2) Aa	89.7 (0.5) Aa	9.7 (0.6) Aa	0.7 (0.1) Aa
		6660	84.5 (1.0) Aa	9.7 (1.0) Ba	5.8 (0.4) ABa	83.8 (0.5) Aa	11.1 (0.5) Aa	5.1 (0.2) Aa	89.3 (0.3) Aa	10.1 (0.3) Aa	0.6 (0.03) Aa
	<i>E. grandis</i>	2220	83.1 (0.8) Aa	9.3 (0.7) Ba	5.8 (0.2) Aa	83.3 (1.2) Aa	12.4 (1.2) Aa	4.2 (0.1) Ab	89.8 (1.1) Aa	9.8 (1.1) Aa	0.4 (0.04) Ba
		3330	84.7 (0.7) Aa	7.8 (0.5) Ba	7.6 (0.5) Aa	83.3 (0.2) Aa	11.9 (0.03) Aa	4.7 (0.1) Aab	89.4 (0.9) Aa	10.2 (0.8) Aa	0.5 (0.04) Ba
		4440	83.8 (1.5) Aa	9.4 (1.8) Ba	6.8 (0.3) Aa	82.8 (1.2) Aa	12.4 (1.1) Aa	4.8 (0.02) Aa	90.1 (0.2) Aa	9.4 (0.2) Aa	0.5 (0.02) Ba
		6660	84.2 (0.9) Aa	9.2 (1.4) Ba	6.7 (0.5) Aa	82.9 (0.6) Aa	11.9 (0.6) Aa	5.2 (0.1) Aa	90.1 (0.7) Aa	9.4 (0.7) Aa	0.5 (0.03) Ba
Paysandú	<i>E. benthamii</i>	2220	82.5 (1.6) cd	10.2 (1.5) bc	7.3 (0.1) Aa	85.3 (1.0) Aa	9.1 (1.0) Aa	5.6 (0.1) Ba	89.4 (0.5) Aa	10.0 (0.6) Aa	0.6 (0.1) Ba
		3330	81.0 (0.3) d	13.0 (0.6) a	5.9 (0.5) Aa	83.2 (1.1) Aa	11.6 (1.2) Aa	5.2 (0.1) Ba	89.7 (0.3) Aa	9.4 (0.6) Aa	1.0 (0.4) Ba
		4440	84.1 (0.4) abc	10.1(0.6) bc	5.8 (0.2) Aa	83.6 (0.5) Aa	10.2 (0.4) Aa	6.2 (0.6) Ba	89.8 (0.3) Aa	9.7 (0.2) Aa	0.5 (0.02) Ba
		6660	81.9 (0.5) cd	11.6 (0.8) ab	6.5 (0.3) Aa	84.1 (0.2) Aa	10.1 (0.3) Aa	5.8 (0.2) Ba	90.1 (0.03) Aa	9.4 (0.1) Aa	0.6 (0.02) Ba

Sites	Species	Planting density (trees ha ⁻¹)	Bark			Leaves			Wood		
			<i>VM</i>	<i>FC</i>	<i>A</i>	<i>VM</i>	<i>FC</i>	<i>A</i>	<i>VM</i>	<i>CF</i>	<i>A</i>
	<i>E. dunnii</i>	2220	83.8 (0.7) abcd	9.0 (0.7) c	7.3 (0.4) Aa	82.5 (0.6) Aa	11.2 (0.3) Aa	6.3 (0.5) Aa	90.4 (0.4) Aa	8.6 (0.5) Aa	1.0 (0.1) Aa
		3330	86.4 (1.6) a	6.0 (1.3) d	7.6 (0.3) Aa	83.9 (0.8) Aa	9.5 (0.7) Aa	6.6 (0.1) Aa	89.6 (0.3) Aa	9.5 (0.3) Aa	0.9 (0.1) Aa
		4440	83.3 (0.8) bcd	9.5 (1.0) bc	7.2 (0.6) Aa	83.5 (0.8) Aa	9.5 (0.6) Aa	7.0 (0.2) Aa	90.9 (0.4) Aa	8.3 (0.4) Aa	0.9 (0.01) Aa
		6660	83.3 (0.8) bcd	9.4 (0.7) bc	7.3 (0.8) Aa	83.3 (0.2) Aa	9.4 (0.2) Aa	7.4 (0.2) Aa	90.1 (0.2) Aa	9.0 (0.1) Aa	0.9 (0.1) Aa
	<i>E. grandis</i>	2220	86.3 (1.7) ab	6.2 (1.1) d	7.5 (0.6) Aa	84.4 (0.5) Aa	9.8 (0.8) Aa	5.8 (0.4) Ba	89.2 (0.6) Aa	10.3 (0.5) Aa	0.5 (0.1) Ba
		3330	83.2 (0.5) cd	9.4 (0.4) bc	7.5 (0.2) Aa	84.5 (0.7) Aa	9.8 (0.7) Aa	5.7 (0.1) Ba	90.1 (0.8) Aa	9.4 (0.8) Aa	0.6 (0.01) Ba
		4440	85.0 (1.1) abc	8.0 (1.1) cd	7.0 (0.8) Aa	83.8 (0.2) Aa	10.6 (0.1) Aa	5.6 (0.1) Ba	90.8 (0.8) Aa	8.7 (0.7) Aa	0.5 (0.1) Ba
		6660	84.9 (0.6) abc	8.1 (0.8) cd	7.0 (0.7) Aa	84.4 (1.5) Aa	9.5 (1.4) Aa	6.2 (0.3) Ba	91.6 (1.4) Aa	7.8 (1.4) Aa	0.6 (0.1) Aa

Table 3

a Mean values ($\pm$ SE) of the UA of the bark, leaf, and wood fractions for the species and plantation densities evaluated in the two sites at the age of 56 months. Different capital letters indicate significant differences between species, and different lowercase letters indicate significant differences between planting densities using the Tukey posterior test of the ANOVA for each site, with a probability level of 5%.

