

## Article

# Calorific Value and Chemical Composition of Five Semi-Arid Mexican Tree Species

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**Abstract:** The current global energy crisis has generated growing interest in looking for alternatives to traditional fossil fuels, presenting lignocellulosic materials as a promising resource for sustainable energy production. In this paper, the calorific values and chemical composition of the trunks, branches, twigs and leaves of five timber species of the semi-arid land of Mexico (*Helietta parvifolia* (Gray) Benth., *Ebenopsis ebano* (Berl.) Barneby, *Acacia berlandieri* (Benth.), *Havardia pallens* (Benth.) Britton & Rose and *Acacia wrightii* (Benth.)) were determined according to international standards. The results highlighted the calorific value ranges of 17.56 to 18.61 MJ kg<sup>-1</sup> in trunks, 17.15 to 18.45 MJ kg<sup>-1</sup> in branches, 17.29 to 17.92 MJ kg<sup>-1</sup> in twigs, and 17.35 to 19.36 MJ kg<sup>-1</sup> in leaves. The pH presented an acidic trend (3.95–5.64). The content of mineral elements varied in trunks (1.09%–2.29%), branches (0.86%–2.75%), twigs (4.26%–6.76%) and leaves (5.77%–11.79%), showing the higher proportion in Ca (57.03%–95.53%), followed by K (0.95%–19.21%) and Mg (0.88%–13.47%). The highest amount of extractives was obtained in the methanolic solvent (3.96%–17.03%). The lignin recorded values of 28.78%–35.84% for trunks, 17.14%–31.39% for branches and 20.61%–29.92% for twigs. Lignin showed a moderately strong correlation ( $r = 0.66$ ) with calorific value, but the best mathematical model was registered with the calorific value depending on the pH and lignin ( $R^2 = 58.86\%$ ).

**Keywords:** calorific value; chemical components; timber species

## 1. Introduction

Wood is one of the main commercial product from the forest [1], and one of the energy sources most used before the industrial revolution [2]. Facing the current crisis in the global energy model, caused by the excessive use of fossil fuels that cause sometimes irreparable damages to the terrestrial biosphere and the environment [3], the interest in finding substitutes for fossil fuels grows daily, proposing alternatives for strengthening a transition to a more sustainable energy model. In this approach, biofuels are the most immediate substitute, since its energy density (energy per unit mass) is similar to that of gasoline (only 20% less) [4]. These biofuels derived from agricultural and/or forestry systems, which are major producers of biomass.

Mexico has a privileged position to generate this kind of energy, since it has a forest area of 126.6 million hectares, equivalent to 64.4% of the national territory [5], of which 25.8 million hectares

are forest, 8.8 million ha of forest with secondary vegetation, 13.1 million ha of rainforests, 21.2 million ha of rainforests with secondary vegetation and 57.6 million ha of arid vegetation. In the latter, representing over 50% of the total area [6–8], approximately 6000 species of angiosperms, of which between 50%–60% are endemic, are recorded [6,9,10]. This rich and immense diversity of arid and semi-arid areas of Mexico have been, according to Rojas [11], important plant resources suppliers. That is the case of the Mexican scrub, which is the most abundant resource and historically the most used in the arid and semi-arid areas of the country [12]. It is used to obtain products for fence construction (as posteria), for the elaboration of agricultural implements and above all, firewood extraction and charcoal production [13].

Despite having favorable natural conditions for the use of forestry sector, it has remained a secondary role in the economic development of the country [14]. Such use is most directed towards timber production. It is estimated that for every tree extracted for timber production, only approximately 20% is used commercially, 40% is left in the field as branches and roots, while the other 40% is underutilized in the sawmilling process in the form of chips, bark and sawdust [2]. The abandonment of these materials in the field has a high environmental impact because of the slow decomposition of potentially high amounts of biomass that, in hot weather, can be a source of fire risk [15].

With these residues, many of the needs in thermal energy can be covered, enabling industries for example, to produce a surplus of heat and electricity, which could help other deficient processes of energy transformation into an integrated complex and may also provide energy for the needs of neighborhood in rural areas [16]. To achieve this expectation, it is necessary to determine if these byproducts comply with international quality standards. Therefore, evaluating the calorific value, which according to the FAO [16], is one of the most important factors indicating the amount of thermal energy that can be obtained by burning a unit mass of the material, as well as some physicochemical features such as ash content, type and content of inorganic elements, is required [17,18]. According to Jara [19], the calorific value of the wood, besides moisture, is greatly influenced by the chemical composition of wood, mainly lignin and extractives.

Knowing these properties and concentrations of the ash elements is vital for energy generation [20], since the elemental chemical composition of a material determines its calorific value, the emitted gases during combustion and the ash composition [21]. Therefore, the aim of this study was to determine the calorific values of five planted species of the semi-arid land of Mexico, and the chemical composition of the different biomass components. Calculating the relationship between calorific values and different aspects of chemical composition could give a better understanding to improve the management of energy production from wood of the investigated area.

## 2. Experimental Section

### 2.1. Collection Site

The study was undertaken at the Forestry Faculty of the Autonomous University of Nuevo León (UANL), located within the coordinates 24°47' north latitude and 99°32' west longitude in a plain region at 430–450 m altitude in the foothills of the Sierra Madre Oriental, Mexico [22]. The regional climate is defined as semi-arid and sub-humid ((A) C (Wo)) in the scheme of Köppen modified by Garcia [23], with two rainy seasons (summer and autumn) and a dry season between November and April. The characteristics of the species under study are shown in Table 1.

**Table 1.** Characteristics of sampled trees.

Common Name	Scientific Name	Families	BD (cm)	DBH (cm)	H (m)	C (m <sup>2</sup> /ind.)
Barreta	<i>Helietta parvifolia</i> (Gray.) Benth.	Rutaceae	4.40	3.05	5.00	6.78
Ébano	<i>Ebenopsis ébano</i> (Berl.) Barneby	Mimosaceae	7.90	5.95	4.80	7.60
Huajillo	<i>Acacia berlandieri</i> Benth	Mimosaceae	3.10	2.05	3.25	8.53
Tenaza	<i>Havardia pallens</i> (Benth.) Britton & Rose.	Mimosaceae	5.20	3.98	4.80	6.72
Uña de gato	<i>Acacia wrightii</i> Benth	Mimosaceae	7.60	4.40	3.70	5.64

BD = Basal diameter; DBH = Diameter at breast height; H = Height; C = Coverage (m<sup>2</sup>/individual) [24].

