agronomy

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# Biomass Identification from Proximate Analysis: Characterization of Residual Vegetable Materials in Andean Areas

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**Abstract:** This work was aimed at the characterization of residual generated biomass from pruned tree species present in the Andean areas of Ecuador as a source of energy, both in plantations and in urban areas, as a response to the change in the energy matrix proposed by the Ecuadorian government. From the proximate analysis (volatiles, ashes, and fixed carbon content), elemental analysis (C, H, N, S, O, and Cl), structural analysis (cellulose, lignin, and hemicellulose content), and higher heating value, the studied species were pine (*Pinus radiata*), cypress (*Cupressus macrocarpa*), eucalyptus (*Eucalyptus globulus*), poplar (*Populus* sp.), arupo (Chionanthus *pubescens*), alder (*Alnus Acuminata*), caper spurge (*Euphorbia laurifolia*), and lime (*Sambucus nigra* L.) trees. We evaluated the influence of the presence of leaves in the biomass. From this characterization, we developed a method based on obtaining the main components for the identification of the biomass's species. If the origin of the biomass was unknown, this method enabled us to identify the species, with all its characteristics. If the origin of the biomass was unknown, this innovative method enabled the identification of the species from the lignocellulosic biomass, with all of its characteristics. Finally, we developed regression models that relate the higher heating value to the elemental, proximate, and structural composition.

**Keywords:** biomass identification; biomass characterization; bioenergy; higher heating value



**Citation:** Velázquez Martí, B.; Gaibor-Chávez, J.; Franco Rodríguez, J.E.; López Cortés, I. Biomass Identification from Proximate Analysis: Characterization of Residual Vegetable Materials in Andean Areas. *Agronomy* **2023**, *13*, 2347. https://doi.org/10.3390/agronomy13092347

Academic Editor: Giuseppe Squillaci

Received: 11 August 2023
Revised: 2 September 2023
Accepted: 5 September 2023
Published: 9 September 2023



## 1. Introduction

The consensus is that fossil energy reserves have a finite nature and that they have a substantial role in exacerbating climate change. Conversely, nuclear energy has significant potential for environmental harm in the event of an accident [1–3]. Due to these developments, the new energy approach highlights renewable energy sources as a substitute to fulfill local energy requirements [4], where biomass acquires a more important role to meet thermal needs [5]. Biomass is characterized as any organic material of biological origin that has not turned into fossilized matter and can be converted into biofuels. This includes materials derived from agriculture (both plant and animal sources), forestry, and related sectors, which encompass fishing and aquaculture. Additionally, biomass encompasses the biodegradable portion of industrial and urban waste (Directiva 2009/28/CE, 2009). Its conversion is carried out by using technologies such as direct combustion, liquefaction, hydrolysis, pyrolysis, gasification, and fermentation, among others [6,7]. To choose between these technologies, one needs to conduct a series of tests and analyses. This includes assessing factors such as moisture, volatile substances, fixed carbon, and ash contents through proximate analysis. Additionally, one should perform elemental analysis to determine the levels of carbon, hydrogen, nitrogen, sulfur, oxygen, and chlorine. Structural analysis is also important, which involves examining components such as lignin, cellulose, hemicellulose, and extractives. Furthermore, conducting thermogravimetric and fermentative analyses is crucial. Lastly, one should calculate both the higher heating value (HHV) and the lower heating value (LHV) to complete the evaluation process. The processes involved in transforming biomass and the quality of the resulting biofuels are contingent on these specific properties [8]. This is why many authors have created mathematical models to predict the higher heating value of biomass from the parameters of each type of analysis [9]. However, despite the fact that the use of biomass in rural areas is beginning to become of interest to farmers in Ecuador, their knowledge of the raw materials to be used as bioenergy is still very limited.

A significant quantity of unused organic material that could potentially be converted into energy can be derived from the maintenance of urban trees and plantations in Ecuador's Bolívar Province. The leftover organic matter, found in both woody and non-woody plant species, exhibits considerable variation based on factors such as the species type, planting density, crop management system, and tree size. At present, these leftover materials are often left in heaps, abandoned, or disposed of through burning in fields, resulting in no immediate advantages. In fact, this practice incurs extra expenses and hinders other agricultural activities. A significant amount of previous work has been published on the study of calculating and/or measuring the energy properties of woody biomass across many species. However, pruning residues are composed of both wood and leaves. The ratio of these components (wood biomass to leaf biomass) can influence the energy characteristics of the biomass overall. In undeveloped countries, where the origin of chipped biomass may be unknown, the development of methods to identify the species is very useful in order to know all of its characteristics such as the calorific power, solid density, and bulk density; elemental analysis (C, H, N, S, O, and Cl) and structural analysis (cellulose, lignin, and hemicellulose content) are among these methods. For this reason, this work proposes a thermochemical characterization of the species, which can be used in this area to identify the species, such as pine (*Pinus radiata*), cypress (*Cupressus macrocarpa*), eucalyptus (*Eucalyptus globulus*), poplar (*Populus* sp.), arupo (*Chionanthus pubescens*), alder (*Alnus acuminata*), and lime (*Sambucus nigra* L.) trees, which are species that are used in urban areas and from which periodic pruning material is obtained, and which can also be considered as energy crops in Andean areas.

In this work, we developed a method for the identification of biomass from proximate analysis (volatile, ash, and fixed carbon content) based on obtaining the main components and through the application of a probability neural net. Proximate analysis is the least expensive method of energy characterization. It is available in most biomass laboratories. Therefore, developing methods to evaluate all the parameters of biomass represents a great innovation. The first step was to identify the biomass; all the parameters can be found in the tables. Nevertheless, in addition, we developed models that relate the higher heating value to the elemental, proximate, and structural composition.

## 2. Materials and Methods

### *2.1. Sampling and Analysis*

Initially, 25 sampling points were chosen from the Province of Bolívar (Ecuador), which included forest, agricultural, and urban areas. This province is at an altitude of 2500 m. The land has a slope from 0 to 30%; the temperature ranges between 6 and 18 °C in the highlands and from 18 to 22 °C in the subtropics; and the precipitation varies from 500 to 2000 mm. The water source derives from the melting of the snow on Chimborazo Volcano.

Pine (*Pinus radiata*), cypress (*Cupressus macrocarpa*), eucalyptus (*Eucalyptus globulus*), poplar (Populus sp.), arupo (*Chionanthus pubescens*), alder (*Alnus acuminata*), caper spurge (*Euphorbia laurifolia*), and lime (*Sambucus nigra* L.) trees were identified.

Twenty-five trees of each species were pruned. The samples were collected immediately after pruning by randomly choosing branches of different diameters, which were stored in airtight bags until they reached the laboratory. Samples of branches with leaves and without leaves were taken in order to evaluate their influence on the biomass properties [10].

After separating the leaves from the wood, the leaves were dried in an oven at a constant temperature of 105 °C. The pieces of wood were initially chipped into 10–15 cm particles. Then, they were dried. Later, the samples were crushed in a mill to bring them to a homogeneous size of 3 mm.

After drying, samples of 1 kg of mixtures of wood and leaves were prepared in the proportions indicated in Table 1 with at least 5 repetitions in each combination.

**Table 1.** Combinations of wood and leaf mixtures to be characterized.

| Percentage of Wood by Mass | Percentage of Leaf by Mass |
|---|---|
| 100% | 0% |
| 90% | 10% |
| 80% | 20% |
| 70% | 30% |
| 60% | 40% |
| 50% | 50% |
| 0% | 100% |

The samples were subjected to proximate analysis (volatiles, ash, and fixed carbon content), elemental analysis (C, H, N, S, O, and Cl), structural analysis (cellulose, lignin, and hemicellulose content), and calorific power. The standards used for the analyses are listed in Table 2.

**Table 2.** Standards of analysis for biomass characterization.

| Standard Reference | Title |
|---|---|
| UNE EN ISO 16559 | Solid Biofuels—Terminology, definitions and descriptions |
| UNE EN ISO 14778 | Solid Biofuels—Sampling—Part 1: Sampling methods |
| UNE EN ISO 14780 | Solid Biofuels—Methods for sample preparation |
| UNE EN ISO 18134-2 | Solid Biofuels—Determination of moisture content—oven drying method. Part 2. Simplified method: Total moisture content. |
| UNE EN ISO 18125 | Solid Biofuels—Determination of calorific value |
| UNE EN ISO 18123 | Solid Biofuels—Determination of Volatile Matter Content |
| UNE EN ISO 18122 | Solid Biofuels—Determination of ash content |
| UNE EN ISO 16948 | Solid Biofuels—Determination of total carbon, hydrogen and nitrogen content—Instrumental Methods |
| UNE-EN ISO 16995 | Solid Biofuels—Methods for determining the water-soluble content of chlorine, sodium and potassium |
| UNE-EN ISO 16994 | Solid Biofuels—Determination of total Sulfur and Chlorine content |
| UNE-EN ISO 16967 | Solid Biofuels—Determination of major elements |

The structural analysis was performed according to the analytical method followed by Van Soest [11].