Sites	Species	Planting density (trees ha ⁻¹)	Bark					Leaves				
			<i>C</i>	<i>H</i>	<i>O</i>	<i>N</i>	<i>S</i>	<i>C</i>	<i>H</i>	<i>O</i>	<i>N</i>	<i>S</i>
-----%----- -----												
Tacuarembó	<i>E. benthamii</i>	2220	49.1 (0.4) Aa	4.6 (0.1) Ba	39.8 (0.8) Ba	0.5 (0.03) Aa	0.01 (0.0) Aa	56.3 (0.4) Ba	5.8 (0.1) Aa	31.2 (0.5) Ba	2.9 (0.1) Aa	0.11 (0.03) Aa
		3330	48.7 (0.4) Aa	4.1 (0.1) Ba	40.9 (0.4) Ba	0.5 (0.03) Aa	0.01 (0.0) Aa	57.0 (0.7) Ba	6.0 (0.03) Aa	29.9 (0.4) Ba	3.2 (0.3) Aa	0.17 (0.02) Aa
		4440	48.9 (0.8) Aa	4.5 (0.03) Ba	39.8 (0.8) Ba	0.6 (0.03) Aa	0.01 (0.0) Aa	56.6 (0.5) Ba	5.8 (0.2) Aa	30.2 (0.5) Ba	2.8 (0.2) Aa	0.19 (0.1) Aa
		6660	48.9 (0.5) Aa	4.5 (0.1) Ba	40.3 (0.6) Ba	0.5 (0.0) Aa	0.01 (0.0) Aa	55.1 (0.4) Ba	5.9 (0.1) Aa	31.5 (0.5) Ba	2.7 (0.1) Aa	0.12 (0.02) Aa
	<i>E. dun nii</i>	2220	47.0 (1.3) Ba	4.8 (0.03) Aa	41.3 (0.7) Ba	0.4 (0.0) Ba	0.01 (0.0) Aa	58.2 (0.5) Aa	6.2 (0.1) Aa	28.0 (0.2) Ca	2.6 (0.3) Aa	0.23 (0.2) Ba
		3330	47.9 (0.3) Ba	4.7 (0.03) Aa	39.7 (0.4) Ba	0.4 (0.03) Ba	0.01 (0.0) Aa	57.6 (0.2) Aa	5.9 (0.1) Aa	28.0 (0.4) Ca	3.2 (0.3) Aa	0.06 (0.01) Ba
		4440	47.6 (0.4) Ba	4.6 (0.1) Aa	40.9 (0.4) Ba	0.4 (0.0) Ba	0.01 (0.0) Aa	58.1 (0.6) Aa	6.2 (0.1) Aa	27.9 (0.9) Ca	2.6 (0.1) Aa	0.08 (0.0) Ba
		6660	47.7 (0.1) Ba	4.6 (0.1) Aa	41.5 (0.3) Ba	0.4 (0.03) Ba	0.01 (0.0) Aa	58.0 (0.4) Aa	6.2 (0.03) Aa	27.9 (0.5) Ca	2.7 (0.1) Aa	0.10 (0.0) Ba
	<i>E. grandis</i>	2220	46.0 (0.1) Ca	4.3 (0.1) Ba	41.6 (0.2) Aa	0.4 (0.0) Ba	0.01 (0.0) Aa	54.7 (0.5) Ca	5.4 (0.1) Ba	32.8 (0.6) Aa	2.8 (0.1) Aa	0.12 (0.01) ABa
		3330	45.9 (0.5) Ca	4.4 (0.2) Ba	41.9 (0.1) Aa	0.4 (0.0) Ba	0.01 (0.0) Aa	54.3 (0.3) Ca	5.5 (0.03) Ba	32.9 (0.3) Aa	2.5 (0.1) Aa	0.10 (0.01) ABa
		4440	46.3 (0.3) Ca	4.4 (0.2) Ba	42.0 (0.2) Aa	0.4 (0.03) Ba	0.01 (0.0) Aa	53.7 (0.4) Ca	5.4 (0.2) Ba	33.4 (0.8) Aa	2.6 (0.2) Aa	0.10 (0.01) ABa
		6660	46.1 (0.2) Ca	4.4 (0.03) Ba	42.4 (0.4) Aa	0.4 (0.0) Ba	0.01 (0.0) Aa	54.0 (0.2) Ca	5.5 (0.1) Ba	32.8 (0.6) Aa	2.4 (0.4) Aa	0.11 (0.01) ABa
Paysandú	<i>E. benthamii</i>	2220	47.8 (0.5) Aa	4.5 (0.03) Aa	40.0 (0.6) Ba	0.4 (0.0) Aa	0.01 (0.0) Aa	57.3 (0.1) Aa	6.0 (0.1) Aa	27.8 (0.3) Ba	3.2 (0.1) Aa	0.13 (0.03) Aa
		3330	48.3 (0.2) Aa	4.7 (0.2) Aa	40.7 (0.2) Ba	0.4 (0.0) Aa	0.01 (0.0) Aa	56.7 (0.4) Aa	5.7 (0.1) Aa	29.6 (0.2) Ba	2.6 (0.2) Aa	0.12 (0.02) Aa
		4440	48.0 (0.2) Aa	4.7 (0.2) Aa	41.1 (0.1) Ba	0.4 (0.0) Aa	0.01 (0.0) Aa	56.0 (0.8) Aa	5.6 (0.1) Aa	29.4 (0.9) Ba	2.6 (0.3) Aa	0.11 (0.01) Aa
		6660	47.8 (0.4) Aa	4.8 (0.1) Aa	40.5 (0.1) Ba	0.4 (0.0) Aa	0.01 (0.0) Aa	57.4 (0.6) Aa	5.9 (0.03) Aa	28.1 (0.7) Ba	2.7 (0.3) Aa	0.12 (0.02) Aa

Sites	Species	Planting density (trees ha ⁻¹)	Bark					Leaves				
			<i>C</i>	<i>H</i>	<i>O</i>	<i>N</i>	<i>S</i>	<i>C</i>	<i>H</i>	<i>O</i>	<i>N</i>	<i>S</i>
	<i>E. dunnii</i>	2220	47.1 (0.6) Ba	4.8 (0.0) Aa	40.4 (0.4) Ba	0.4 (0.0) Aa	0.01 (0.0) Aa	57.3 (0.2) Aa	5.9 (0.1) Aa	27.8 (0.1) Ba	2.5 (0.2) ABa	0.09 (0.02) Ba
		3330	47.4 (0.2) Ba	4.8 (0.03) Aa	39.8 (0.4) Ba	0.4 (0.0) Aa	0.01 (0.0) Aa	57.2 (0.7) Aa	5.9 (0.1) Aa	27.7 (1.0) Ba	2.5 (0.03) ABa	0.08 (0.0) Ba
		4440	46.8 (0.2) Ba	4.8 (0.1) Aa	40.8 (0.3) Ba	0.4 (0.0) Aa	0.01 (0.0) Aa	56.3 (0.1) Aa	5.8 (0.03) Aa	28.9 (0.04) Ba	2.0 (0.2) ABa	0.07 (0.01) Ba
		6660	46.6 (0.9) Ba	4.6 (0.1) Aa	41.1 (0.3) Ba	0.4 (0.0) Aa	0.01 (0.0) Aa	56.6 (1.1) Aa	5.8 (0.1) Aa	28.0 (1.4) Ba	2.3 (0.2) ABa	0.07 (0.01) Ba
	<i>E. grandis</i>	2220	46.6 (0.03) Ba	4.7 (0.1) Aa	40.9 (0.7) Aa	0.4 (0.0) Aa	0.01 (0.0) Aa	54.1 (0.8) Ba	5.6 (0.2) Aa	32.2 (0.6) Aa	2.3 (0.1) Ba	0.08 (0.01) Ba
		3330	46.2 (0.3) Ba	4.7 (0.2) Aa	41.2 (0.3) Aa	0.4 (0.0) Aa	0.01 (0.0) Aa	54.2 (0.7) Ba	5.7 (0.1) Aa	32.1 (0.9) Aa	2.2 (0.1) Ba	0.08 (0.01) Ba
		4440	46.2 (0.4) Ba	4.8 (0.1) Aa	41.6 (0.5) Aa	0.4 (0.0) Aa	0.01 (0.0) Aa	54.0 (0.7) Ba	5.5 (0.1) Aa	32.6 (0.8) Aa	2.2 (0.1) Ba	0.07 (0.0) Ba
		6660	46.0 (0.4) Ba	4.6 (0.2) Aa	42.0 (0.4) Aa	0.4 (0.0) Aa	0.01 (0.0) Aa	54.6 (0.3) Ba	5.6 (0.1) Aa	31.1 (0.7) Aa	2.4 (0.03) Ba	0.08 (0.01) Ba

Table 3

b Mean values ($\pm$ SE) of the *UA* of the bark, leaf, and wood fractions for the species and plantation densities evaluated in the two sites at the age of 56 months. Different capital letters indicate significant differences between species and different lowercase letters indicate significant differences between planting densities, by means of the Tukey test *posteriori* of the ANOVA, for each site, with a probability level of 5%.