## 2.2. Sampling and Sample Preparation

All trees were randomly obtained from 30-year-old experimental plantations, with height from 3.25 to 5 m (Table 1), in April 2014 (spring). Three trees of each of the five studied species were cut down and separated into four biomass components (trunks, branches, twigs and leaves). The trunks had diameters ranged from 4 to 8 cm and a length of 1 m, the diameters of branches were from 2 to 3 cm with a length of 0.5 m, twigs had diameters < 2 cm and a length of 0.5 m. After cutting them into small pieces of about 20 cm length, three samples were obtained per biomass component and per tree, resulting in 180 incremental samples. The samples were splintered, dried outdoor and ground in a Wiley cutting mill (Model 4 Bench, 115 V, 50/60 Hz). The wood meal obtained was classified based on the mesh opening. Chemical analyses were performed with sawdust fraction containing particles from 40 mesh (425 µm) to 60 (250 µm), according to the standard T 257 cm-85 [25].

## 2.3. Determination of Calorific Value

The calorific value was determined according to ISO 17225-1 [26]. A prefabricated pellet from 1 g of each sample of wood meal was placed in a quartz crucible together with 500 µL of paraffin (46,260 J g<sup>-1</sup>). The crucible was placed in the suspension bracket of a combustion vessel and a cotton thread was firmly attached to the ignition wire and immersed in the paraffin to ensure a correct ignition. Then, 5 mL water was added to the vessel. After closing the vessel, oxygen was added with a pressure of 30 atmospheres to ensure a complete combustion. The analyses were done with a calorimeter IKA, C 7000. Results are given in MJ kg<sup>-1</sup> dry matter.

## 2.4. Chemical Analysis and Determination of Ash Content

The pH determination was performed according to the methodology described by Sandermann and Rothkamm [27]. The ash content was determined in accordance with ISO 17,225-1 [26], by incinerating about 2 g of samples of wood meal in porcelain crucibles in a furnace (Nabertherm, L 24/11/P320) with sufficient ventilation to enable a complete incineration. First, the temperature was increased up to 250 °C to calcinate the sample and afterwards up to 550 °C. The temperature of 550 °C was held for 2 h to ensure a complete incineration. The results are given in w-% dry matter.

The constituent elements of ash were identified and quantified by a partial microanalysis on a X-ray spectrometer coupled to a scanning electron microscope JEOL model JSM -6400. The operating conditions were 20 kV and 8.5 s [28].

The extractives contained in the wood meal (8 to 13 g) were determined by solid–liquid successive extraction with different solvents of increasing polarity, using 200 mL of cyclohexane, acetone, methanol and distilled water in Soxhlet [29]. The extraction periods were 6 h with each solvent. The separation of solvents from extractives was performed using a rotavapor Yamato, BM 100 at 45 °C temperature, applying vacuum with reduced pressure. The extractives for each solvent were calculated by dividing the mass of the anhydrous extractive by the mass of the anhydrous sample in percent. The total extractives were calculated as the sum of the percentages of all extractives of a sample. The material after successive extraction, was designated as extractive-free wood meal and an aliquot of it was used for determination of lignin content, in accordance with the technique from Runkel and Wilke [30].

Fifty milliliters of sulfuric acid (72%) and 50 mL of hydrobromic acid (40%) were added to 1 g sample of extractive-free wood meal. The suspension was stirred and allowed to stand for 2 h. Next, 200 mL of distilled water was added and the solution was boiled for 5 minutes. After cooling to room temperature, the samples were filtered in a Buchner funnel and washed until the suspension was acid-free. Finally, the samples were dried at 103 °C to constant weight. The lignin content was calculated by dividing the difference of the masses of the dried sample before and after lignin extraction by the mass of the dried extractive-free sample, and the results is given in w-%.

### 2.5. Statistical Analysis

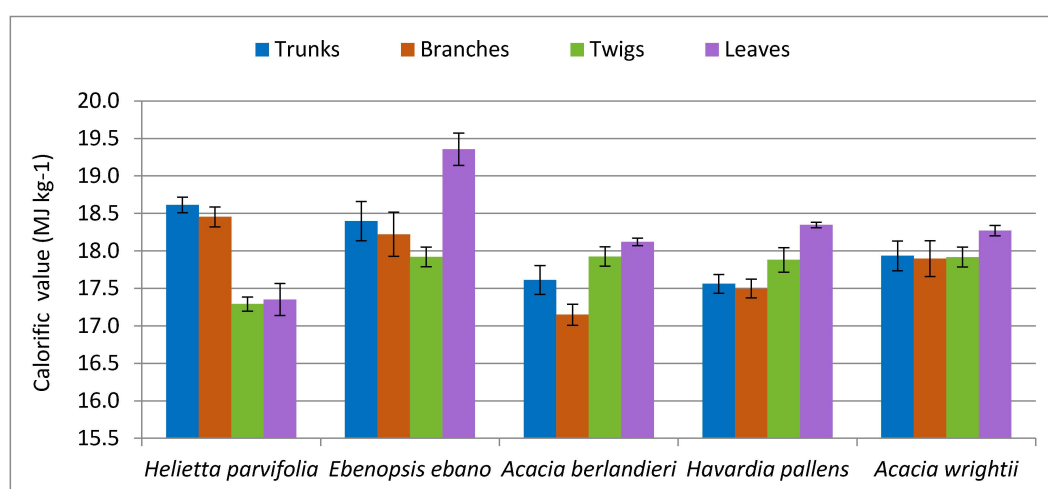
To verify the significance of differences between single results of the analyzed parameters, an analysis of variance was performed, and the multiple comparison test of Tukey ( $p \leq 0.05$ ), using the species and the different biomass components per tree as criteria. Analogously, a multiple regression analysis was performed by Pearson method in order to determine the relationship of each of the variables with its calorific value. These analyses were performed using the Statistical Package STATGRAPHICS Centurion XVI [31].