### *2.2. Biomass Identifier*

In order to obtain a biomass species identification system, a principal component analysis (CPA) was applied. This is a statistical technique of information synthesis, or dimension reduction (number of variables). In other words, faced with a database with many variables, the objective is to reduce them to a smaller number, losing as little information as possible. The main components are a linear combination of the original variables, and they are also independent from each other.

If p variables are available, the coordinates of individual $i$ in component 1 and 2 are given by Equations (1) and (2), in which $x_{ij}$ is the standardized value of variable $j$ in individual $i$, that is, the average is subtracted and divided by the standard deviation; $v_{j1}$ and $v_{j2}$ are the weights of each variable in components 1 and 2, respectively.

$$y_{i1} = x_{i1}v_{11} + x_{i2}v_{21} + \ldots + x_{ip}v_{p1} \tag{1}$$

$$y_{i2} = x_{i1}v_{12} + x_{i2}v_{22} + \ldots + x_{ip}v_{p2} \tag{2}$$

The principal components $y_{i1}$ and $y_{i2}$ represent new coordinates chosen in such a way as to include the greatest possible variance. For $n$ individuals, the values of component 1 can be expressed in the matrix form

$$\begin{pmatrix} y_{11} \vdots y_{n1} \end{pmatrix} = \begin{pmatrix} x_{11} \ \ldots \ x_{1p} \vdots \ \ldots \ \vdots x_{n1} \ \ldots \ x_{np} \end{pmatrix} \begin{pmatrix} v_{11} \vdots v_{p1} \end{pmatrix}$$

$$y_1 = Xv_1$$

To obtain the weights $v_1$, Equation (3) is maximized, which is equivalent to obtaining the first eigenvector of the matrix $S = X^T X$, such that $v_1^T v_1 = 1$

$$varY_1 = \frac{1}{n} y_1^T y_1 = \frac{1}{n} v_1^T X^T X v_1 = \frac{1}{n} v_1^T S v_1 \tag{3}$$

To obtain the weights $v_2$, Equation (4) is maximized, which is equivalent to obtaining the second eigenvector of the matrix $S = X^T X$,such that $v_2^T v_1 = 0$, $v_2^T v_2 = 1$

$$cov(Y_1, Y_2) = \frac{1}{n} y_2^T y_1 = \frac{1}{n} v_2^T X^T X v_1 = \frac{1}{n} v_2^T S v_1 \tag{4}$$

The two output values, one per component, are associated with the biomass species, defining classification areas through the application of an additional probabilistic neural network (PNN), applied through the Statgraphics software.

This implies the application of two-stage neural systems PCA + PNN, which is a novelty to refine the classification.

The probabilistic neural network (PNN) is a unidirectional network made up of four layers: the input layer, the hidden pattern layer, the sum layer, and the output decision layer, whose operation results from the Bayesian network and the kernel Fisher discriminant analysis statistical algorithm [12].

The input layer is made up of $a$ neurons, where $a$ is the number of variables that allow classification. Since the PNN takes the output of the principal components, 2 variables enter the PNN ($a = 2$), forming a two-dimensional vector $\vec{y}_i$ $(y_{i1}, y_{i2})$, obtained from the application of the linear combinations of each principal component.

The hidden pattern layer is made up of $n$ neurons, one for each sample used for training. We applied 175 samples for training; therefore, the hidden layer had 172 neurons. Each of the neurons in the hidden layer belongs to one of the possible classes $C = \{C_1, C_2, \ldots C_k\}$, where $C_1$ is pine (*Pinus radiata*), $C_1$ is cypress (*Cupressus macrocarpa*), $C_3$ is eucalyptus (*Eucalyptus globulus*), $C_4$ is poplar (*Populus* sp.), $C_5$ is arupo (*Chionanthus pubescens*), $C_6$ is alder (*Alnus Acuminata*), $C_6$ is caper spurge (*Euphorbia laurifolia*), and $C_7$ is lime (*Sambucus nigra* L.).

The input layer standardizes the values, subtracting the average from each one and dividing the standard deviation of the training individuals in each class. Later, the input neurons feed each of the neurons in the hidden layer.

The hidden layer calculates the distances from the standardized input vector $\vec{y}_{ei}$ to each of the vectors or training patterns $\vec{p}_j$ through the kernel normal standard probability density function, as shown in Equation (5), where $\sigma_k$ is 1, since the input variables are standardized in each group. $h_{ijk}$ represents the chances that an individual with input variables $\vec{y}_{ei}(y_{ei1}, y_{ei2})$, when compared to an individual $j$ pattern, belongs to class $k$.

$$h_{ijk} = \left(2\pi\sigma_k^2\right)^{-a/2} e^{-\frac{(\vec{y}_i - \vec{p}_j)^T (\vec{y}_i - \vec{p}_j)}{2\sigma_k^2}} \tag{5}$$

In the sum layer, the conditional probability or likelihood that each vector $\vec{y}_{ei}$ (the input data) belongs to the $i$-th class is calculated by Equation (6), where $n_k$ is the number of patterns of class $k$ used in the training, $h_{ijk}$, with this being the values obtained from function (6) that belong to the class $k$.

$$P(v \in C_k) = \frac{1}{n_k} \sum_{i=1}^{n_k} h_{ijk} \tag{6}$$

The output layer selects the class with the highest plausibility, according to Equation (7)

$$classify(C_1, C_2, \ldots, C_k) = P\ (v \in C_k) \tag{7}$$

Maximum probability areas are delimited from the PNN for the possible ranges of $y_{ei1}$ and $y_{ei2}$.

After training, another 200 samples are used in order to validate the system.

## 3. Results and Discussion

### *3.1. Calorific Power*

Tables 3 and 4 show the statistical summaries of HHV and LHV. Standardized bias and standardized kurtosis analyze the distribution shape, which can be used to assess whether the sample comes from a normal distribution. Values of these statistics outside the range of −2 to +2 would indicate significant deviations from normality, which would tend to invalidate many of the statistical procedures that are usually applied to these data. In this case, the variables were within the range. Therefore, the average and the standard deviation allowed us to determine the percentage of samples with HHV and LHV values in a defined interval. We can observe that the HHV of the species studied was between 17 and 19.5 MJ/kg, and the LHV varied between 15 and 17 MJ/kg.

**Table 3.** Statistical description of the HHV in the species studied.

| | Average (MJ/kg) | Standard Deviation | Variation Coefficient | Minimum | Maximum | Standard Bias | Standardized Kurtosis |
|---|---|---|---|---|---|---|---|
| Alder | 18.36 | 0.45 | 2.47 | 17.37 | 19.51 | −1.18 | 1.10 |
| Poplar | 18.61 | 0.55 | 2.95 | 17.70 | 19.12 | −1.36 | 1.19 |
| Arupo | 18.41 | 0.34 | 1.87 | 18.08 | 18.97 | 1.32 | 1.11 |
| Cypress | 17.50 | 0.31 | 1.74 | 17.12 | 17.87 | −0.04 | −0.71 |
| Eucalyptus | 17.46 | 0.33 | 1.89 | 17.25 | 18.04 | 1.89 | 2.02 |
| Pine | 18.52 | 0.39 | 2.11 | 18.14 | 19.03 | 0.51 | −1.13 |
| Caper spurge | 18.82 | 0.33 | 1.77 | 18.37 | 19.21 | −0.34 | −0.55 |
| Lime tree | 18.22 | 0.65 | 3.57 | 17.12 | 19.21 | −0.46 | −1.36 |

Figure 1 shows the LSD intervals of the ANOVA analysis that decomposes the variance of HHV [MJ/kg]. It can be observed that the cypress and eucalyptus species had a significantly lower higher heating value than the poplar, lime tree, arupo, alder, and cypress.

