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Additional Information

1 **COMPLETE CHARACTERIZATION OF PRUNING WASTE FROM THE**
2 **LECHERO TREE (*Euphorbia laurifolia* L.) AS RAW MATERIAL FOR**
3 **BIOFUEL**

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14 **Abstract**

16 The aim of this study is to conduct a complete characterization of the pruning waste
17 from the lechero tree. This tree species is of particular relevance in Ecuador for its use
18 as biomass since it yields large amounts of pruning waste, it has a high propagation
19 capacity and very fast growth, for both the trunk and branches. The pruning waste
20 consists of a mixture of wood and leaves, which are subjected to caloric analysis,
21 elemental analysis, proximate analysis, thermogravimetric analysis and fermentability.
22 The average dry pruned biomass obtained per tree is 9.95 kg, with a 1.49 kg standard
23 deviation. The average ratio of leaves in pruned biomass is the 40%. Regression model
24 to determine pruning waste biomass from plant measurements was obtained with 0.7 of
25 r^2 . The calorific value of these residues is 19 MJ/kg average. N and ash content is

26 influenced by leaf content. A leaf content less than 25% represent N content lower than
27 1%, and 6% ash content. Prediction models to higher heat value (kJ/kg) based on
28 elemental, proximate and structural analysis is presented.

29 Keywords: bioenergy, renewable energy, agricultural biomass

30 INTRODUCTION

31

32 Research on sources of renewable energy has become of great importance in the 21st
33 century since fossil energy (coal, oil, natural gas, etc.) does not comply with the
34 sustainability principles and environmental respect established for the well-being of
35 humanity. Biomass resulting from pruning waste can be used as a source of energy.
36 Several studies have aimed to quantify this resource [1]. However these studies must be
37 supplemented with assessment of the energetic properties of the biomass [2].

38

39 The aim of this work has been to assess the waste wood obtained from pruning the
40 lechero tree (*Euphorbia laurifolia* L.) cultivated in the Bolivar province, Ecuador. The
41 lechero tree is of particular relevance in Ecuador to be used as biomass due to this tree
42 has traditionally been grown as bushes to define boundary lines between plots, mainly
43 on sloped terrain where cereals are cultivated (mainly corn), as it helps to fix the soil
44 and prevent erosion. It has a high propagation capacity and very fast growth, for both
45 the trunk and branches. Because of this, it is heavily pruned every year in order to avoid
46 excessive growth. This activity produces a great amount of waste material, [3-4]. Up to
47 now the quantification of the amount of available biomass from dendrometry has not
48 been done. This is one of objective of this work.

49 Besides its use as boundary between plots, the leaves and latex available abundantly in
50 the wood of the lechero have been employed traditionally in medicinal applications [5-
51 6]. The need to fix the soil in order to prevent erosion has led to its widespread
52 cultivation in the Bolivar province.

53

54 A complete characterization is a multi-analytical endeavor. The first important
55 parameter is calorific value, the amount of energy released after combustion. The
56 presence of latex in the plant structures could have a significant influence on the energy
57 obtained. To know if the energy is acceptable, it is necessary to perform a dendrometric
58 assessment to calculate the amount of pruning waste available based on the sizes of the
59 plant, such as its height, diameter of the trunk and diameter of the crown. There have
60 been successful results from working with other tree species such as *Plananus*
61 *hispanica* L. [7], *Sophora Japonica* [8], olive trees [9], almond trees [10], among others.
62 By establishing equations that can determine the total amount of raw materials based on
63 easily measurable variables in the plant, and the energy in them, it is possible to carry
64 out spatial inventories and logistic planning for collection and transportation of the
65 materials. Dendrometric characterization is usually paired with determining the mix
66 percentage of wood and leaves in the raw material, as well as its moisture content.