## 3. Results and Discussion

### 3.1. Calorific Value

Figure 1 shows the calorific values on dry basis of the different biomass components from the five species tested as average values from each data of each combination of species and biomass component of a tree. Calorific values of trunks and branches representing the main parts used for energy production were in range from 17.15 to 18.61 MJ kg<sup>-1</sup> with the highest values for trunks of *Helietta parvifolia* (*H. parvifolia*): 18.61 MJ kg<sup>-1</sup> and *Ebenopsis ebano* (*E. ebano*): 18.40 MJ kg<sup>-1</sup>. Looking to the values for the different biomass components of each species, *H. parvifolia* and *E. ebano* showed the highest differences with values of 17.29 MJ kg<sup>-1</sup> for twigs of *H. parvifolia* and 19.36 MJ kg<sup>-1</sup> for leaves of *E. ebano*. Calorific values of different biomass components from the other three species, *Acacia berlandieri* (*A. berlandieri*), *Havardia pallens* (*H. pallens*) and *Acacia wrightii* (*A. wrightii*), were in a closer range with values from 17.50 to 18.44 MJ kg<sup>-1</sup>, with the exception of branches from *A. berlandieri* (17.22 MJ kg<sup>-1</sup>).

In contrast, very high values were observed in leaves of the others four species, which reached a maximum of 19.36 MJ kg<sup>-1</sup> in *E. ebano*. This can be attributed to the high extractives content, since according to Kollmann [32], they tend to increase the calorific value.



**Figure 1.** Calorific value of five planted timber species of the semi-arid land of Mexico, in different biomass components.

The calorific values of the present study are similar to those found by Quirino *et al.* [33] in eucalyptus, and are within the range of 17.882 to 19.629 J.g<sup>-1</sup> reported by Francescato *et al.* [34] for conifers, allowing consideration of the use of these five species from the semi-arid land in Mexico for energy purposes.

### 3.2. Chemical Constituents

Table 2 recapitulates the means and standard deviations of the chemical constituents for each species in the trunks, branches, twigs and leaves segments.

**Table 2.** Chemical constituents and standard deviations in different biomass components of five planted timber species of the semi-arid land of Mexico.

Species	Biomass Components	pH	Ash <sup>1</sup>	Extractives <sup>1</sup>	Lignin <sup>2</sup>
<i>Helietta parvifolia</i>	T	5.64 ± 0.23	1.70 ± 0.60	14.56 ± 1.08	35.94 ± 1.01
	B	4.89 ± 0.35	1.38 ± 0.36	10.38 ± 0.97	31.39 ± 0.61
	M	4.93 ± 0.21	6.76 ± 1.50	32.08 ± 0.52	20.61 ± 0.37
	L	5.30 ± 0.03	11.79 ± 1.29	—	—
<i>Ebenopsis ebano</i>	T	4.84 ± 0.06	2.28 ± 0.49	38.12 ± 1.05	35.43 ± 0.20
	B	4.92 ± 0.13	2.57 ± 0.44	11.99 ± 2.13	28.08 ± 0.34
	M	5.08 ± 0.02	5.14 ± 0.48	24.95 ± 0.48	29.92 ± 0.59
	L	5.17 ± 0.35	7.18 ± 0.80	—	—
<i>Acacia berlandieri</i>	T	3.90 ± 0.04	2.03 ± 0.59	11.97 ± 0.27	28.78 ± 0.54
	B	4.98 ± 0.06	2.75 ± 0.12	9.16 ± 1.99	21.04 ± 1.68
	M	4.78 ± 0.01	5.89 ± 1.53	30.48 ± 0.18	26.56 ± 0.30
	L	4.89 ± 0.31	5.77 ± 0.12	—	—
<i>Havardia pallens</i>	T	3.95 ± 0.01	1.85 ± 0.46	12.10 ± 1.94	32.21 ± 0.69
	B	5.07 ± 0.53	2.34 ± 0.65	10.99 ± 1.42	20.18 ± 1.39
	M	4.73 ± 0.12	4.82 ± 0.73	31.81 ± 1.06	28.51 ± 0.25
	L	5.14 ± 0.04	8.26 ± 1.46	—	—
<i>Acacia wrightii</i>	T	4.21 ± 0.41	1.09 ± 0.38	26.84 ± 1.29	33.94 ± 2.67
	B	4.61 ± 0.04	0.86 ± 0.28	19.37 ± 0.11	17.14 ± 1.48
	M	5.02 ± 0.11	4.26 ± 0.76	22.01 ± 0.43	29.04 ± 0.88
	L	5.05 ± 0.08	8.18 ± 1.21	—	—
P		0.375	0.000 **	0.019 *	0.014 *

<sup>1</sup> Components in percentage based on the dry weight of the original sample; <sup>2</sup> Components in percentage based on the dry weight of the samples free of extracts; T = Trunks, B = Branches, M = Twigs, L = Leaves and P = Probability at 5% for each chemical constituent: \* significant value ( $p \leq 0.05$ ), \*\* highly significant value ( $p < 0.01$ ).

#### 3.2.1. pH

The pH varied from 3.90 to 5.64 (Table 2), reflecting an acidic trend of the species studied in its different biomass components. For all species except *Helietta parvifolia*, the trunks presented lower values compared to the other components, which means there is a tendency to become more acidic in the stem. This coincides with the results found for hardwoods by McNamara *et al.* [35]. Similar results have been reported in the heartwood and sapwood of *Pinus montezumae* and *Pinus. pseudostrobus* [11], with values of 4.81 and 4.94, respectively.

However, there were no significant differences ( $p > 0.05$ ) between species and biomass components, which can be attributed to a higher amount of acetic acid, acyl compound, and the interaction between them, as shown in some species of hardwoods [36,37].