Sites	Species	Planting density (trees ha ⁻¹)	Wood				
			<i>C</i>	<i>H</i>	<i>O</i>	<i>N</i>	<i>S</i>
			-----%				
Tacuarembó	<i>E. benthamii</i>	2220	51.0 (0.3) Ba	4.8 (0.03) Aa	43.5 (0.4) Aa	0.2 (0.0) Aa	0.01 (0.0) Aa
		3330	50.7 (0.4) Ba	4.7 (0.1) Aa	44.0 (0.4) Aa	0.2 (0.0) Aa	0.01 (0.0) Aa
		4440	51.0 (0.7) Ba	4.8 (0.1) Aa	43.5 (0.7) Aa	0.2 (0.06) Aa	0.01 (0.0) Aa
		6660	50.6 (0.7) Ba	5.0 (0.1) Aa	43.8 (0.7) Aa	0.2 (0.03) Aa	0.01 (0.0) Aa
	<i>E. dunnii</i>	2220	51.0 (0.6) Ba	4.8 (0.03) Aa	43.4 (0.5) Aa	0.1 (0.03) Aa	0.01 (0.0) Aa
		3330	50.6 (0.5) Ba	4.8 (0.2) Aa	43.6 (0.3) Aa	0.2 (0.0) Aa	0.01 (0.0) Aa
		4440	50.6 (0.6) Ba	4.8 (0.1) Aa	43.8 (0.5) Aa	0.2 (0.03) Aa	0.01 (0.0) Aa
		6660	51.1 (0.9) Ba	4.9 (0.1) Aa	43.2 (0.8) Aa	0.2 (0.0) Aa	0.01 (0.0) Aa
	<i>E. grandis</i>	2220	51.3 (0.7) Aa	4.8 (0.1) Aa	43.2 (0.7) Aa	0.2 (0.03) Aa	0.01 (0.0) Aa
		3330	51.7 (0.1) Aa	4.9 (0.03) Aa	42.8 (0.1) Aa	0.2 (0.03) Aa	0.01 (0.0) Aa
		4440	51.3 (0.5) Aa	4.8 (0.1) Aa	43.2 (0.5) Aa	0.2 (0.03) Aa	0.01 (0.0) Aa
		6660	51.5 (0.9) Aa	4.9 (0.1) Aa	42.9 (0.9) Aa	0.2 (0.0) Aa	0.01 (0.0) Aa
Paysandú	<i>E. benthamii</i>	2220	49.8 (0.1) Aa	5.0 (0.1) Aa	44.4 (0.2) Aa	0.1 (0.03) Aa	0.01 (0.0) Aa
		3330	49.9 (0.0) Aa	5.0 (0.03) Aa	44.0 (0.4) Aa	0.2 (0.03) Aa	0.01 (0.0) Aa
		4440	50.0 (0.1) Aa	5.1 (0.1) Aa	44.3 (0.4) Aa	0.1 (0.0) Aa	0.01 (0.0) Aa
		6660	50.1 (0.1) Aa	5.0 (0.2) Aa	44.2 (0.2) Aa	0.1 (0.03) Aa	0.01 (0.0) Aa
	<i>E. dunnii</i>	2220	49.3 (0.2) Ba	4.9 (0.1) Aa	44.7 (0.2) Aa	0.1 (0.0) Aa	0.01 (0.0) Aa
		3330	49.8 (0.4) Ba	5.0 (0.03) Aa	44.0 (0.4) Aa	0.1 (0.03) Aa	0.01 (0.0) Aa
		4440	49.4 (0.3) Ba	4.9 (0.1) Aa	44.8 (0.3) Aa	0.1 (0.0) Aa	0.01 (0.0) Aa
		6660	47.3 (1.6) Ba	5.1 (0.2) Aa	46.6 (1.3) Aa	0.1 (0.0) Aa	0.01 (0.0) Aa
	<i>E. grandis</i>	2220	50.1 (0.2) Aa	4.9 (0.03) Aa	44.4 (0.1) Aa	0.1 (0.0) Aa	0.01 (0.0) Aa
		3330	50.1 (0.2) Aa	4.8 (0.1) Aa	44.4 (0.2) Aa	0.1 (0.03) Aa	0.01 (0.0) Aa
		4440	49.9 (0.1) Aa	4.9 (0.1) Aa	44.6 (0.1) Aa	0.1 (0.0) Aa	0.01 (0.0) Aa
		6660	49.9 (0.1) Aa	4.9 (0.03) Aa	44.5 (0.1) Aa	0.1 (0.0) Aa	0.01 (0.0) Aa

Table 4

Values of the *O/C* and *H/C* atomic ratios ($\pm$ S.E.) of the biomass fractions for all species and planting densities in both sites at the age of 56 months. Different capital letters indicate significant differences between species and different lowercase letters indicate significant differences between planting densities, by means of the Tukey test *posteriori* of the ANOVA, for each site, with a probability level of 5%.