**Table 4.** Statistical description of the LHV in the species studied.

| | Average (MJ/kg) | Standard Deviation | Variation Coefficient | Minimum | Maximum | Standard Bias | Standardized Kurtosis |
|---|---|---|---|---|---|---|---|
| Alder | 16.73 | 0.32 | 1.92% | 16.82 | 17.50 | −0.81 | −0.78 |
| Poplar | 16.94 | 0.37 | 1.84% | 16.32 | 17.11 | −0.18 | −0.94 |
| Arupo | 16.59 | 0.32 | 1.97% | 16.25 | 17.12 | 1.15 | 0.99 |
| Cypress | 15.39 | 0.29 | 1.89% | 15.06 | 15.75 | 0.13 | −0.95 |
| Eucalyptus | 15.40 | 0.28 | 1.84% | 15.21 | 15.89 | 1.83 | 1.91 |
| Pine | 16.59 | 0.37 | 2.26% | 16.28 | 17.07 | 0.46 | −1.11 |
| Caper spurge | 16.84 | 0.32 | 1.91% | 16.02 | 17.20 | −0.28 | −0.82 |
| Lime tree | 16.16 | 0.71 | 4.39% | 15.06 | 17.74 | −0.35 | −1.41 |

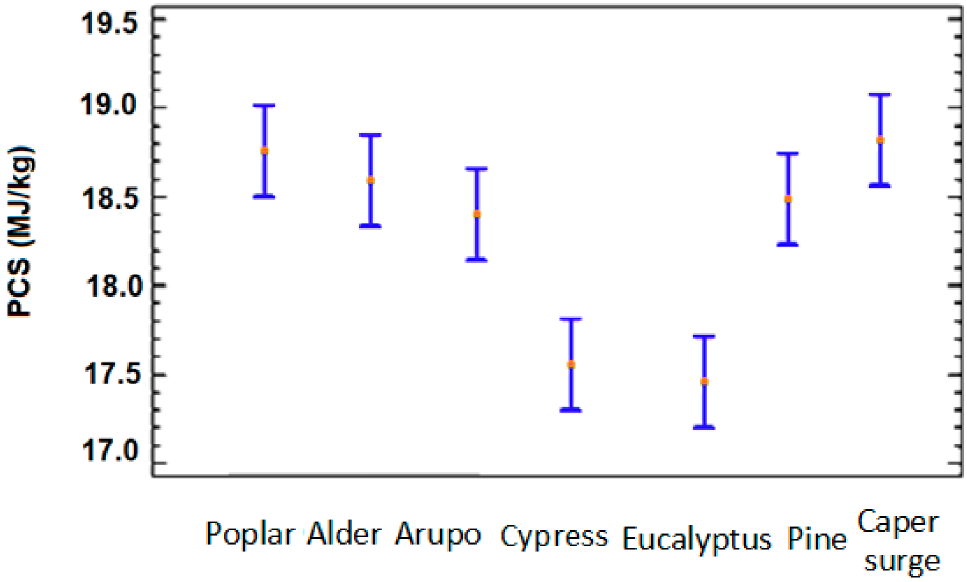



**Figure 1.** LSD intervals of the analysis of variance on the HHV at the 95% confidence level.

### *3.2. Elemental and Proximate Analysis*

The characterization parameters of the different materials are shown in Table 5. The normality of the distribution of all the variables was verified.

No significant differences could be observed between the studied species. The volatiles content was around 80% of the weight. The ash content was less than 3%, except in caper spurge, which was 5.44%. The nitrogen content was less than 1%. The average higher heating value was 18.35 MJ/kg.

Table 6 shows the Pearson correlation coefficients between each pair of variables. These correlation coefficients range from −1 to +1, and they measure the strength of the linear relationship between variables. The asterisk indicates the statistical significance of the estimated correlations with P-values of less than 0.05, which indicate correlations significantly different from zero, with a confidence level of 95.0%.

The % of ashes, volatiles, and fixed carbon showed a significant negative linear relationship between them. This was obvious since, as any of the fractions increased, the other two decreased. The values of these three variables were complementary. On the other hand, we can observe that the content of hydrogen and oxygen influenced the content of volatiles and fixed carbon. Since the analyzed samples were dry, the hydrogen and oxygen present were associated with structural carbohydrates (cellulose, hemicellulose, and lignin), not with water. This can be demonstrated by the fact that the content of these elements barely influenced the calorific power. If the samples were wet, the content of hydrogen and oxygen would be negatively related to the calorific power, since a large content of these elements is linked to the presence of water [10,13]. Apart from that, nitrogen was more closely related to fixed carbon and the carbon content was strongly related to the higher heating value of the samples.

**Table 5.** Proximate and elemental analysis of the species studied.

| | | % Ashes | % Volatiles | % Fixed Carbon | %C | %N | %H | %O | HHV (MJ/kg) |
|---|---|---|---|---|---|---|---|---|---|
| Poplar | Average | 1.29 | 82.21 | 16.5 | 44.152 | 0.642 | 3.917 | 0.873 | 18.334 |
| | Standard deviation | 0.04 | 0.32 | 0.317 | 1.042 | 0.0295 | 0.235 | 1.571 | 0.081 |
| Alder | Average | 1.05 | 82.126 | 16.824 | 51.354 | 0.483 | 3.562 | 38.96 | 18.558 |
| | Standard deviation | 0.06 | 0.438 | 0.383 | 0.649 | 0.016 | 0.086 | 0.684 | 0.466 |
| Arupo | Average | 1.76 | 83.453 | 14.787 | 49.275 | 0.578 | 3.453 | 41.546 | 18.503 |
| | Standard deviation | 0.07 | 0.257 | 0.237 | 1.101 | 0.016 | 0.073 | 0.987 | 0.408 |
| Cypress | Average | 2.19 | 81.341 | 16.469 | 49.446 | 0.459 | 3.769 | 39.68 | 17.306 |
| | Standard deviation | 0.06 | 0.136 | 0.09 | 1.517 | 0.025 | 0.0225 | 1.454 | 0.201 |
| Eucalyptus | Average | 2.19 | 83.45 | 14.36 | 48.998 | 0.477 | 3.405 | 40.519 | 17.554 |
| | Standard deviation | 0.06 | 0.66 | 0.663 | 1.4476 | 0.022 | 0.179 | 1.4692 | 0.422 |
| Caper spurge | Average | 5.44 | 83.04 | 11.52 | 44.97 | 0.51 | 4.777 | 0.417 | 18.64 |
| | Standard deviation | 1.18 | 1.17 | 1.826 | 0.4 | 0.065 | 0.455 | 0.3099 | 0.556 |
| Pine | Average | 1.05 | 82.13 | 16.82 | 51.354 | 0.483 | 3.563 | 38.96 | 18.525 |
| | Standard deviation | 0.06 | 0.44 | 0.383 | 0.649 | 0.016 | 0.086 | 0.684 | 0.467 |
| Lime tree | Average | 2.22 | 80.07 | 17.71 | 50.999 | 0.981 | 3.715 | 38.522 | 18.838 |
| | Standard deviation | 0.05 | 0.39 | 0.33 | 0.41 | 0.03 | 0.05 | 0.48 | 0.32 |

**Table 6.** Pearson correlation coefficients (* significant value with 95% level of confidence).

| | % Ashes | % Volatiles | % Fixed Carbon | % C | % N | % H | % O | HHV (MJ/kg) |
|---|---|---|---|---|---|---|---|---|
| % Ashes | | −0.49 * | −0.03 | −0.07 | −0.02 | 0.0023 | −0.09 | −0.10 |
| % Volatiles | −0.49 * | | −0.85 * | −0.35 | −0.45 | −0.60 * | 0.54 * | −0.23 |
| % Fine carbon | −0.03 | −0.85 * | | 0.44 | 0.53 * | 0.69 * | −0.57 * | 0.33 |
| % C | −0.07 | −0.35 | 0.44 | | 0.13 | 0.2675 | −0.93 * | 0.86 * |
| % N | −0.014 | −0.45 | 0.53 * | 0.13 | | 0.3214 | −0.17 | 0.51 * |
| % H | 0.0023 | −0.60 * | 0.69 * | 0.27 | 0.32 | | −0.45 | 0.04 |
| % O | −0.09 | 0.54 * | −0.57 * | −0.93 * | −0.17 | −0.4455 | | −0.19 |
| HHV (MJ/kg) | −0.10 | −0.23 | 0.33 | 0.86 * | 0.51 * | 0.0395 | −0.19 | |

As there were no significant differences in the parameters of the proximate and elemental analysis, it was not possible to identify the sample immediately, especially if it was crushed material. This encourages us to investigate the possibility of devising identification methods based on these analyses in order to be able to assess the traceability of materials at a commercial level.

### *3.3. Structural Analysis*

In Table 7, we can observe that the content of cellulose, hemicellulose, lignin, and extractives was strongly influenced by the composition of the samples in terms of the percentage of wood and leaves. In all species, the analysis of variance showed that there were significant differences between the different types of mixture. We can see that the content of leaves decreased the mass percentages of cellulose, hemicellulose, and lignin, and increased the percentage of extractives.