#### 3.2.2. Ash Content

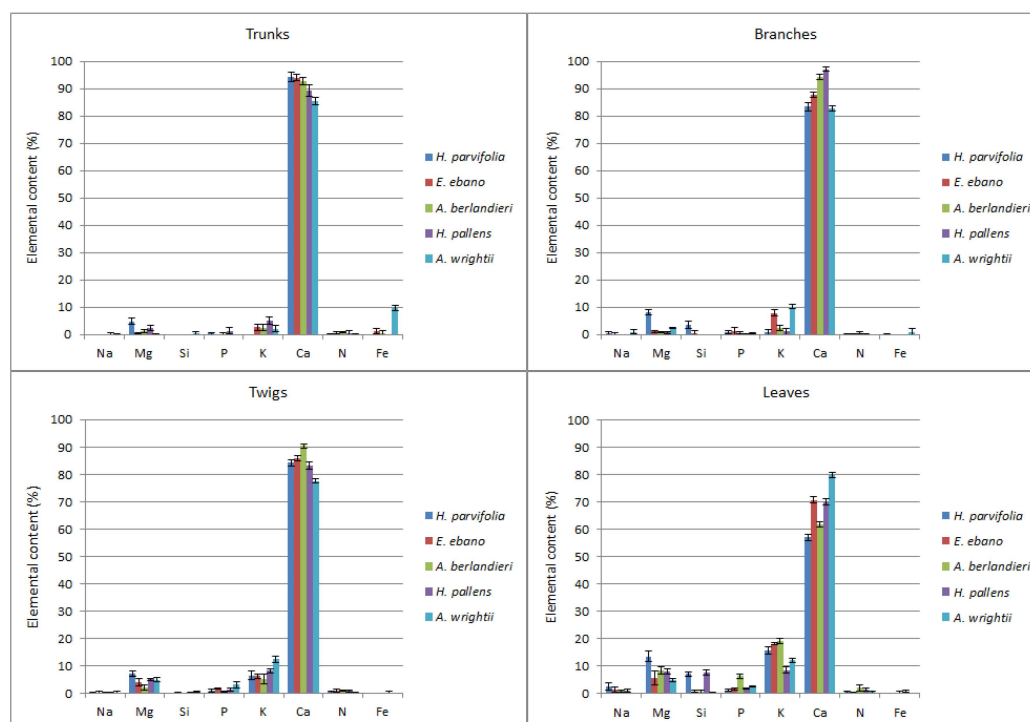
The ash content presented a similar pattern for all species, in an ascendant order of the biomass components: trunk < branches < twigs < leaves, with values from 1.09% to 2.29% for trunks, 0.86% to 2.75% for branches, 4.26% to 6.76% for twigs and 5.77% to 11.79% for leaves (Table 2). For *H. parvifolia*, *A. berlandieri* and *A. wrightii*, slight deviations from the general pattern could be recognized, i.e., the values for branches of *H. parvifolia* and *A. wrightii* were slightly higher than for trunks and for

*A. berlandieri* the order was changed between twigs and leaves with a slightly higher amount of ash in twigs. The analysis of variance showed highly significant differences ( $p < 0.001$ ) between species and between biomass components of trees. A similar result has been reported by Young and Guinn [38], in the distribution of 12 inorganic elements in various parts of the tree (roots, bark, wood and leaves), determining that the inorganic content varies depending on the environmental conditions in which the tree develops. The lowest values were recorded in the trunks (1.09%) and branches (0.86%) of *A. wrightii*, while the highest amount of ash was presented in the leaves of *H. parvifolia*. The high ash content in twigs and especially in leaves confirms the demineralization of the trunk towards leaves. This is because before the fall of the leaves, the sap is concentrated in them and at detaching, demineralizes the trunk [39].

By determining the chemical composition of *Haematoxylum brasiletto*, Ávila and Rutiaga [40] found ash values of 4.31% in sapwood and 2.88% in heartwood, values similar to those obtained in this study, for branches and trunks, respectively. However, the same authors reported up to 18.20% in the bark of this species.

### 3.2.3. Mineral Elements

The proportional disposition of mineral elements in the different biomass components of the five investigated species of the Mexican semi-arid land are presented in Figure 2. The absolute amounts of inorganic compounds correspond with the ash content given in Table 2.



**Figure 2.** Mineral elements content (%) of five planted timber species of the Mexican semi-arid land in different biomass components (trunks, branches, twigs and leaves).

Figure 2 shows very clearly that calcium (57.03%–95.53%) is the main mineral element in all biomass components of all species, followed by potassium (0.95%–19.21%) and magnesium (0.88% to 13.47%). These results represent the typical distribution of mineral elements in trees, as has also been observed by Fengel and Wegener [36] and Rojas [11], who found large amounts of these elements in wood ashes of four conifers (*Abies religiosa*, *Pinus montezumae*, *P. pseudostrobus* and *P. leiophylla*), with values up to 80%. According to Hon and Shiraishi [41], these elements can exist in the wood as oxalates, carbonates and sulfates. These three elements belong to the group of seven elements that are



named macro elements or macronutrients (magnesium, phosphorus, sulfur, potassium, calcium, and nitrogen), necessary for plants growth [42].

In all samples of all biomass components of the trees, traces of Nitrogen (0.17%–1.53%), Phosphorus (0.06%–5.51%), Sodium (0.02%–1.3%), and Silicon (0.004%–7.59%) were found. The registered range of these elements is very wide, compared to the findings by Martinez-Perez *et al.* [43] of 0.04% to 1.20% in the bark of six fruit trees.

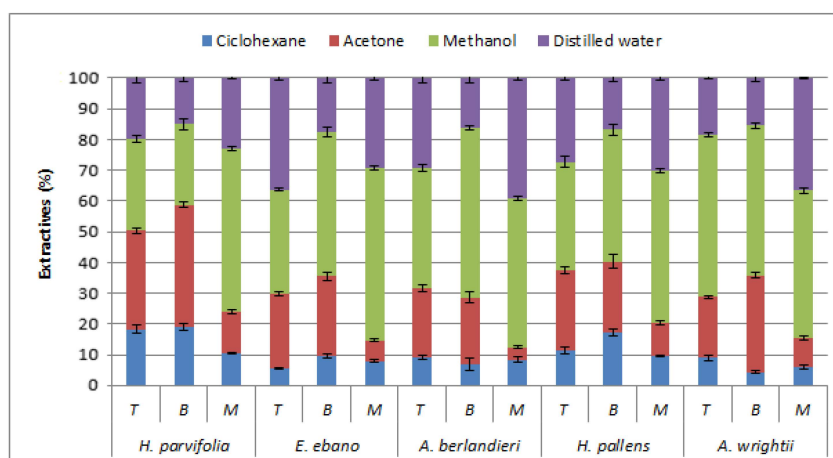
The results for sodium also showed a wide range with maximum values as reported by Correa-Méndez *et al.* [44] for ashes of sawdust and chips, 1.4% and 1.0%, respectively. These values are lower, but in the same magnitude as the results (2.0%–4.4%) found by Revilla [45], when analyzing wood of *P. cembroides*, *P. johannis*, *P. pinceana* and *P. maximartinezii*. For the content of Phosphorous, Correa-Mendez *et al.* [44] reported average values of 4.9% in the ashes of sawdust and 4.0% in the chips, which are again similar to the upper limit of the range obtained in the present work.