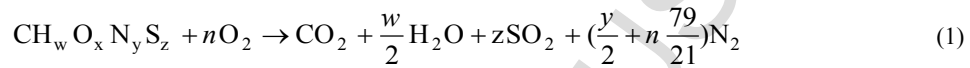
67

68 The elemental analysis is of vital importance as well. This consists of determining the
69 amount of the most important elements present in the material, mainly carbon C,
70 hydrogen H, nitrogen N, oxygen O, sulfur S and chlorine Cl. The content of N, S and Cl
71 is limited by biomass standardization norms because combustion can turn these
72 elements into corrosive acids, damaging thermal installations [11-12].

73

74 The C, H, N and O content is used to define the empirical formula for the material and
 75 model its complete combustion (Eq. 1). This model makes it possible to calculate the
 76 amount of oxygen necessary to achieve this (Eq. 2), and therefore, the amount of
 77 stoichiometric air needed (Eq. 3). The relation between the air necessary for complete
 78 combustion and the real amount entered into a device is called “excess air parameter”,
 79 λ (Eq. 4). If this parameter is bigger than 1, complete combustion will be achieved, if it
 80 is smaller than 1, application of heat will result in pyrolysis or carbonization. For this
 81 reason, performing an elemental analysis is extremely important [13].

82



$$\text{Oxygen moles: } n = 1 + \frac{w}{4} + z - \frac{x}{2} \quad (2)$$

$$\text{Air (m}^3\text{N/kg of biomass)} = \frac{22,39 \cdot 10^{-3}}{0,21} \cdot \left(\frac{m_C}{12,011} + \frac{1}{4} \frac{m_H}{1,008} + \frac{m_S}{32,060} - \frac{m_O}{32,000} \right) \quad (3)$$

$$\lambda = \frac{\text{Required air}}{\text{Stoichiometric air}} \quad (4)$$

83

84 m_C , m_H , m_S y m_O stand for carbon, hydrogen, sulfur and oxygen mass present in the
 85 sample, measured as grams for every kilogram of biomass. The denominators
 86 correspond to their atomic weight. The N means the volume of air is measured under
 87 normal conditions.

88

89 In addition to know the amount of air necessary for complete combustion, the carbon
 90 content in biofuels is used to calculate the amount of CO_2 previously absorbed by the
 91 plant, and consequently, the amount of CO_2 emitted to the atmosphere by its
 92 combustion. This way it is possible to know the balance and carry out a carbon footprint
 93 analysis.

94

95 Other analyses that must be performed during characterization are the proximate and
96 structural analyses. The proximate analysis consists of determining the amount of ash,
97 volatiles and fixed carbon present in the organic matter. The ash is used to estimate the
98 amount of residue to evacuate after combustion; the volatiles to know the mass of gas
99 formed during pyrolysis. Both affect calorific value significantly. The structural
100 analysis consists of determining the amount of lignin, cellulose, hemicellulose and
101 extractives present in the raw material. These structures influence the kinetics of the
102 pyrolysis and possible fermentability [14].

103

104 The thermogravimetric analysis is used to study the kinetics of the pyrolysis, according
105 to temperature ramp, type of atmosphere and air flow [15-16].

106

107 Fermentation can be an alternative to direct combustion. Microbiologic action
108 decomposes the organic matter into biofuels such as alcohol and methane.

109

110 The aim of this study is to conduct a complete characterization of the pruning waste
111 from the lechero tree. The pruning waste consists of a mixture of wood and leaves,
112 which are subjected to caloric analysis, elemental analysis, proximate analysis,
113 thermogravimetric analysis and fermentability.

114

115 **MATERIALS AND METHODS**

116

117 *Study Area*

118

119 The study was conducted in the Bolivar province (Ecuador); this province is located in

120 the central area of Ecuador, on the western Andes. Its capital is the city of Guaranda. It
121 is characterized by deep valleys in the high Andes, which serve as agricultural areas. Its
122 climate is subtropical, with a long (May - October) dry season. The land has slopes of
123 20 to 30%, the temperature oscillates between 6 and 18°C in the highlands, and 18 and
124 22°C in the subtropic; rainfall is between 500 and 2000 mm.