**Table 7.** Structural analysis of the species studied (mean ± standard deviation).

| | % Wood | % Sheets | % Cellulose | % Hemicellulose | % Lignin | % Extractives |
|---|---|---|---|---|---|---|
| Poplar | 100 | 0 | 46.16 ± 0.49 | 19.98 ± 0.20 | 7.25 ± 0.25 | 26.60 ± 0.68 |
| | 50 | 50 | 32.04 ± 0.41 | 15.67 ± 0.54 | 8.95 ± 0.38 | 43.33 ± 0.36 |
| | 0 | 100 | 21.59 ± 1.10 | 12.01 ± 0.22 | 12.21 ± 0.13 | 54.18 ± 0.24 |
| Alder | 100 | 0 | 47.57 ± 1.41 | 16.63 ± 0.11 | 7.97 ± 0.32 | 28.87 ± 0.47 |
| | 50 | 50 | 36.28 ± 0.42 | 14.07 ± 0.22 | 7.85 ± 0.05 | 41.80 ± 0.35 |
| | 0 | 100 | 15.72 ± 0.93 | 15.76 ± 0.93 | 6.49 ± 0.60 | 62.02 ± 0.34 |
| Arupo | 100 | 0 | 52.18 ± 0.47 | 19.27 ± 0.21 | 5.30 ± 0.17 | 23.24 ± 0.47 |
| | 50 | 50 | 37.93 ± 0.50 | 15.22 ± 0.23 | 5.55 ± 0.14 | 41.29 ± 0.74 |
| | 0 | 100 | 22.31 ± 1.69 | 12.69 ± 2.49 | 14.49 ± 3.47 | 59.60 ± 0.19 |
| Cypress | 100 | 0 | 54.43 ± 1.81 | 14.32 ± 0.42 | 19.13 ± 0.71 | 12.12 ± 0.31 |
| | 50 | 50 | 30.09 ± 1.63 | 12.13 ± 0.86 | 10.08 ± 0.15 | 47.70 ± 0.18 |
| | 0 | 100 | 17.63 ± 0.62 | 9.48 ± 0.10 | 11.40 ± 0.26 | 64.55 ± 0.24 |
| Eucalyptus | 100 | 0 | 54.64 ± 1.19 | 24.62 ± 0.24 | 5.57 ± 0.21 | 15.17 ± 0.28 |
| | 50 | 50 | 35.15 ± 1.23 | 13.39 ± 0.51 | 3.86 ± 0.52 | 47.60 ± 0.14 |
| | 0 | 100 | 22.88 ± 0.51 | 6.57 ± 0.78 | 2.48 ± 0.37 | 68.06 ± 0.28 |
| Caper spurge | 100 | 0 | 37.18 ± 0.58 | 15.05 ± 0.64 | 7.59 ± 0.85 | 33.27 ± 0.38 |
| | 50 | 50 | 23.46 ± 0.18 | 12.05 ± 0.17 | 5.10 ± 0.24 | 56.16 ± 0.63 |
| | 0 | 100 | 10.79 ± 0.044 | 7.24 ± 0.29 | 2.48 ± 0.15 | 78.50 ± 0.34 |
| Pine | 100 | 0 | 54.74 ± 0.31 | 39.67 ± 1.52 | 14.28 ± 0.37 | 13.93 ± 0.12 |
| | 50 | 50 | 37.06 ± 1.31 | 28.48 ± 0.96 | 10.93 ± 0.47 | 37.41 ± 0.28 |
| | 0 | 100 | 20.67 ± 0.68 | 16.63 ± 0.53 | 8.19 ± 0.25 | 58.63 ± 0.45 |
| Lime tree | 100 | 0 | 51.18 ± 0.56 | 17.48 ± 0.54 | 10.81 ± 0.33 | 20.52 ± 0.65 |
| | 50 | 50 | 27.43 ± 0.90 | 14.45 ± 0.50 | 8.72 ± 0.22 | 49.40 ± 0.35 |
| | 0 | 100 | 12.43 ± 0.61 | 10.68 ± 0.38 | 6.08 ± 0.27 | 70.81 ± 1.21 |

On the other hand, significant differences can be observed between the species, which can be classified into two groups:

(a). Species with high cellulose content: lime tree, pine tree, eucalyptus, cypress, and arupo;
(b). Species with low cellulose content: caper spurge, alder, and poplar.

### *3.4. Regression Models*

A valid regression model for determining the higher heating value from elemental analysis for all the studied species is presented below. Due to the uncertainty in the composition of wood and leaves when the biomass arrives at the processing plant, a general method is proposed, which was obtained from samples with different compositions. We observed that the presented model explains 94% of the variability in the calorific power. The $r^2_{aj}$ 0.93 is presented in order to compare the proposed model with other models with a different number of variables.

$$r^2 = 94.07\%$$

$$r^2_{aj} = 93.01\%$$

$$\text{Standard deviation of the residues} = 0.45\ \text{MJ/kg}$$

$$\text{Mean absolute error (MAE)} = 0.32$$

$$\text{Durbin-Watson statistic} = 2.1906\ (p = 0.4130)$$

$$\text{HHV (MJ/kg)} = -34.3184 + 0.737288\cdot\%\text{Cd} + 1.41779\cdot\%\text{N} + 0.767188\cdot\%\text{O} - 0.192502\cdot\%\text{Volatiles}$$

The standard error of the estimate shows that the standard deviation of the residues was 0.45 MJ/kg. This value can be used to construct limits for new observations. The mean absolute error (MAE) of 0.32 was the average value of the residuals. The Durbin–Watson (DW) statistic examines the residuals in order to determine if there is any significant correlation based on the order in which they occur in the data file. Since the P-value was higher than 0.05, there was no indication of serial autocorrelation in the residuals at a 95.0% confidence level.

This model was validated with a set of 25 samples different from those used to obtain it. To perform this, we analyzed the values provided by the model and those obtained from the analyses through the paired samples test, based on the Student t-distribution.

### *3.5. Principal Component Analysis*

This type of analysis seeks to define new coordinates and a linear combination of all the variables by collecting the maximum variability in the population. These new coordinates are called principal components and allow the representation of individuals in a biphasic scatter diagram. Table 8 shows the coefficients of the standardized variables of the proximate analysis (% ashes, % volatile, and % fixed carbon) for the calculation of each of the main components applied to the data of the eight evaluated species.

**Table 8.** Weights of the variables for the calculation of the components for the differentiation of 8 species.

| | **Component 1** | **Component 2** |
|---|---|---|
| % Ashes | 0.488337 | 0.716929 |
| % Volatiles | 0.503154 | −0.697145 |
| % Fixed carbon | −0.712996 | −0.000936423 |

The weight of each variable can be seen in Figure 2. This graph facilitated an interpretation of the influence of each of the variables on the components. The higher heating value influenced component 1 and 2 in an almost similar way; however, fixed carbon influenced component 1 more than component 2 in a positive way, whereas the volatiles influenced component 2 more than component 1, and their influence was negative. On the contrary, the ash had a negative influence on component 2 and a positive influence on component 1.

Based on this, it can be deduced that the samples located in the first quadrant of the biphasic diagram have a higher high-heat value and fixed carbon than the volatile ones. The samples in the second quadrant have a high content of volatiles and higher heating value. The samples in the third quadrant have a high volatile content, but the higher heating value is lower. The samples in the fourth quadrant have a high ash content and a high calorific power.

This result enables us to propose a biomass identification system, since the main components obtained from the proximate analysis and higher heating value distribute each species in an area of the diagram. Figure 3a shows the average values of the samples ($n$ = 10) and we can observe that the eight species are distributed separately. This is a major innovation since we did not find a similar identification system in the bibliography.