These elements affect the ash melting behavior, the deposit formation, the fly ash and aerosol emissions as well as corrosion and the utilization or disposal of the ashes [46]. Ca and Mg usually increase the ash melting point, while K and Na decrease it [47,48]. Low melting alkali and aluminosilicates may also significantly decrease the ash melting point [49]. This can also cause sintering or slag formation in the combustion chamber [46].

### 3.2.4. Extractive Compounds

The extractives content varied significantly ( $p \leq 0.05$ ) both between species and by biomass components, ranging from 11.97% to 38.12% in trunks, 9.16% to 19.37% in branches and 22.01% to 31.81% in twigs (Table 2). For *H. parvifolia*, *A. berlandieri* and *H. pallens*, considerably higher amounts were found in twigs compared to trunks and branches. Looking to *E. ebano*, the value for trunks was significant higher than for the other sections and for *A. wrightii*, the results for all sections were relatively close together. Mostly higher values for trunks than for branches are in accordance to the results of Rojas [11] reported with conifers, caused by the general higher percentage of extractives in heartwood compared to sapwood.

The proportions of extractives obtained from the solvents of increasing polarity are presented in Figure 3. The maximum amounts are found in the methanol fraction, with the higher values for twigs of *H. parvifolia* (17.03%), *E. Ebano* (13.96%), *A. berlandieri* (14.62%) and *H. pallens* (15.60%), and trunks of *E. ebano* (13.72%) and *A. wrightii* (14.41%). Lower amounts of extractives were obtained in the cyclohexane fraction, in the range of 0.67% to 3.36%, but higher than the range of 1.03% to 1.33% found by Ávila and Rutiaga [40] in sapwood, heartwood and bark of *Haematoxylum brasiletto*.



**Figure 3.** Amounts of extractives from five timber species of the semi-arid land of Mexico, in different biomass components (T = trunk, B = branches and M = twigs) with different solvents.

In general, a sequential pattern of decreasing amounts of extractives depending on the solvent was observed: Methanol > Distilled water > Acetone > Cyclohexane (Figure 3). This pattern of lower solubility in nonpolar solvents, followed by higher solubility in solvents of medium polarity and decreasing again in the aqueous extraction was also observed by successive extraction of heartwood from *Andira inermis* [28] and heartwood from *Enterolobium cyclocarpum* [50].

The content of extractives influences the physical and mechanical properties of the tree, by decreasing the moisture content [51,52], which is an important factor in term of energy. The yields obtained in this work are higher than the range of 2.4% to 7.7% reported for species of pine [36,53,54]. This indicates that the species of the semi-arid land of Mexico are less vulnerable to different changes in humidity, improving its availability for energy production.

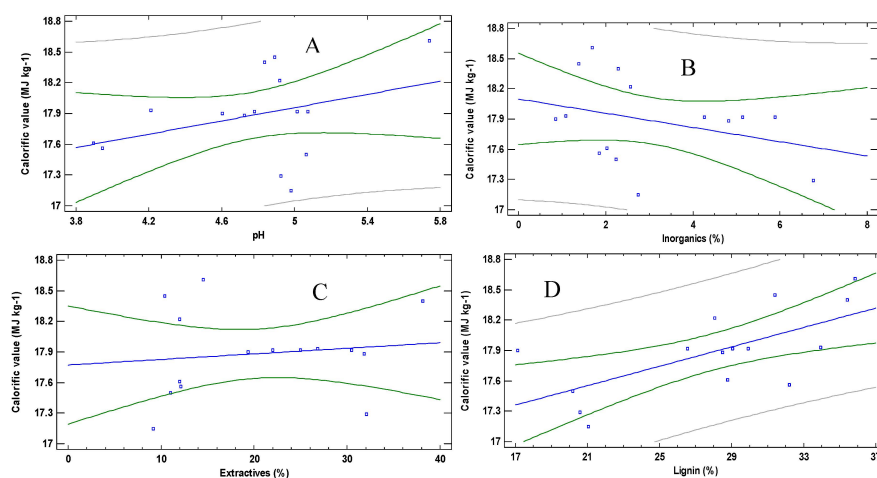
### 3.2.5. Runkel Lignin

The content of lignin varied significantly ( $p \leq 0.05$ ) from 28.78% to 35.84% for trunks, 17.14% to 31.39% for branches and 20.61% to 29.92% for twigs (Table 2). The range of the lignin amounts obtained from trunks is higher than from heartwood of the tropical wood species *Dalbergia granadillo* (26.25% to 26.50%) and *Platymiscium lasiocarpum* (25.25% to 25.95%) found by Rutiaga *et al.* [55]. The trunks presented the highest percentage of lignin for all the species, followed by twigs and with the lowest amounts for branches, with the exception of *H. parvifolia*, with a reversed order for the amounts in twigs and branches. Looking to the variance of the results within each section of each species, only moderate differences were found, confirming the observation of Fonseca [54], who did not find significant differences for the lignin content of *Pinus oocarpa* and *P. maximinoi*.

The ranges registered both for branches as twigs of the species studied included the highest value published by Bernabé *et al.* [56] for pines, in wood of *Pinus leiophylla* (28.5%) and by Rutiaga [57] for the heartwood of *Pinus pseudostrobus* (27.6%).

### 3.3. Correlations between Calorific Value and Chemical Components in Different Sections of the Studied Species

The correlation analyses were done with data from the woody biomass components of the trees without data for leaves. The calorific value correlated with chemical components (Figure 4) showed a tendency to decrease with a higher value of ash content (Figure 4B), as noted in the literature [36,43]. This tendency for calorific value is the reversed of lignin (Figure 4D) and the pH (Figure 4A), with correlation coefficients of 0.66 and 0.36, respectively (Table 3). Only a weak correlation of increasing calorific value with increasing amount of extractables could be noticed, with a correlation coefficient of 0.13 (Figure 4D).



**Figure 4.** Linear regressions and error bounds at 95% confidence interval of the calorific value in function of chemical constituents (A: pH, B: Inorganics, C: extractives and D: lignin) of five timber species of the Mexican semi-arid land.



**Table 3.** Equations of linear regression and multiple correlations between calorific value (CV) and chemical constituents of the studied timber species of the Mexican semi-arid land.