Site	Species	Planting density (trees ha ⁻¹)	Bark		Leaves		Wood	
			<i>O/C</i>	<i>H/C</i>	<i>O/C</i>	<i>H/C</i>	<i>O/C</i>	<i>H/C</i>
Tacuarembó	<i>E. benthamii</i>	2220	0.61 (0.04) Ba	1.11 (0.07) Ba	0.42 (0.11) Ba	1.23 (0.10) Aa	0.64 (0.01) Aa	1.11 (0.02) Aa
		3330	0.63 (0.06) Ba	1.01 (0.07) Ba	0.39 (0.19) Ba	1.25 (0.22) Aa	0.65 (0.01) Aa	1.10 (0.03) Aa
		4440	0.61 (0.03) Ba	1.09 (0.05) Ba	0.40 (0.23) Ba	1.23 (0.36) Aa	0.64 (0.001) Aa	1.12 (0.03) Aa
		6660	0.62 (0.04) Ba	1.10 (0.07) Ba	0.43 (0.06) Ba	1.28 (0.07) Aa	0.65 (0.003) Aa	1.17 (0.02) Aa
	<i>E. dunnii</i>	2220	0.66 (0.07) Ba	1.23 (0.02) Aa	0.36 (0.02) Ca	1.27 (0.08) Aa	0.64 (0.02) ABa	1.13 (0.05) Aa
		3330	0.62 (0.02) Ba	1.16 (0.03) Aa	0.36 (0.11) Ca	1.23 (0.11) Aa	0.65 (0.03) ABa	1.12 (0.04) Aa
		4440	0.65 (0.02) Ba	1.16 (0.05) Aa	0.36 (0.15) Ca	1.27 (0.28) Aa	0.65 (0.02) ABa	1.13 (0.04) Aa
		6660	0.65 (0.01) Ba	1.14 (0.03) Aa	0.36 (0.03) Ca	1.27 (0.06) Aa	0.64 (0.01) ABa	1.14 (0.02) Aa
	<i>E. grandis</i>	2220	0.68 (0.01) Aa	1.12 (0.04) ABa	0.45 (0.04) Aa	1.18 (0.06) Aa	0.63 (0.02) Ba	1.12 (0.02) Aa
		3330	0.69 (0.02) Aa	1.13 (0.07) ABa	0.45 (0.14) Aa	1.20 (0.15) Aa	0.62 (0.01) Ba	1.12 (0.04) Aa
		4440	0.68 (0.01) Aa	1.14 (0.07) ABa	0.47 (0.20) Aa	1.20 (0.27) Aa	0.63 (0.02) Ba	1.12 (0.01) Aa
		6660	0.69 (0.01) Aa	1.13 (0.02) ABa	0.46 (0.03) Aa	1.22 (0.08) Aa	0.58 (0.03) Ba	1.19 (0.02) Aa
Paysandú	<i>E. benthamii</i>	2220	0.63 (0.04) Ca	1.13 (0.04) Ba	0.36 (0.04) Ba	1.26 (0.08) Aa	0.67 (0.01) Ba	1.20 (0.03) Aa
		3330	0.63 (0.003) Ca	1.15 (0.08) Ba	0.39 (0.02) Ba	1.21 (0.06) Aa	0.66 (0.01) Ba	1.19 (0.004) Aa
		4440	0.64 (0.01) Ca	1.16 (0.07) Ba	0.39 (0.09) Ba	1.20 (0.12) Aa	0.67 (0.01) Ba	1.21 (0.04) Aa
		6660	0.64 (0.02) Ca	1.20 (0.03) Ba	0.37 (0.09) Ba	1.22 (0.10) Aa	0.66 (0.01) Ba	1.19 (0.07) Aa
	<i>E. dunnii</i>	2220	0.64 (0.03) Ba	1.21 (0.02) Aa	0.36 (0.01) Ba	1.23 (0.06) Aa	0.68 (0.01) Aa	1.19 (0.05) Aa
		3330	0.63 (0.02) Ba	1.22 (0.03) Aa	0.36 (0.14) Ba	1.22 (0.19) Aa	0.66 (0.02) Aa	1.20 (0.01) Aa
		4440	0.65 (0.01) Ba	1.23 (0.02) Aa	0.38 (0.01) Ba	1.22 (0.01) Aa	0.68 (0.02) Aa	1.17 (0.03) Aa
		6660	0.66 (0.04) Ba	1.19 (0.07) Aa	0.37 (0.19) Ba	1.22 (0.21) Aa	0.74 (0.08) Aa	1.29 (0.03) Aa
	<i>E. grandis</i>	2220	0.66 (0.03) Aa	1.19 (0.06) Aa	0.45 (0.08) Aa	1.23 (0.12) Aa	0.67 (0.01) Ba	1.16 (0.01) Aa
		3330	0.67 (0.02) Aa	1.21 (0.05) Aa	0.45 (0.09) Aa	1.25 (0.11) Aa	0.67 (0.01) Ba	1.15 (0.02) Aa

4440	0.68 (0.01) Aa	1.23 (0.06) Aa	0.45 (0.08) Aa	1.22 (0.13) Aa	0.67 (0.01) Ba	1.17 (0.02) Aa
6660	0.69 (0.02) Aa	1.20 (0.06) Aa	0.43 (0.06) Aa	1.23 (0.12) Aa	0.67 (0.004) Ba	1.16 (0.01) Aa

Similar results were obtained at Paysandú site, and the planting density did not affect the contents of the elements in any of the fractions evaluated. *E. grandis* maintained superiority in the *O* contents of the bark and leaves, and *E. benthamii* presented the highest contents of *C* in the bark and *N* and *S* in the leaves. The wood of *E. dunnii* presented the lowest values of the analyzed compounds of the three species. In turn, these two species register the lowest *O/C* values in the three biomass fractions, while the *H/C* ratio remains unchanged with few changes, as in the other site.

The *H/C* and *O/C* relationships represented through the Van Krevelen diagram show similar results with the wood and bark fractions clearly differentiating from the leaves regarding the second of the mentioned indices (Fig. 1). For the wood and bark fractions, *E. grandis* is the species that has the best *O* and *C* ratios, whereas for *E. benthamii* and *E. dunnii* the best relationship was recorded in the leaves. When considering the biomass as a mix of fractions derived from the whole tree, *E. grandis* is the species that shows the greatest potential for the different thermal conversion processes in the sites evaluated (Fig. 2). In any case, an evident similarity is observed between the evaluated species. The *VM/FC* index also shows that *E. grandis* and *E. dunnii* show the largest values basically due to the differences recorded in the composition of the bark (Fig. 3) since statistically similar values are obtained in the other fractions.

Relationships between the analyzed variables and prediction models

The simple correlation values of the components of *UA* and *PA* with *HHV* are generally higher with some of the elements of the first of those mentioned (Table 5 and Figures S1 to S6 Supplementary material). The highest values obtained with *C* in the bark and leaves fractions and with *O* in this same fraction of the tree biomass stand out. These components have a low correlation in the wood fraction, although significantly different from 0. For this reason, high correlation values of the atomic *O/C* ratio with *HHV* are also obtained in the bark and leaves (Figure S7, Supplementary material). With the *PA* parameters, moderate to low correlation values with *HHV* are obtained in all fractions.

Table 5
Simple correlation values of the *PA* and *UA* parameters with the *HHV* for each fraction, jointly considering the sites, species, and planting densities.

Fraction	<i>C</i>	<i>H</i>	<i>O</i>	<i>N</i>	<i>VM</i>	<i>FC</i>	<i>A</i>	<i>O/C</i>	<i>H/C</i>
Bark	0.91 ***	0.16 ns	-0.40 *	0.17 ns	-0.30 *	0.53 **	-0.40 *	-0.83 ***	-0.38 ***
leaves	0.89 ***	0.69 ***	-0.80 ***	0.46 ***	0.23 *	-0.14 ns	0.0 ns	-0.87 ***	0.03 ns
Wood	0.56 ***	0.18 ns	-0.53 ***	0.22 *	0.0 ns	0.0 ns	-0.36 **	-0.59 ***	-0.12 ns

These associations ultimately explain the *HHV* prediction capacity of the models adjusted for each tree fraction evaluated (Table 6). The models with the highest precision in estimating *HHV* were obtained with the bark and leaves fractions with high levels of *Adjusted*² and low levels of error and *BIAS*. The model with the lowest *HHV* prediction capacity is obtained with the wood fraction, although with lower error values than with the other fractions of the tree biomass. The model to estimate the *HHV* of the bark shows a tendency to underestimate the values for the laboratory measurement, which is corroborated by the relatively high value obtained in the *BIAS* compared to the other fractions (Fig. 4). On the contrary, the model adjusted for the leaf fraction presents comparatively reduced *BIAS* values and higher error levels.

Table 6

Adjust *HHV* prediction models based on each fraction's *UA* and *PA* parameters, jointly considering the sites, species, and plantation densities. The values expressed in % are calculated based on the average of the measured *HHV* values.