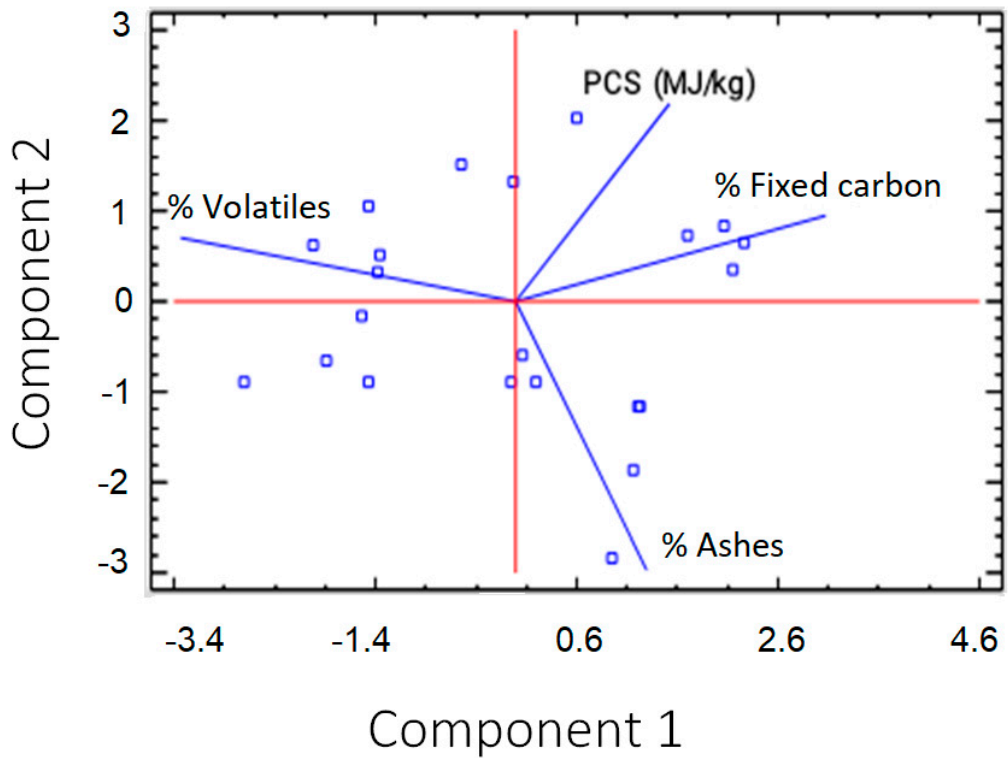
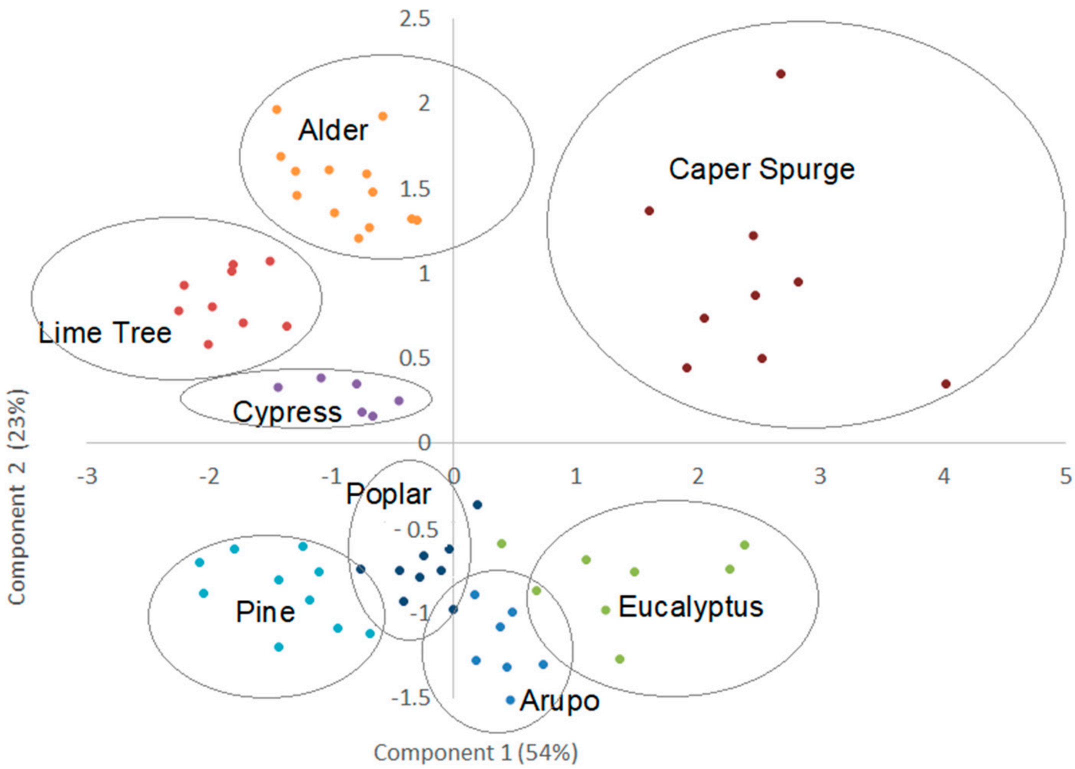
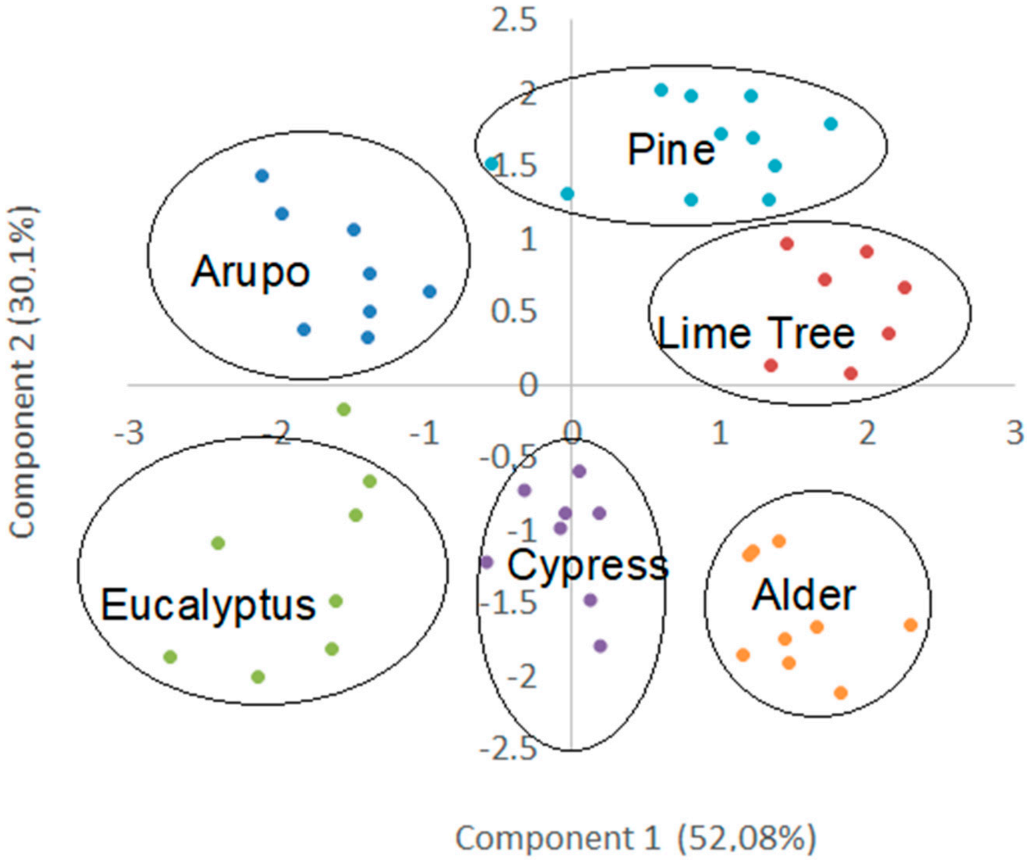



**Figure 2.** Two-phase diagram for variable influence analysis.




**(a)**

**Figure 3.** *Cont*.




(**b**)

**Figure 3.** Biphasic diagrams of the principal components: (**a**) for 8 species (**b**) for 6 species.

The calculation of the main components for the eight studied species was carried out with Equations (8) and (9), in which the values of the variables in the equation were standardized by subtracting their average and dividing them by their standard deviations.

$$CP1 = 0.488337 \cdot \%Ashes + 0.503154 \cdot \%Volatiles - 0.712996 \cdot \%\ Fixed\ Carbon \tag{8}$$

$$CP2 = 0.716929 \cdot \%Ashes + -0.697145 \cdot \%Volatiles - 0.000936423 \cdot \%\ Fixed\ Carbon \tag{9}$$

Due to the fact that the pine tree, poplar, eucalyptus, and arupo species are very close in the biphasic dispersion diagram (Figure 3a), we analyzed the possibility of better discriminating these species by carrying out another principal component analysis exclusively with six species (Figure 3b). The new values of the coefficients of each of the variables can be seen in Table 9. When only the samples of the pine tree, cypress, eucalyptus, arupo, alder, and lime tree species were used, the first principal component had the following equation:

$$CP1 = 0.563214 \cdot HHV\ (MJ/kg) - 0.76697 \cdot \%Ashes - 0.674207 \cdot \%Volatiles + 0.618112 \cdot \%\ Fixed\ Carbon$$

The second principal component had the following equation:

$$CP2 = 0.307495 \cdot HHV\ (MJ/kg) + 0.262354 \cdot \%Ashes + 0.184166 \cdot \%Volatiles + 0.246231 \cdot \%\ Fixed\ Carbon$$

**Table 9.** Weights of the variables in components 1 and 2 for differentiation of 6 species.

| | Component 1 | Component 2 |
|---|---|---|
| HHV (MJ/kg) | 0.307495 | 0.563214 |
| % Ashes | 0.262354 | −0.76697 |
| % Volatiles | −0.674207 | 0.184166 |
| % Fixed carbon | 0.618112 | 0.246231 |

### 3.6. Implementation of the Probabilistic Neural Network

Table 10 shows the results of using the trained neural network to classify observations of the eight species. Among the 150 cases used to train the model, 94.5% were correctly classified. We can observe that of the 25 poplar samples, 22 were correctly classified, but 2 samples were classified as eucalyptus. Of the 25 eucalyptus samples, 23 were correctly classified; however, 3 were classified as poplar. This means that both species were very close in terms of their own characteristics of the proximate analysis, which means that there was a percentage of error in the classification between 8 and 12%. That is, the samples of these species were correctly discriminated between 88 and 92%. On the other hand, there were six pine tree samples that were classified as poplar.