N°	Parameters	Equations	R <sup>2</sup>	r	P
1	CV & pH	CV = 16.3406 + 0.323322 × pH	13.13	0.36	0.184
2	CV & Inorganics	CV = 18.0988 − 0.070599 × Inorganics	9.77	−0.31	0.257
3	CV & Extractives	CV = 17.7722 + 0.00546609 × Extractives	1.59	0.13	0.654
4	CV & Lignin	<b>CV = 16.5477 + 0.0478768 × Lignin</b>	<b>44.04</b>	<b>0.66</b>	<b>0.007*</b>
5	CV, pH, Inorganics	CV = 16.2072 + 0.411899 × pH − 0.0951561 × Inorganics	29.90	−	0.119
6	CV, pH, Extractives	CV = 16.2524 + 0.320308 × pH + 0.00501283 × Extractives	14.47	−	0.392
7	CV, pH, Lignin	<b>CV = 14.8803 + 0.343794 × pH + 0.0488191 × Lignin</b>	<b>58.86</b>	−	<b>0.005*</b>
8	CV, Inorganics, Extractives	CV = 17.8816 − 0.123761 × Inorganics + 0.018522 × Extractives	22.53	−	0.216
9	CV, Inorganics, Lignin	CV = 16.7467 − 0.0400171 × Inorganics + 0.0451078 × Lignin	47.03	−	0.022*
10	CV, Extractives, Lignin	CV = 16.5365 + 0.000864855 × Extractives + 0.0476448 × Lignin	44.08	−	0.031*

R<sup>2</sup> = determination coefficient, r = correlation coefficient, P = probability at 5%, \* significant value ( $p \leq 0.05$ ).

As for the lignin, the correlation coefficient of 0.66 has been registered (Table 3), indicating a moderately strong correlation with the calorific value, which can be justified in 44% of cases (R<sup>2</sup>). The resulting model can be applied for future observations, as it is statistically significant ( $p < 0.05$ ). This result agrees with that reported by Francescato *et al.* [34], who pointed out that high lignin values in combustible materials increases their fuel quality. Guadalfajara [39] reports a high energy content in conifers compared to deciduous wood, caused by their high resin content with calorific value of about 38 MJ kg<sup>−1</sup> and their higher content of lignin, with calorific value of about 25 MJ kg<sup>−1</sup>.

According to Rojas [11], lignin is one of the world's largest industrial wastes products when it is disposed as derivatives of lignin in sulfite liquor in pulp production from wood. This residue is generally proposed as fuel for generating heat but with the disadvantage of an extremely high sulfur content.

Significant differences ( $p \leq 0.05$ ) were registered between calorific value, extractives and lignin; but with R<sup>2</sup> = 44.08%, similar to what is stated between calorific value and lignin, *i.e.*, the influence from adding extractives to the model is negligible.

However, adding ash content instead of extractives, the model was improved, with R<sup>2</sup> = 47% ( $p = 0.02$ ), although the inorganics had a negative effect on the calorific value. When considering the pH and lignin, the highest value of R<sup>2</sup> (58.86%) was obtained. Therefore, acidity and lignin together have a significant influence on the calorific value ( $p = 0.005$ ).

#### 4. Conclusions

The evaluation of the chemical constituents of five tree species from the semi-arid land of Mexico allowed knowing their patterns of variation within and between species and, especially, their energy value. The pH reflected an acidic trend in all biomass components of all species. The amount and composition of mineral elements varied depending on species and biomass components, with the general ascendant order trunk < branches < twigs < leaves, with calcium as the major element in the ashes of these species. The extractives showed the sequential pattern Methanol > Distilled Water > Acetone > Cyclohexane, according to a decreasing gradient performance, with a greater proportion in twigs for *H. parvifolia*, *E. ebano* and *A. berlandieri*, and in trunks for *E. ebano* and *A. wrightii*. For lignin, the trunks presented the greater percentage in all species, followed by twigs, except in *H. parvifolia* where a greater percentage of lignin was reported in branches than in twigs. The calorific value showed higher values in trunks than in branches. However, the greatest value was recorded in leaves of *E. ebano*. On the correlations studied, lignin and acid resulted determinant in the energy potential. However, the total inorganic content is a factor to consider, as it indicates monitoring is needed for its use as energy.