Fraction	Models	<i>Bias</i>		<i>MAE</i>		<i>RMSE</i>		<i>Radjusted</i> ²	<i>HHV</i>	<i>HHV</i>
									<i>estimated</i>	<i>measured</i>
									<i>average</i>	<i>average</i>
Bark	$HHV = -2058.29 + 417.51 \cdot C$	84.4	0.5%	170.1	1.0%	278.7	1.6%	0.83	17766	17681
Leaves	$HHV = -860.81 + 423.32 \cdot C + 281.07 \cdot N$	-31,2	0.1%	314.9	1.3%	402.4	1.7%	0.80	23567	23598
Wood	$HHV = 14644.71 + 102.5 \cdot C$	-0.1	0.001%	138.1	0.7%	191.8	1.0%	0.35	19750	19804

Wood fuel quality

The analysis of variance indicates that *E. benthamii* and *E. dunnii* have the highest *Wdw* values in both sites and that it does not depend on the planting density (Table S2, Supplementary material). The superiority of these species concerning the *Wdw* of *E. grandis* is more noticeable at Paysandú, although the values of the plantation densities are similar to those of Tacuarembó. The *FVI* results showed similar results between species and plantation densities, but *E. dunnii* had lower values at Paysandú. The mean values of *Wdw* and *FVI* of the species and plantation densities at Paysandú seem higher than those of Tacuarembó, although this was not confirmed statistically.

The partial correlation values of the *FVI* with the variables related to its calculation show that the most significant relative weight has the *A* content negatively ($r = -0.89$ and -0.91) (Table S3, Supplementary material). *Wdw* has a moderate relationship with *FVI* ($r = 0.4-0.7$), while *LHV* has a correlation value very close to 0.

Discussion

The results confirmed the hypothesis that the *Eucalyptus* species affects the wood's different parameters related to its energy behavior. However, the hypothesis of the influence of planting density on the aforementioned indicators was not confirmed. The information obtained shows that from the point of view strictly of the composition of the biomass, the silvicultural management decision is based on the type of species to be used. Although the tree population has a neutral effect on the characteristics of the biomass, the energy yield per unit area and the sustainability of this type of plantation must be considered. In this sense, it has been determined in previous studies that the use of the wood fraction in low plantation densities is what would allow achieving the best levels of sustainability from the point of view of energy efficiency and nutrient extraction [39]. On the other hand, there is no doubt that the use of the bark and leaves fractions would contribute to total biomass productivity, although the latter adds a certain complexity to biomass harvesting and extraction operations. The hypothesis was also confirmed that it is feasible to obtain prediction models for the caloric content of wood for each biomass fraction, which depends on the *C* content.

Energetic value

The analysis of the *LHV* values shows that in both sites, the wood fraction has the same levels for the three species evaluated, which is consistent with what has been reported in the literature for different *Eucalyptus* species [40, 41]. Although it is known that *Eucalyptus* species have different lignin and extractive contents [42, 43], which are associated with differences in *LHV*, the composition of the species evaluated in this study is likely relatively similar to each other. As will be analyzed later, of the parameters evaluated in this study, only *C*, *O*, and *A* show a moderate relationship with the *LHV* of the wood, but that ultimately does not explain the results obtained from this variable. On the other hand, with the bark and leaves fractions, it is observed that in both sites, the highest values recorded with *E. benthamii* and *E. dunnii* are associated with the high *C* contents and low *O* contents recorded. The high energy contents contained in the carbon-carbon bonds compared to the carbon-oxygen bonds [2] ultimately explain the higher *LHV* values of the bark and leaves of both species. In both sites, the differences recorded in the leaf fraction are of greater magnitude than those obtained with the bark, the latter being of little importance since it is considered a value greater than $1,250 \text{ J} \cdot \text{g}^{-1}$ at an industrial level [44]. Plantation density (like other silvicultural parameters) has no effect on *LHV* in all biomass fractions and in both sites in the same way, as reported in several studies with *Eucalyptus* species [10, 45].

Regarding the ash content and considering the combustion of the different fractions of the tree (as a function of the relative weight of each one in the total biomass) it is observed that all species have values lower than 1.5%. This allow those species to be categorized as suitable

for domestic use according to the standard (UNE-EN ISO 17225-4 2021) [46]. On average for both sites and plantation densities, the lowest values are obtained with *E. benthamii* and *E. grandis* (0.6 and 0.5%, respectively) while *E. dunnii* has a value of 0.8%.

Chemical parameters

Proximate analysis

Generally, the values obtained for this component are similar to those reported by several authors evaluating different biomass fractions of *Eucalyptus* species [47–49]. At the Tacuarembó site, the most significant variability recorded between the evaluated species is observed in the bark, with the highest levels of *VM* in *E. dunnii* and *E. grandis*, while the highest *FC* content is obtained in *E. benthamii*. On the other hand, the wood fraction representing around 77% of the total weight of the tree biomass in these tests [34] has the exact contents of these parameters except for the *A*, in which *E. grandis* is the species with the lowest values. *VM* are derived from cellulose and hemicelluloses, so biomass with high contents of this component is more reactive and, therefore, has more significant volatilization potential and can be converted to bio-oil [50, 51]. In turn, the low *A* contents improve the quantity and quality of the bio-oil obtained by reducing the solids content and avoiding secondary vaporization reactions [52]. It is also verified that high *A* contents reduce volatilization and increase scale formation, which reduces thermal efficiency and increases operating costs [5].

Regarding the *FC*, it is observed that *E. benthamii* is the one that shows the most significant potential for biochar production but given the reduced contribution of the bark to the total biomass of the tree (approximately 12%), the superiority of this species for such purposes It has no industrial implications. Considering that the sum of both fractions is 90% of the total weight, *E. grandis* stands out for its more significant potential for obtaining bio-oil through the pyrolysis process due to the high content of *VM* and low contents of *A*. These two characteristics also make it a species with an exciting biomass for another thermomechanical conversion process, such as gasification [9, 22, 53]. At the Paysandú site, a somewhat different behavior is observed in the sense that in the wood fraction, *E. dunnii* stands out with the lowest *A* contents in the same way as in the leaves, but it has already been commented on the little contribution that this fraction makes to the total biomass. The interaction between the species and the density detected in the fraction lacks practical implications since there is no defined relationship between both parameters, adding to the little contribution to the total biomass. Therefore, at this site, *E. dunnii* has the advantage of having the lowest content of mineral residues, although this has no impact on energy performance, as previously analyzed.

Ultimate Analysis

The values obtained for this parameter are within what is expected for different types of biomass of *Eucalyptus* species [18, 28, 54]. In both sites, the effect of plantation density on these elements is not detected, unlike what was reported by [10] where the *C* and *N* contents are higher in the smaller spacings even though these results are considered scarce. Relevance and that did not affect the final energy result. From the point of biomass composition, *C*, *O*, and *H* are the most important because they contribute primarily to *HHV* [19]. At the Tacuarembó site, in the wood fraction, *E. grandis* stands out with the highest *C* values, while in the bark and leaves, the highest *C* and *H* values are obtained with *E. benthamii* and *E. dunnii*. The higher *O* contents recorded with *E. grandis* in these fractions reduce its potential concerning the other species, although this is of secondary importance due to the high but comparative nature of the wood fraction. The atomic ratios *O/C* and *H/C* are also used to measure the energy content of solid fuels since high levels of *O* and *H* reduce energy values [55]. From this point of view, the three species have a similar potential, considering the similar values obtained in the composition of the wood fraction (See Table S4 Supplementary material). At the Paysandú site, *E. benthamii* and *E. grandis* show the most significant energy potential due to their high *C* content, particularly in the wood fraction, although a similar result is also obtained in the other biomass fractions. In all cases, it is obtained that the values of *N* and *S* are shallow, so the gases resulting from combustion are expected to have reduced levels of N_2O and SO_2 . The *O/C* and *H/C* atomic ratios also confirm the better behavior of these species in terms of high levels of tar and total volatiles and low gas yields during the pyrolysis process [56].