**Table 10.** Results from the neural network trained to classify observations of the 8 species.

| Current Species | Sample Size | Prediction | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | Poplar | Alder | Arupo | Cypress | Eucalyptus | Caper Spurge | Pine | Lime Tree |
| Poplar | 25 | 23 (92%) | 0 (0.00%) | 0 (0.00%) | 0 (0.00%) | 2 (8%) | 0 (0.00%) | 0 (0.00%) | 0 (0.00%) |
| Alder | 25 | 0 (0.00%) | 25 (100%) | 0 (0.00%) | 0 (0.00%) | 0 (0.00%) | 0 (0.00%) | 0 (0.00%) | 0 (0.00%) |
| Arupo | 25 | 0 (0.00%) | 0 (0.00%) | 25 (100%) | 0 (0.00%) | 0 (0.00%) | 0 (0.00%) | 0 (0.00%) | 0 (0.00%) |
| Cypress | 25 | 0 (0.00%) | 0 (0.00%) | 0 (0.00%) | 25 (100%) | 0 (0.00%) | 0 (0.00%) | 0 (0.00%) | 0 (0.00%) |
| Eucalyptus | 25 | 3 (12%) | 0 (0.00%) | 22 (88%) | 0 (0.00%) | 0 (0.00%) | 0 (0.00%) | 0 (0.00%) | 0 (0.00%) |
| Caper spurge | 25 | 2 (8%) | 0 (0.00%) | 0 (0.00%) | 0 (0.00%) | 0 (0.00%) | 23 (92%) | 0 (0.00%) | 0 (0.00%) |
| Pine | 25 | 4 (6%) | 0 (0.00%) | 0 (0.00%) | 0 (0.00%) | 0 (0.00%) | 0 (0.00%) | 21 (94%) | 0 (0.00%) |
| Lime tree | 25 | 0 (0.00%) | 0 (0.00%) | 0 (0.00%) | 0 (0.00%) | 0 (0.00%) | 0 (0.00%) | 0 (0.00%) | 25 (100%) |

Percentage of training cases correctly classified: 94.5%.

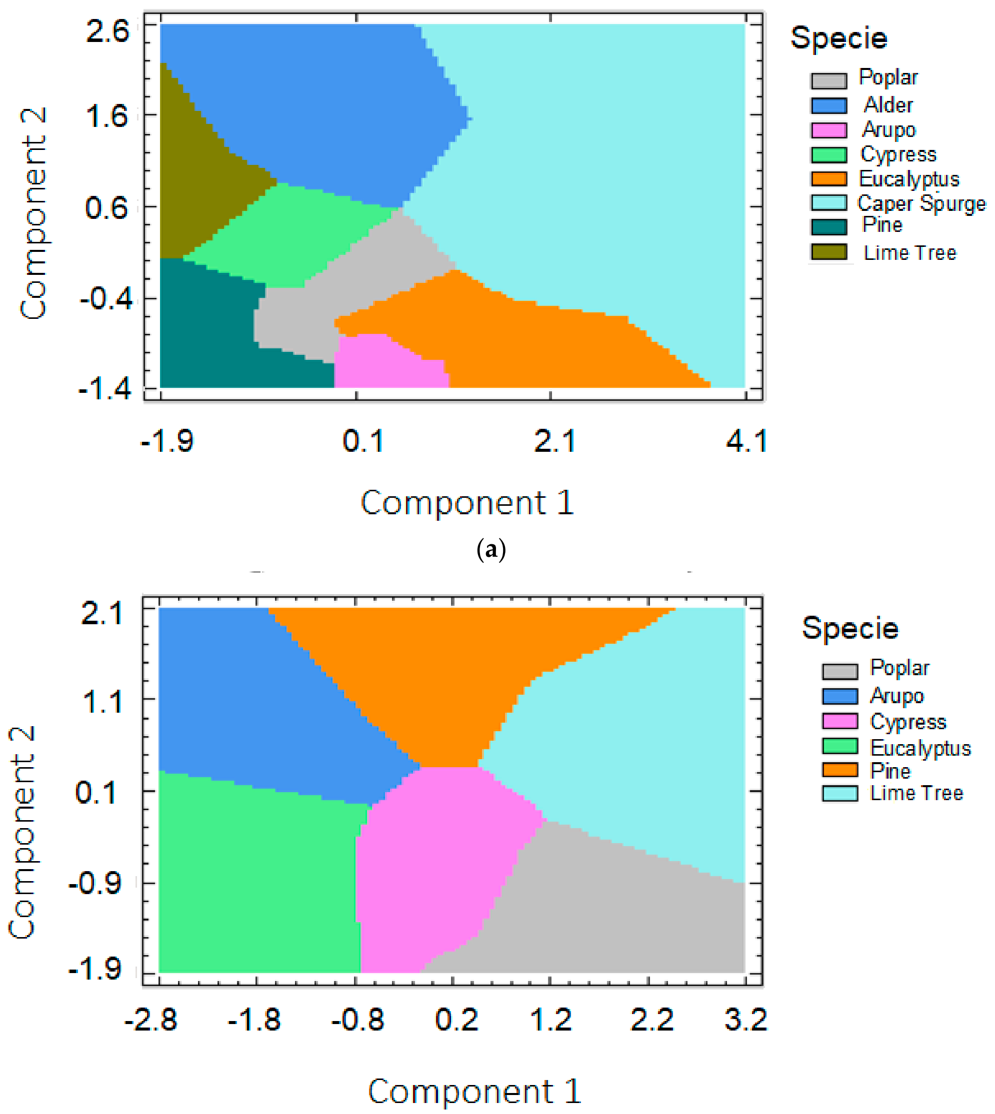
In order to check whether the classification percentage of the eucalyptus samples could be improved, the analysis of the probabilistic neural network was repeated for six species only (Table 11). Then, we observed that 8 of the 25 eucalyptus samples were classified as arupo (32%).

Figure 4 shows the identification areas of the different species from the application of the probabilistic neural network to the main components obtained from the variables of the proximate analysis. Figure 4a shows the identification areas when variables from eight different species are used. Figure 4b shows the identification areas when six different species are used.

**Table 11.** Results of the neural network trained to classify observations of the 6 species.

| Current Species | | Prediction | | | | | |
|---|---|---|---|---|---|---|---|
| | | **Alder** | **Arupo** | **Cypress** | **Eucalyptus** | **Caper Spurge** | **Pine** |
| Alder | 25 | 25 (100%) | 0 (0.00%) | 0 (0.00%) | 0 (0.00%) | 0 (0.00%) | 0 (0.00%) |
| Arupo | 25 | 25 (0.00%) | 25 (100%) | 0 (0.00%) | 0 (0.00%) | 0 (0.00%) | 0 (0.00%) |
| Cypress | 25 | 0 (0.00%) | 0 (0.00%) | 25 (100.%) | 0 (0.00%) | 0 (0.00%) | 0 (0.00%) |
| Eucalyptus | 25 | 0 (0.00%) | 8 (32.00%) | 0 (0.00%) | 17 (68.00%) | 0 (0.00%) | 0 (0.00%) |
| Caper spurge | 25 | 0 (0.00%) | 0 (0.00%) | 0 (0.00%) | 0 (0.00%) | 25 (100%) | 0 (0.00%) |
| Pine | 25 | 0 (0.00%) | 0 (0.00%) | 0 (0.00%) | 0 (0.00%) | 0 (0.00%) | 25 (100%) |

Percentage of training cases correctly classified: 94.6%.




(**a**)

(**b**)

**Figure 4.** Decision areas for species identification: (**a**) 8 species and (**b**) 6 species based on proximate analysis and calculation of principal components.

We can observe that the areas constituted closed convex regions, and that there were no islands in which there could be classification errors. In the validation of these areas, we obtained a percentage of success in the identification of the species of 96.30%.

### 3.7. The Effect of the Leaves

In Figure 5, we can see that the content of leaves in the biomass increased the percentage of ashes. When the biomass was made up exclusively of wood, all species, except caper spurge, have an ash content of less than 3%. However, they exceeded this value when the leaf content exceeded 40%, and the ash percentage could reach 10% in the lime tree and caper spurge.