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## References

1. Orea, U.V.; Carballo, L.R.A.; Cordero, E.M. Apuntes sobre la composición química de la madera. Monography published. 2004. Available online: <http://www1.monografias.com/trabajos15/composicion-madera/composicion-madera.shtml> (accessed on 22 September 2015).
2. Twenergy. La biomasa forestal se abre paso en México. 2014. Available online: <http://twenergy.com/a/la-biomasa-forestal-se-abre-paso-en-mexico-1225> (accessed on 28 July 2015).
3. Gutiérrez, Y. Crisis energética en el mundo. 2012. Available online: <http://www.miambiente.com.mx/sustentabilidad1/crisis-energetica-en-el-mundo> (accessed on 16 August 2015).
4. Mediavilla, M. Una visión global de la crisis energética. *Revista. El Ecologista*. N° 73. 2012. Available online: <http://www.ecologistasenaccion.org/article8042.html> (accessed on 19 June 2015).
5. Semarnat (Secretaría de Medio Ambiente y Recursos Naturales). Compendio de Estadística Ambientales. 2010. Available online: <http://aplicaciones.semarnat.gob.mx/estadisticas/compendio2010/index.html> (accessed on 23 June 2015).
6. Rzedowski de Calderón, G.; Rzedowski, J. Presentación. Guía para los autores y normas editoriales. Flora del Bajío y de Regiones Adyacentes. In *Fascículo Complementario I*; Instituto de Ecología A.C. Centro Regional del Bajío: Pátzcuaro, Michoacan, Mexico, 1991.
7. Instituto Nacional de Estadística, Geografía e Informática (INEGI). *Carta de uso del suelo y vegetación. Hoja Pachuca*; Esc. 1:1 000 000; Sistema meteorológico mexicano: Mexico City, Mexico, 1997.
8. González, M.F. *Las Zonas Áridas y Semiáridas de México y su Vegetación*; Secretaría de Medio Ambiente y Recursos Naturales, Instituto Nacional de Ecología: Mexico City, Mexico, 2012.
9. Toledo, V.M.; Ordoñez, M.J. The biodiversity scenario of México: A review of terrestrial habitats. In *Biological Diversity of Mexico: Origins and Distribution*; Ramamoorthy, T.P., Bye, R., Lot, A., Fa, J., Eds.; Oxford University Press: New York, NY, USA, 1993; pp. 757–777.
10. Challenger, A. *Utilización y Conservación de los Ecosistemas Terrestres de México. Pasado, Presente y Futuro*; Comisión Nacional para el Conocimiento y Uso de la Biodiversidad-Instituto de Biología, Universidad Nacional Autónoma de México: Mexico City, Mexico, 1998.
11. Rojas, L.L. Evaluación de la Composición química y Propiedades físicas de Madera y Corteza de Cuatro coníferas Para la Producción de Bioenergía. Tesis de Maestría, Facultad de Ciencias Forestales, Universidad Autónoma de Nuevo León, México, 2013; p. 55.
12. García-Hernández, J.; Jurado, E. Characterization of scrub in pristine conditions at Linares, N.L., Mexico. *Ra Ximhai* **2008**, *1*, 1–21.
13. Correa, J.B. Evaluación y cuantificación de los cambios del uso del suelo mediante imágenes de Satélite en los municipios de Linares y Hualahuises, N.L. Tesis Profesional, Fac. de Ciencias Forestales, U.A.N.L., México, 1996; p. 47.
14. Elizondo, A. El mercado de la madera en México. Informes en Productos Mexicanos de Madera Certificada. Dirección General de Investigación en Política y Economía Ambiental. Instituto Nacional de Ecología, 2006. Available online: [www.ine.gob.mx/dgipea/bosq\\_madera.html](http://www.ine.gob.mx/dgipea/bosq_madera.html) (accessed on 10 October 2015).
15. Borja, V.M. *Aprovechamiento de los Residuos Forestales Para uso Energético*; Universidad Politécnica de Valencia: España, Spain, 2006.
16. FAO. *Conservación de Energía en las Industrias Mecánicas Forestales*; FAO: Rome, Italy, 1991; p. 93.
17. García, R.; Pizarro, C.; Lavín, A.G.; Bueno, J.L. Characterization of Spanish biomass wastes for energy use. *Bioresour. Technol.* **2012**, *103*, 249–258. [CrossRef] [PubMed]

18. Vassilev, S.V.; Baxter, D.; Andersen, L.K.; Vassileva, C.G.; Morgan, T.J. An overview of the organic and inorganic phase composition of biomass. *Fuel* **2012**, *94*, 1–33. [[CrossRef](#)]
19. Jara, E.R.P. *O Poder calorífico de Algumas Madeiras que Ocorrem no Brasil*; Instituto de Pesquisas Tecnológicas: São Paulo, Brasil, 1989; p. 6.
20. Werkelin, J.; Skrifvars, B.J.; Zevenhoven, M.; Holmbom, B.; Hupa, M. Chemical forms of ash-forming elements in woody biomass fuels. *Fuel* **2010**, *89*, 481–493. [[CrossRef](#)]
21. Cunha, M.P.; Pontes, C.L.; Cruz, F.I.; Cabral, M.F.; Cunha Neto, Z.B.; Barbosa, A.P. Estudio Químico de 55 especies lenhosas para geracao de energia em caldeiras. In 3°. *Encontro Brasileiro em madeiras e em estruturas de madeira. Anais, v.2*; Instituto Brasileiro da Madeira e das Estruturas de Madeira (Ibramem): Sao Carlos, Brasil, 1989.
22. Foroughbakhch, R.P.; Hernández-Piñero, J.L.; Carrillo-Parra, A. Adaptability, growth and firewood volume yield of multipurpose tree species in semiarid regions of Northeastern Mexico. *Int. J. Agric. Pol. Res.* **2014**, *2*, 444–453.
23. García, E. *Modificaciones al Sistema de Clasificación Climática de Koppen Para Adaptarlo a las Condiciones de la República Mexicana*, 3r ed.; UNAM: México D.F., 2004; p. 252.
24. Maginot, N.H.; Rahim, F.P.; Artemio, C.P.; Lidia-Rosaura, S.C. Estimation of Timber Production of Five Species of the Tamaulipas Thorny Shrubs Growing in Native Stands and Plantations. *OJF* **2014**, *4*, 239–248. [[CrossRef](#)]
25. Technical Association for Pulp and Paper Industry (TAPPI). *TAPPI Test Methods (1994–1995)*; TAPPI Press: Atlanta, GA, USA, 2000.
26. ISO 17225, 1. *Solid Biofuels—Fuel Specifications and Classes—Part 1: General Requirements*; International Organization for Standardization: Geneva, Switzerland, 2014.
27. Sandermann, W.; Rothkamm, M. Über die Bedeutung der pH-Werte von Handelshölzern und deren Bedeutung für die Praxis. *Holz. Roh. Werkst.* **1959**, *17*, 433–440. [[CrossRef](#)]
28. Téllez, S.C.; Ochoa-Ruiz, H.G.; San Juan-Dueñas, R.; Rutiaga-Quiñones, J.G. Componentes químicos del duramen de *Andira inermis* (W. Wright) DC. (Leguminosae). *Rev. Chapingo. SER CIE* **2010**, *16*, 87–93.
29. Schwanninger, M.; Hinterstoisser, B. Comparison of the classical wood extraction method using a soxhlet apparatus with an advanced extraction method. *Holz. Roh. Werkst.* **2002**, *60*, 343–346. [[CrossRef](#)]
30. Runkel, R.; Wilke, K.D. Zur Kenntnis des thermoplastischen Verhaltens von Holz. *Holz. Roh. Werkst.* **1951**, *9*, 260–270. [[CrossRef](#)]
31. Statistical Graphics Corporation. Statgraphics Centurion (Computer Program) Version XV. Warrenton: Statistical Graphics Corporation, 2002. Available online: [www.statgraphics.com](http://www.statgraphics.com) (accessed on 21 July 2015).
32. Kollmann, F. *Tecnología de la Madera y sus Aplicaciones*; Instituto Forestal de Investigaciones y Experiencias y Servicio de la Madera: Madrid, España, 1959; Volume 1.
33. Quirino, W. Poder calorífico da madeira e de materiais ligno-celulósicos. *Rev. Madeira* **2005**, *89*, 100–106.
34. Francescato, V.; Antonini, E.; Bergomi, L.Z.; Metschina, C.; Schnedl, C.; Krajnc, N.; Kosciuk, K.; Gradziuk, P.; Nocentini, G.; Stranieri, S. *Wood Fuels Handbook*; AIEL—Italian Agriforestry Energy Association: Legnano, Italy, 2008.
35. McNamara, W.S.; Sullivan, S.E.; Higgins, J.C. pH Measurements on northeastern woods. *Wood Sci.* **1970**, *3*, 48–51.
36. Fengel, D.; Wegener, G. *Wood Chemistry, Ultrastructure, Reactions*; Walter de Gruyter: Berlin, Germany, 1989; p. 415.
37. Volz, K.R. Influence of inorganic content on the pH of bark. *Holz-Zentralbl.* **1971**, *97*, 1783.
38. Young, H.E.; Guinn, V.P. Chemical elements in complete mature trees. *Forest. Prod. J.* **1966**, *21*, 56–59.
39. Guadalfajara, A.B. Producción de sal Culinaria de Alta Calidad con Tecnologías Renovables. Tesis, Escuela Técnica superior de Ingeniería (ICAI), Universidad Pontificia Comillas de Madrid, Spain, 2015; p. 125.
40. Ávila-Calderón, L.E.; Rutiaga-Quiñones, J.G. Chemical components of the wood and bark of *Haematoxylum brasiletto* Karsten (Leguminosae). *Madera y Bosque* **2014**, *20*, 153–158.
41. Hon, D.; Shiraichi, N. *Wood and Cellulosic Chemistry*, 2nd ed.; Marcel Dekker: New York, NY, USA, 2001; p. 914.
42. Gil, M.F. *Elementos de Fisiología Vegetal*; Ediciones Mundi-Prensa: Madrid, España, 1995.
43. Martínez-Pérez, R.; Pedraza-Bucio, F.E.; Apolinar-Cortes, J.; López-Miranda, J.; Rutiaga-Quiñones, J.G. Poder calorífico y material inorgánico en la corteza de seis árboles frutales. *Rev. Chapingo SER CIE* **2012**, *18*, 375–384.