Implications for thermal conversion of biomass

The relationships between *C*, *H*, *O*, *VM* and *FC* components serve as indicators of the potential thermal conversion processes of different raw materials. The most frequently used indicators are the Van Krevelen diagram and the *MV/FC* ratio which can be applied to characterize the reactivity of the biofuel. According to the Van Krevelen diagram, the values obtained with the wood and bark fractions indicate that all species have the potential to provide bio-oil (through pyrolysis) while the leaves have a more appropriate composition to produce CH_4 (through gasification) [57, 58]. Although some authors indicate that the lowest values of the *O/C* and *H/C* indices correspond to high levels of *HHV* [59], in this case the first of the mentioned is the best predictor of the caloric content of all fractions. The greatest effect of the *O* content on the *HHV* is due to the high contents of this component within lignocellulosic biomass [60]. Analyzing the 3 fractions together for both sites based considering these parameters, *E. grandis* is the species with the best prospects for obtaining fuel. Regarding the

reactivity of the biomass expressed through the *VM/FC* index [61, 62], *E. grandis* and *E. dunnii* show the highest values based on the differences determined in the bark and the relative weight of this fraction in the total biomass. Both indices are coherent since both point to *E. grandis* as the species with the highest energy potential, which is confirmed by the *HHV* values obtained from the fractions of this species.

Silvicultural Implications

Implementing short rotation systems for producing some fuel implies that the energy yield per unit area depends mainly on aspects of forestry, such as plantation density and harvest shift. The results previously obtained relativize the effect of the *Eucalyptus* species and highlight the growth rate, which depends on the factors mentioned above [12]. These studies indicate that the optimal harvest time from the point of view of energy yield occurs close to 4 years, so the results obtained in this evaluation provide complementary information on the characteristics of the biomass obtained in that period. The results obtained in this study show that the evaluated species do not differ significantly in terms of energy content due to the small margin of difference detected between them in the different parameters evaluated. This situation is particularly evident in the wood fraction due to the relative weight it represents over the total biomass, which in turn is the fraction that determines the lowest extraction of nutrients from the soil [34]. On the other hand, the logistics for using fractions such as leaves and branches require equipment whose operating costs are only sometimes economically viable. In this sense, the use of wood and bark has comparative advantages concerning the other fractions of the tree. From this point of view, the choice of species is likely to be unimportant in practical terms, and attention should focus on differences in biomass productivity, which is associated with planting density and harvest age.

Relationships between parameters and HHV prediction

Considering the set of parameters evaluated, it is observed that the components of elemental *UA* show a better relationship with *HHV*, as also reported by other authors evaluating *Eucalyptus* species [24] and other types of biomass [63, 64]. However, in some cases, highly accurate *HHV* estimation models have been obtained from the *PA* components [65] or a combination of both components [19]. According to Hosokai et al. [29], fuels produce heat due to the recombination of chemical bonds between their elements, and therefore, it is expected that the estimation of *HHV* from the *UA* components is more precise compared to other elements in the fuel composition. However, it must be considered that the determination of *UA* requires more expensive equipment and analysts with more outstanding training compared to the determination of *PA* [66, 67]. In our study, the highest correlations with *HHV* in all fractions are obtained with *C* and *O* (and the relationships between both), agreeing with what was reported by [68, 69], who evaluated different biomass types, including *Eucalyptus*. As mentioned above, this is due to i) the release of energy that occurs during the oxidation of carbon (element in more significant proportion) and ii) the reduction of oxygen (second element in more significant proportion). Although the *C* and *O* contents of all fractions are relatively similar, the correlation values with *HHV* are noticeably different, which could be explained by differences in the contents of variables not measured in this case, such as lignin [70] and carbohydrates [67]. The content of *A* has a moderate and antagonistic relationship with the *HHV* aspect, which has also been identified by some authors as a variable that improves the prediction capacity of the models [25, 71]. In the case of the relationship with *FVI*, the relative weight is more remarkable because it is an inert material that directly affects combustion.

The adjusted models to estimate the *HHV* with greater precision based on *C* and *N* have *Adjusted*² values somewhat lower than those reported in the literature obtained with different types of *Eucalyptus* biomass [65, 68]. However, the *BIAS* and error indicators (*MAE* and *RMSE*) are lower, showing the usefulness of their use, considering that they do not reach 2% of the measured value of *HHV*. This result is equivalent to, on average, levels lower than 500 J.g⁻¹, which, in practical terms, can have little impact on the energy result. The model to estimate the *HHV* of the bark overestimates the values concerning those measured in a tiny proportion, while the model to estimate the *HHV* of the leaves underestimates the observed values in an even smaller proportion. The correlation errors (*MAE*) for both fractions are of the order of 1%, which indicates the high precision obtained with the *r* calculated between both parameters. The *BIAS* obtained with the model to estimate the *HHV* of wood is practically 0. According to García et al. [68], the *BIAS* (by definition) does not consider absolute values and, therefore, is not a good indicator of the precision of a model since negative errors of similar magnitude neutralize large positive errors. Other authors evaluating different types of biomass also affirm that *MAE* values lower than 7% are an indicator of good precision models for estimating *HHV* [27].

Energy density of wood

Although in short rotation crops with *Eucalyptus* species whole trees are harvested at young age, the leaves and the bark represent only around 15% of the total weight of the biomass. Considering logistic costs, the most economical extraction method is chipping all the aboveground biomass in the field. However, pursuing more sustainable practices it is of interest to evaluate the energy content of the wood since this predominant fraction has the lowest nutrient content.

The practical implications of our findings are evident in the differences observed in the *Wdw* values and *FVI* results. Despite the high levels of *A* recorded by *E. benthamii* and *E. grandis* at both sites, the *FVI* results only show significant differences in favor of these species at the Paysandú site. This is due to the high relative weight that this component has with respect to *Wdw* and *LHV* in the calculation of this index. The negative weight of *A* on this index, as reported by several authors evaluating different forest species [15], further emphasizes the practicality of our findings. At the Tacuarembó site, these species are the ones with the highest levels of *FVI*, but these differences are not significant. The highest *Wdw* values at both sites are recorded with *E. benthamii* and *E. dunnii*, consistent with previous studies in the same region as that of the trials evaluated in this study [72]. It's important to note that different types of biomes with similar *LHV* values can produce fuels with different energy contents due to variations in the components that have been mentioned in these topics [52].

Conclusions

This study includes determining a broad set of parameters to evaluate the energy potential of silvicultural systems with different *Eucalyptus* species in short rotation.