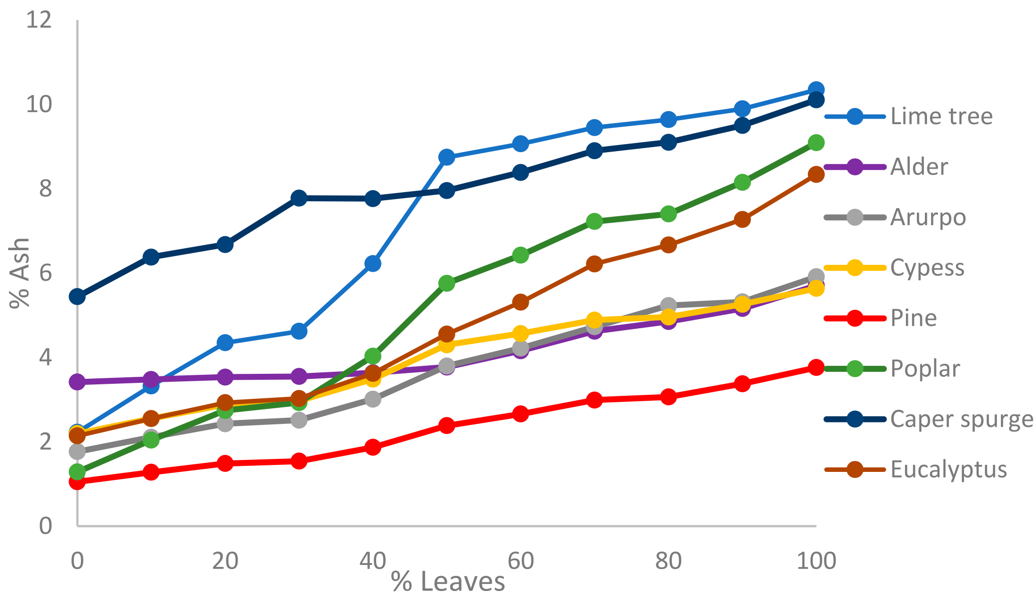



**Figure 5.** Variation in ash content with the percentage of leaves in the sample.

As shown in Figure 6, the presence of leaves had little influence on the higher heating value in these species, with no significant differences between the different types of mixtures, except in the lime tree, in which the higher heating value decreased from 19 MJ/kg in 100% wood samples to 16.5 MJ/kg in 100% leaf samples. On the other hand, in Table 12, we verify that the presence of dry leaves did not raise the nitrogen content above 3.5% in any species. The sulfur content in the wood of the species studied was negligible, at less than 0.01%. We can observe that, although it increased with the presence of leaves, the sulfur content in the samples of 100% leaves was very low, except in poplar, which did not exceed 0.4%. This means that the formation of oxidizing agents will be small and tolerable for current thermal installations.

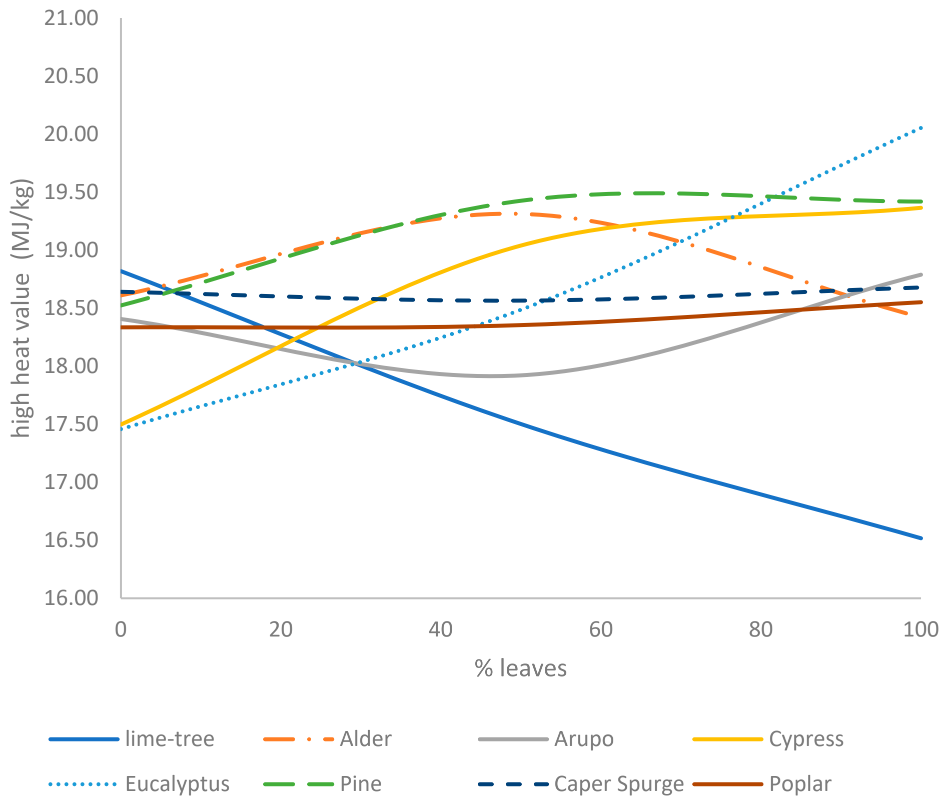



**Figure 6.** Variation in higher heating value with the percentage of leaves in the sample.

**Table 12.** Variation in calorific value, nitrogen, and sulfur percentages with the presence of leaves in pruning biomass.

| | % Wood | % Leaves | PC (MJ/kg) | %N | %S |
|---|---|---|---|---|---|
| Poplar | 100 | 0 | 18.33 | 0.69 | 0.12 |
| | 50 | 50 | 18.35 | 1.50 | 0.21 |
| | 0 | 100 | 18.55 | 2.20 | 0.37 |
| Alder | 100 | 0 | 18.61 | 0.83 | 0.00 |
| | 50 | 50 | 19.31 | 1.94 | 0.00 |
| | 0 | 100 | 18.42 | 3.63 | 0.04 |
| Arupo | 100 | 0 | 18.41 | 0.59 | 0.00 |
| | 50 | 50 | 17.92 | 1.05 | 0.00 |
| | 0 | 100 | 18.79 | 2.59 | 0.04 |
| Cypress | 100 | 0 | 17.50 | 0.48 | 0.00 |
| | 50 | 50 | 19.04 | 0.63 | 0.00 |
| | 0 | 100 | 19.36 | 0.98 | 0.00 |
| Eucalyptus | 100 | 0 | 17.46 | 0.50 | 0.00 |
| | 50 | 50 | 18.49 | 0.71 | 0.00 |
| | 0 | 100 | 20.05 | 1.34 | 0.00 |
| Caper spurge | 100 | 0 | 18.64 | 0.55 | 0.42 |
| | 50 | 50 | 18.56 | 1.75 | 0.06 |
| | 0 | 100 | 18.68 | 2.73 | 0.07 |
| Pine | 100 | 0 | 18.52 | 0.47 | 0.00 |
| | 50 | 50 | 19.43 | 0.89 | 0.00 |
| | 0 | 100 | 19.42 | 1.13 | 0.00 |
| Lime tree | 100 | 0 | 18.82 | 1.06 | 0.00 |
| | 50 | 50 | 17.50 | 2.16 | 0.01 |
| | 0 | 100 | 16.52 | 3.72 | 0.12 |

## 4. Discussion

Researchers around the world are working on elemental, proximate, structural, thermogravimetric, and fermentative analyses. The results shown in this work present several novelties: firstly, the available materials were analyzed in the Andean province of Ecuador, where the production of bioenergy resources has not yet been developed. Secondly, we proposed a characterization system that allowed the analyzed materials to be identified. Even without knowing its origin, it allowed us to find out the species of wood and, later on, its characteristics, through a proximate analysis.

Carbon, hydrogen, and oxygen are the main components of biomass. Out of the three, carbon generally has a direct correlation with the higher heating value (HHV) [14,15]. This was demonstrated in this work, in which it was verified that the contents of N and S in the studied species were not problematic. The concentration of N and S in biomass is important because they are involved in the generation of NOx, $SO_2$, and $SO_3$ gas. Cl produces acid emissions with a corrosive effect during combustion. This makes these elements undesirable in the composition of biomass [16]. The contents of C in biomass can range between 42 and 71%; H, between 3 and 11%; O, between 16 and 49%; N, between 0.1 and 12%; S, between 0.01 and 2.3%; and Cl, between 0.01 and 0.9% [17]. The results shown in the tables show that the species are in the typical ranges of materials used for solid biofuels. Similarly, CP (dry basis) ranges between 17 and 20 MJ $kg^{-1}$, which is very different from wood forests (pine tree with 21 MJ $kg^{-1}$) and fruit forests (19 MJ $kg^{-1}$). In wet biomass, the values obtained decrease depending on the moisture content [18].

Biomass contains a variable amount of cellulose, hemicellulose, and lignin, and small amounts of lipids, proteins, simple sugars, and starch. Moreover, it contains inorganic constituents and a fraction of water. Out of all of them, cellulose, hemicellulose, and lignin are the three main constituents [6,19]. The combination of cellulose, hemicellulose, and lignin is known as lignocellulose, which accounts for about half of the matter produced in photosynthesis and represents the most abundant renewable organic resource on Earth [19]. The structural analysis of biomass is especially important in the development of production processes for other fuels and chemical products, as well as in the study of the combustion phenomenon. On the other hand, these analyses can be useful for the determination of higher heating value (HHV) [20]. Along with cellulose, hemicellulose, lignin, ashes, or minerals, there are other materials in biomass known as extractives, which correspond to fatty acids, resin acids, tannins, sugars, terpene oligomers, sterols, hydrocarbons, etc. The amount of them that appears depends on the species, the part of the tree, the time of year, and other factors. The extractives have a higher heating value of about 35 MJ $kg^{-1}$, which is very interesting for energy applications [20]. Proximate analyses consist of determining the content of volatile matter, fixed carbon, and ash present in the biomass [16,19]. It is interesting to study these parameters to know how biomass combusts. For example, some ash content can be related to certain combustion and ignition problems; on the other hand, the higher heating value of biomass increases when fixed carbon and volatile material increase [19]. A large number of scientific articles are based on the evaluation of the fermentability of waste [21–23] or on its gasification by pyrolysis in the absence of oxygen from structural analysis. All the references shown demonstrate the great topicality and worldwide interest of this type of research.