44. Correa-Méndez, F.; Carrillo-Parra, A.; Rutiaga-Quiñones, J.G.; Márquez-Montesino, F.; González-Rodríguez, H.; Jurado-Ybarra, E.; Garza-Ocañas, F. Contenido de humedad y sustancias inorgánicas en subproductos maderables de pino para su uso en pélets y briquetas. *Rev. Chapingo SER CIE* **2014**, *20*, 77–88.
45. Revilla, G.E. Química de la Madera de Cuatro Pinos Mexicanos de la Subsección Cembroides. Tesis, Universidad Autónoma Chapingo, Chapingo, Texcoco, Edo. de México, México, 2011.
46. Biedermann, F.; Obernberger, I. Ash-related problems during biomass combustion and possibilities for a sustainable ash utilization, 2005. Available online: <http://www.bios-bioenergy.at/uploads/media/Paper-Biedermann-AshRelated-2005-10-11.pdf> (accessed on 22 December 2015).
47. Obernberger, I. *Nutzung fester biomasse in verbrennungsanlagen unter besonderer berücksichtigung des verhaltens aschebildender elemente, schriftenreihe "Thermische Biomassenutzung"*; DBV-Verlag der Technischen Universität Graz: Graz, Austria, 1997.
48. Van Loo, S.; Koppejan, J. *Handbook of Biomass Combustion and Co-Firing*; Bioenergy task 32; International Energy Agency (IEA): Amsterdam, Netherlands, 2002.
49. Miles, T.R. *Alkali Deposits Found in Biomass Power Plants*; Research Report NREI/TP-443-8142-SAND 96-8225; National Renewable Energy Laboratory: Oakridge, TN, USA, 1996; Volume I and II.
50. Ramos-Pantaleón, D.; Ávila-Calderón, L.E.A.; Ochoa Ruíz, H.G.; Rutiaga- Quiñones, J.G. Contenido de sustancias extraíbles en la madera de *Enterolobium cyclocarpum* (Jacq.) Griseb. (*Leguminosae*). *Cienc. Nicolaita* **2011**, *53*, 7–19.
51. Poblete, H.; Rodríguez, S.; Zárate, M. *Extraíbles de la Madera, sus Características y Efectos Sobre la Utilización de esta Materia Prima*; Publicación docente núm. 34; Facultad de Ciencias Forestales; Universidad Austral de Chile: Valdivia, Chile, 1991; p. 51.
52. Ávila, L.E.; Herrera, M.A. Efecto de los extraíbles en tres propiedades físicas de la madera de *Enterolobium cyclocarpum* procedente de Michoacán, México. *Bosque* **2012**, *33*, 115–120. [[CrossRef](#)]
53. Rodríguez, L.M.E. Determinación de los componentes químicos de la madera de pino blanco (*Pinus pseudostrobus* Lindl.) proveniente de la finca Las Victorias, Patzún, Chimaltenango. Tesis Profesional, Escuela de Ingeniería Química, Universidad de San Carlos de Guatemala, Ciudad de Guatemala, Guatemala, 2005; p. 90.
54. Fonseca, M.R. Determinación de la composición química de la madera de pino candelillo (*Pinus maximinoi* H.E. Moore) procedente de la finca Río Frío, Tactic, Alta Verapaz. Tesis Profesional, Escuela de Ingeniería Química, Universidad de San Carlos de Guatemala, 2006; p. 125.
55. Rutiaga-Quiñones, J.G.; Pedraza Bucio, F.E.; López Albarrán, P. Componentes químicos principales de la madera de *Dalbergia granadillo* Pittier y de *Platymiscium lasiocarpum* Sandw. *Rev. Chapingo SER CIE* **2010**, *16*, 179–186. [[CrossRef](#)]
56. Bernabé-Santiago, R.; Ávila-Calderón, L.E.A.; Rutiaga-Quiñones, J.G. Componentes químicos de la madera de cinco especies de pino del municipio de Morelia, Michoacán. *Madera Bosques* **2013**, *19*, 21–35.
57. Rutiaga Quiñones, J.G. *Chemische und biologische Untersuchungen zum Verhalten dauerhafter Holzarten und ihrer Extrakte gegenüber holzabbauenden Pilzen*; Buchverlag Gräffeling: München, Germany, 2001; p. 201 S.