The results obtained indicate that the *Eucalyptus* species and plantation densities evaluated have similar potential aptitudes for fuel production through different thermochemical processes. From the point of view of the predominant fractions in these production systems (wood and bark), the evaluated species show different potentialities. *E. grandis* combine the highest values of *VM* and *C* and the best levels of the *O/C* ratio. The thermal conversion potential indicators suggest that in general all biomasses can be used for pyrolysis and gasification processes to obtain high viscosity bio-oil and CO, respectively. Considering the results obtained with the different planting densities, these differences surely lose relevance in terms of energy production per hectare. Therefore, the decision of the silvicultural system to implement must be based on aspects related to the productivity of biomass per unit of area and time as well as issues related to the sustainability of this type of crops in the long term (e.g., [12, 34]). The *HHV* estimation models of the different biomass fractions are based on some elements of the *UA* through which it is possible to obtain a relatively high precision. The parameters with the greatest predictive capacity for *HHV* are *C* to a greater extent than *N* and *A*.

Declarations

Competing Interests

The authors declare no competing interests.

Author contribution

FR, C R-C and L C-L planned and designed the research. FR and C R-C conducted fieldwork and performed experiments. AH and NT contributed to data elaboration and analysis. FR, LC-L, CR, AH y NT wrote the manuscript.

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Data availability

Data will be made available on request.

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Figures

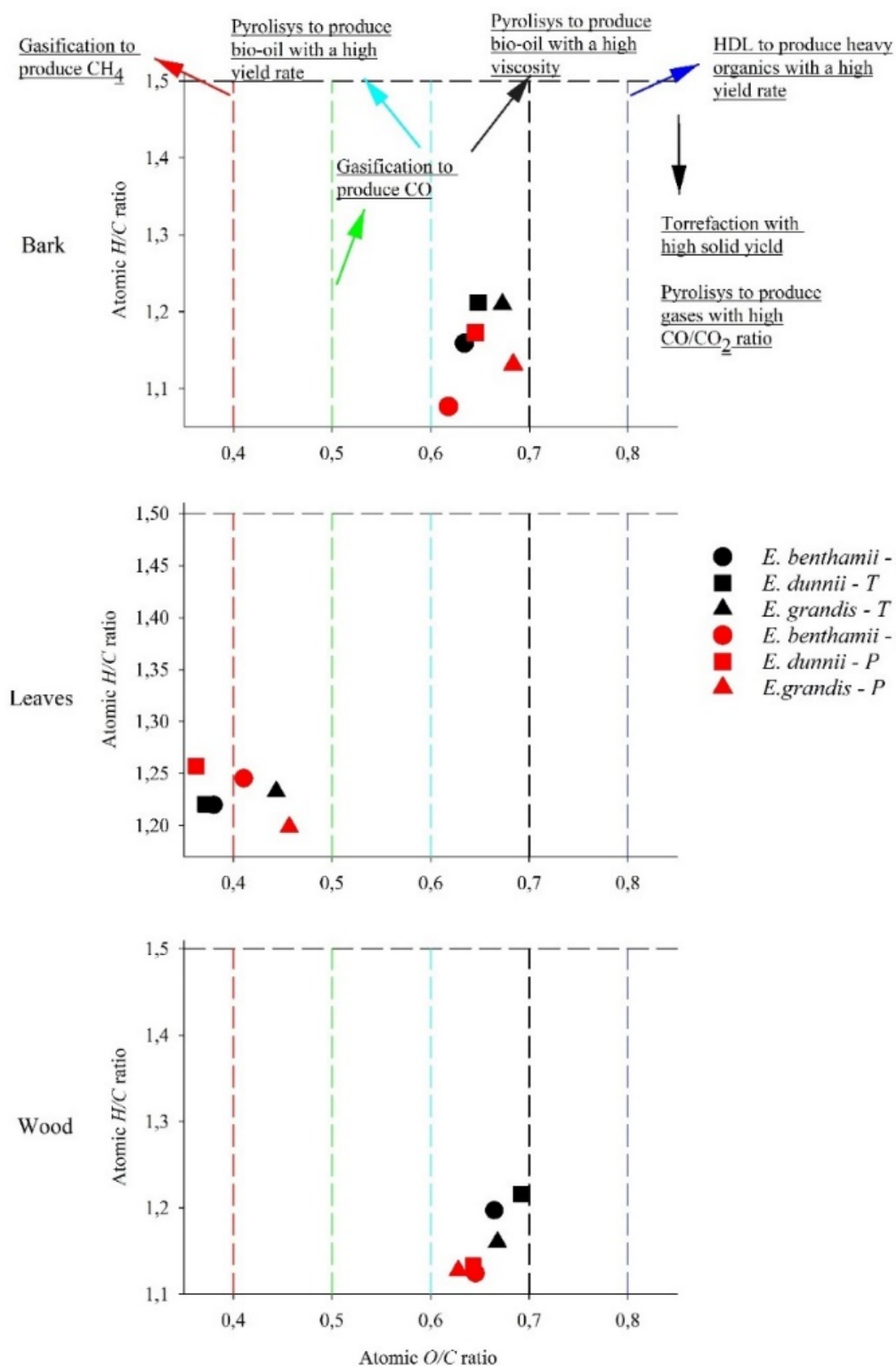


Figure 1

Average levels of H/C vs O/C atomic ratios in each biomass fraction of the species and their thermal conversion potential according to the Van Krevelen diagram at each site (based on Wang et al. [58]).

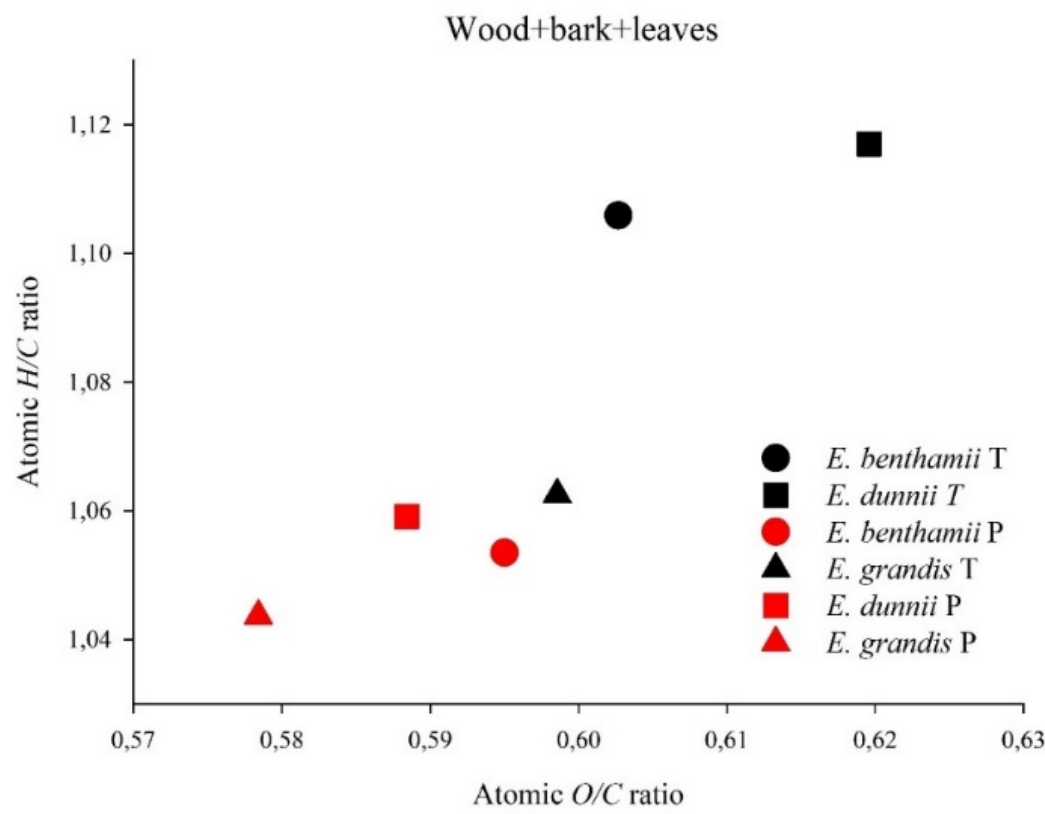


Figure 2

Average levels of the H/C vs O/C atomic ratios of the species considering the mix of the fractions based on the relative weight with respect to the total weight of biomass at each site (based on Resquin et al. [34]).