## 5. Conclusions

The studied species (pine (*Pinus radiata*), cypress (*Cupressus macrocarpa*), eucalyptus (*Eucalyptus globulus*), poplar (*Populus* sp.), arupo (*Chionanthus pubescens*), alder (*Alnus acuminata*), and lime (*Sambucus nigra* L.)) presented a higher heating value which was enough to consider their use as solid biofuel. The nitrogen and sulphur contents were low. They did not exceed the limits considered inadequate for the formation of oxidants that could affect the materials of thermal installations.

Although the presence of leaves in the pruning biomass increased the percentage of ash, N, and S content, it did not significantly affect the suitability of the materials as biofuels.

The percentage of wood and leaves in the samples significantly influenced the content of cellulose, hemicellulose, lignin, and extractives. The leaf content decreased the mass percentages of cellulose, hemicellulose, and lignin, and increased the percentage of extractives.

The studied species did not present significant differences in the parameters of the proximate and elemental analysis. This means that it was not possible to identify the sample immediately, especially if it was crushed material. This encourages investigating the possibility of devising identification methods based on these analyses in order to assess the traceability of materials at a commercial level.

The combination of principal component analysis with a probabilistic neural network proved to be an effective method to identify the species from the ash, volatile, and fixed carbon content. The percentage of correctly classified cases was approximately 95%. This is very useful if the nature of the material that reaches a plant before being used as biofuel is unknown.

**Author Contributions:** B.V.M. performed the conceptualization, methodology, validation, formal analysis, investigation, writing—original draft preparation, writing—review and editing, and funding acquisition. J.G.-C. performed the formal analysis and funding acquisition. J.E.F.R. performed the methodology and validation. I.L.C. performed the writing—review and editing. All authors have read and agreed to the published version of the manuscript.

**Funding:** This research received no external funding.

**Institutional Review Board Statement:** Not applicable.

**Informed Consent Statement:** Not applicable.

**Data Availability Statement:** The datasets from the current study are available from the corresponding author upon reasonable request.

**Acknowledgments:** This work was carried out within the framework of the work "Analysis of the implementation of biomass exploitation chains in rural communities in the province of Bolívar (Ecuador)" of the ADSIEO-COOPERATION program of the Polytechnic University of Valencia (UPV). The Ecuadorian Energy Exploitation Research Network of Biomass (ECUMASA) and the IBEROMASA Network of the Ibero-American Program of Science and Technology for Development (CYTED) participated in this program.

**Conflicts of Interest:** The authors declare no conflict of interest.

## References

1. Ferre, A.J.C.; Martínez, J.A.L. Briquettes of plant remains from the greenhouses of Almería (Spain). *Span. J. Agric. Res.* **2009**, *7*, 525–534. [CrossRef]
2. Callejón-Ferre, A.J.; Velázquez-Martí, B.; López-Martínez, J.A.; Manzano-Agugliaro, F. Greenhouse crop residues: Energy potential and models for the prediction of their higher heating value. *Renew. Sustain. Energy Rev.* **2011**, *15*, 948–955. [CrossRef]
3. Callejón-Ferre, A.J.; Carreño-Sánchez, J.; Suárez-Medina, F.J.; Pérez-Alonso, J.; Velázquez-Martí, B. Prediction models for higher heating value based on the structural analysis of the biomass of plant remains from the greenhouses of Almería (Spain). *Fuel* **2014**, *116*, 377–387. [CrossRef]
4. Demirbas, A.H.; Demirbas, I. Importance of rural bioenergy for developing countries. *Energy Convers. Manag.* **2007**, *48*, 2386–2398. [CrossRef]
5. Manzano-Agugliaro, F.; Alcayde, A.; Montoya, F.G.; Zapata-Sierra, A.; Gil, C. Scientific production of renewable energies worldwide: An overview. *Renew. Sustain. Energy Rev.* **2013**, *18*, 134–143. [CrossRef]
6. Demirbas, M.F. Biorefineries for biofuel upgrading: A critical review. *Appl. Energy* **2009**, *86*, S151–S161. [CrossRef]
7. Zhang, L.; Xu, C.; Champagne, P. Overview of recent advances in thermo-chemical conversion of biomass. *Energy Convers. Manag.* **2010**, *51*, 969–982. [CrossRef]
8. Yin, C.-Y. Prediction of higher heating values of biomass from proximate and ultimate analyses. *Fuel* **2011**, *90*, 1128–1132. [CrossRef]
9. Vargas-Moreno, J.M.; Callejón-Ferre, A.J.; Pérez-Alonso, J.; Velázquez-Martí, B. A review of the mathematical models for predicting the heating value of biomass materials. *Renew. Sustain. Energy Rev.* **2012**, *16*, 3065–3083. [CrossRef]
10. Velázquez-Martí, B. *Aprovechamiento de la Biomasa Para Uso Energético*, 2nd ed.; Barcelona: Reverté, Spain, 2018.

11. Van Soest, P.J.; Wine, R.H. Determination of lignin and cellulose in acid-detergent fiber with permanganate. *J. Assoc. Off. Anal. Chem.* **1968**, *51*, 780–785. [CrossRef]
12. Specht, D.F. Probabilistic neural networks. *Neural Netw.* **1990**, *3*, 109–118. [CrossRef]
13. Sajdak, M.; Velazquez-Marti, B. Estimation of pruned biomass form dendrometric parameters on urban forests: Case study of Sophora japonica. *Renew. Energy* **2012**, *47*, 188–193. [CrossRef]
14. Telmo, C.; Lousada, J.; Moreira, N. Proximate analysis, backwards stepwise regression between gross calorific value, ultimate and chemical analysis of wood. *Bioresour. Technol.* **2010**, *101*, 3808–3815. [CrossRef]
15. Pérez-Arévalo, J.J.; Callejón-Ferre, A.J.; Velázquez-Martí, B.; Suárez-Medina, M.D. Prediction models based on higher heating value from the elemental analysis of neem, mango, avocado, banana, and carob trees in Guayas (Ecuador). *J. Renew. Sustain. Energy* **2015**, *7*, 053122. [CrossRef]
16. Vassilev, S.V.; Baxter, D.; Andersen, L.K.; Vassileva, C.G. An overview of the chemical composition of biomass. *Fuel* **2010**, *89*, 913–933. [CrossRef]
17. Velázquez-Martí, B.; Estornell, J.; López-Cortés, I.; Martí-Gavilá, J. Calculation of biomass volume of citrus trees from an adapted dendrometry. *Biosyst. Eng.* **2012**, *112*, 285–292. [CrossRef]
18. Saidur, R.; Abdelaziz, E.A.; Demirbas, A.; Hossain, M.S.; Mekhilef, S. A review on biomass as a fuel for boilers. *Renew. Sustain. Energy Rev.* **2011**, *15*, 2262–2289. [CrossRef]
19. Arin, G.; Demirbas, A. Mathematical modeling the relations of pyrolytic products from lignocellulosic materials. *Energy Sources* **2004**, *26*, 1023–1032. [CrossRef]
20. Khan, A.A.; de Jong, W.; Jansens, P.J.; Spliethoff, H. Biomass combustion in fluidized bed boilers: Potential problems and remedies. *Fuel Process. Technol.* **2009**, *90*, 21–50. [CrossRef]
21. Pardão, J.; Diaz, I.; Raposo, S.; Manso, T.; Lima-Costa, M.E. Sustainable bioethanol production using agro-industrial by-products. In Proceedings of the 4th IASME/WSEAS International Conference Energy, Environment, Ecosystems and Sustainable Development, Crete Island, Greece, 24–26 July 2007; pp. 149–153.
22. Sarris, D.; Matsakas, L.; Aggelis, G.; Koutinas, A.A.; Papanikolaou, S. Aerated vs non-aerated conversions of molasses and olive mill wastewaters blends into bioethanol by Saccharomyces cerevisiae under non-aseptic conditions. *Ind. Crops Prod.* **2014**, *56*, 83–93. [CrossRef]
23. Yu, M.; Li, J.; Chang, S.; Du, R.; Li, S.; Zhang, L.; Fan, G.; Yan, Z.; Cui, T.; Cong, G.; et al. Optimization of ethanol production from NaOH-pretreated solid state fermented sweet sorghum bagasse. *Energies* **2014**, *7*, 4054–4067. [CrossRef]