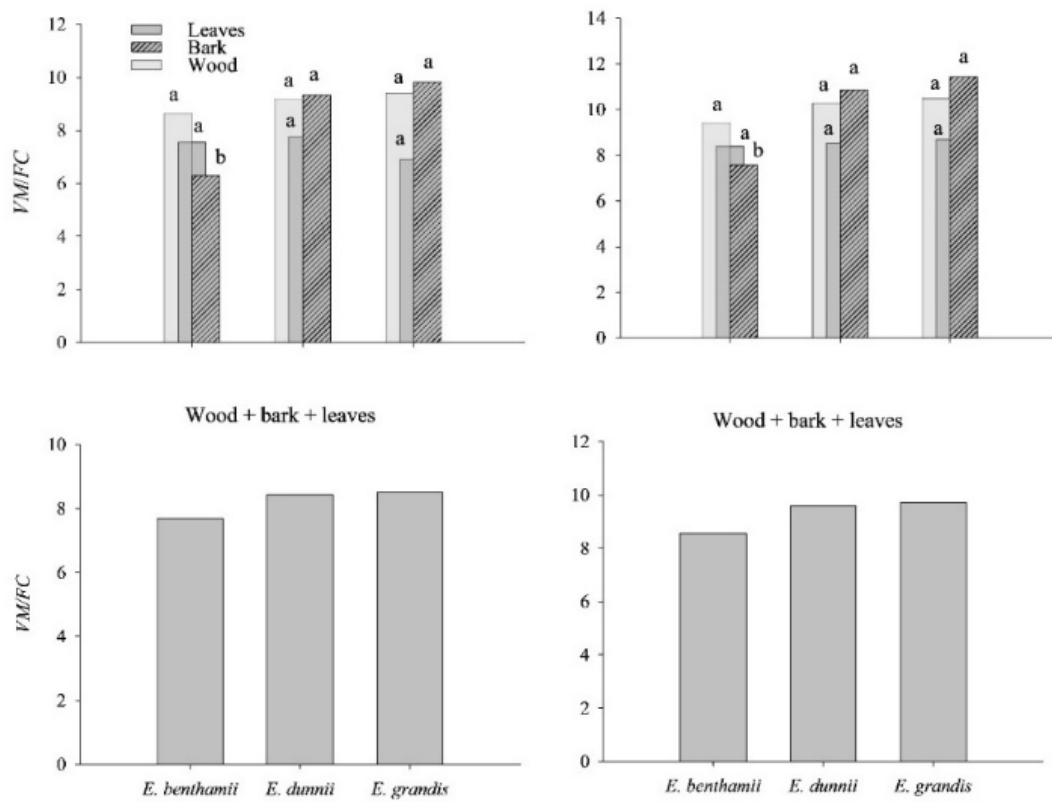


Figure 3

Average values of the VM/CF index in the biomass fractions and mix (depending on the relative weight of each one in relation to the total) the species at the Tacuarembó (left) and Paysandú (right) sites (based on Resquin et al. [34]).

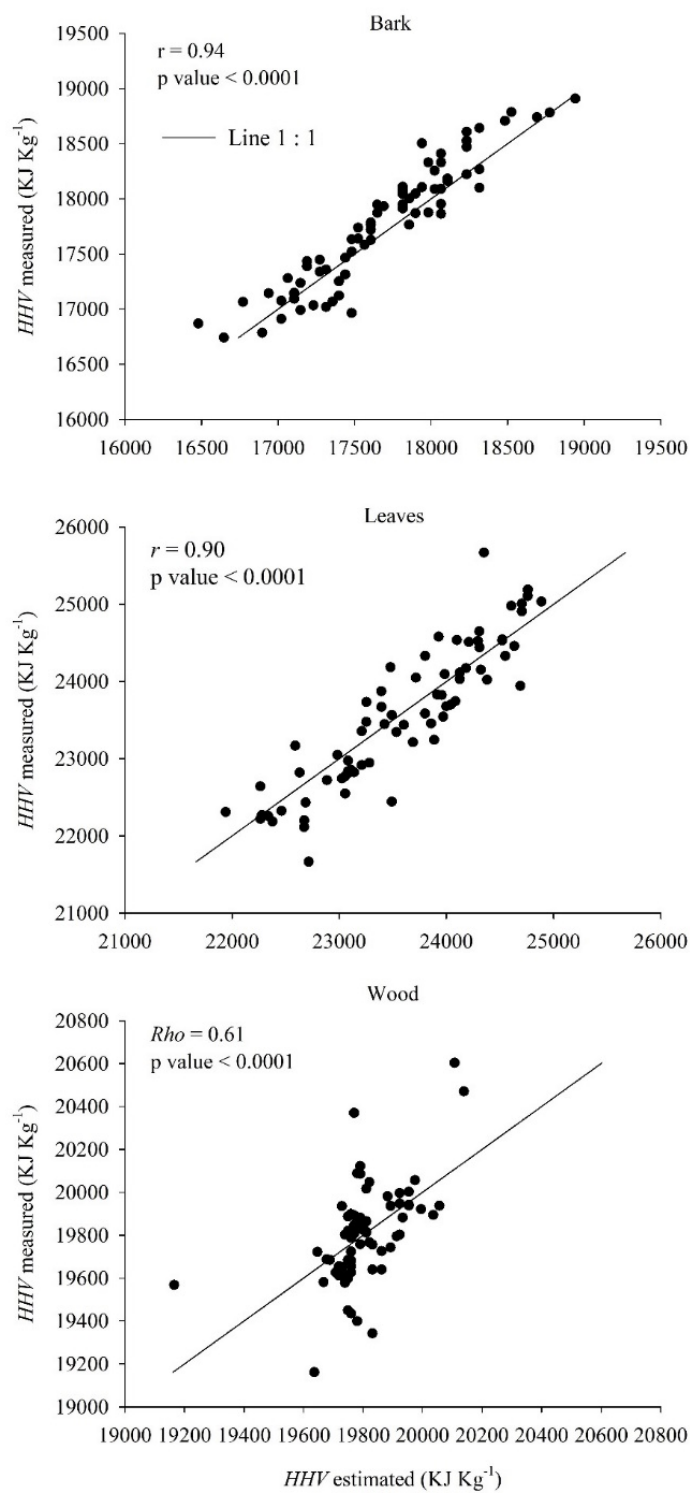


Figure 4

Measured vs estimated values of *HHV* for the bark, leaf, and wood fractions, considering the results obtained in the sites, species, and planting densities.

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