125 The lechero tree (*Euphorbia laurifolia* L.), while not exactlu a crop, is widely grown in
126 the area as boundary between plots or fencing for livestock. Its wood is used as raw
127 material for house construction. It also contains latex, which is used as glue as well as
128 plaster. This plant is also used in traditional medicine treatments of liver conditions,
129 infected abscesses and warts. This plant is still given both traditional and ornamental
130 use in the Ecuadorian mountains.

131

132 This tree yields large amounts of pruning waste, as it has a high propagation capacity
133 and very fast growth, for both the trunk and branches. Additionally, its location on the
134 periphery of land plots facilitates the extraction and transportation of the residual
135 biomass, as it can be done on the same locations as the pruning.

136

137 It is widely distributed in Colombia, Venezuela, Guyana, Ecuador, Peru and Bolivia. In
138 Ecuador it is well represented in every Andean province, from 1500 to 3000 m above
139 sea level.

140

141 Depending on handling it is considered either a bush or tree. It has milky latex in its
142 branches and leaves. The inflorescence has five fleshy lobes alternating with glands and
143 some internal bracts. It has several male flowers growing around a single central female
144 flower with pedicels. Its fruits consists of three joined nuts.

145

146 Samples were collected in five Andean locations, between 2673 and 2900 m above sea
147 level (Table 1).

148

149 *Dendrometric analysis*

150

151 A characterization of the plants, by measuring trunk diameter, crown diameter, height
152 from the crown to the ground, total height of the tree and last year of pruning (Figure 1),
153 was performed before an operator proceeded to prune the trees. Stem and crown
154 diameter (D_t and D_c) was measured with a diameter tape with precision 0.001 m. The
155 crown diameter was determined by averaging measurements of the long axis with a
156 diameter taken at right angle. Tree height (H) was determined with a Vertex IV
157 hypsometer with precision 0.01 m. The Vertex IV hypsometer uses ultrasonic pulses
158 together with a transponder fixed to a tree. After pruning, the obtained mass was
159 weighted with a dynamometer, forming sheaves with the woody material. Since pruning
160 was performed while leaves were still on the branches, 5 branches were taken from each
161 tree after pruning and the leaves were removed manually, weighting the branches both
162 before and after removal of the leaves to calculate the percentage of leaf and wood
163 mass. Subsequently, wood samples were taken in plastic containers to determine
164 moisture content via laboratory analysis. Moisture content in the leaves was measured
165 as well. The obtained moisture content value was then used to correct the measured
166 weight and obtain the mass of the dry matter.

167

168 The thermochemical characterization of the pruning waste was conducted according to
169 the standardized norms in Table 2. Samples with different percentages of wood and leaf

170 matter were studied: 100% wood, 90% wood/10% leaves, 80% wood/20% leaves, 70%
171 wood/30% leaves, 60% wood/40% leaves, 50% wood/50% leaves, 100% leaves. It is
172 very useful to perform this analysis with different percentages since pruning waste can
173 have different ratios, in turn affecting the final biofuel obtained [7,9,17]

174

175

176 *Calorific value*

177

178 In order to determine calorific value, a portion of the sample, previously dried and
179 crushed, was burned in an LECO AC-500 isoperibolic calorimeter, according to
180 conditions specified in the EN 14918 norm. The sample was placed in a crucible then
181 inserted in a pump with oxygen at 3000 kPa. The pump was entered into the calorimeter
182 in a tray of water, where the temperature was periodically registered. Activation energy
183 was transmitted through a resistance.

184

185 *Elemental analysis*

186

187 A Truspec CHN LECO elemental analyzer was used to determine content of carbon,
188 hydrogen, nitrogen and sulfur, in accordance with the EN ISO 16948 norm. The process
189 consists of burning a known mass from the sample in the presence of oxygen, so it turns
190 into ash and gaseous products during combustion. These gaseous products consist
191 mostly of carbon dioxide, water vapor, nitrogen and/or nitrogen oxides, oxides and
192 sulfur oxoacids. These fractions are drawn by helium into different detectors to
193 determine each of the elements.

194

195 *Proximate analysis*

196

197 The method used to measure ash content in solid biofuels is specified in EN ISO 18122
198 norm. The sample used had a minimum mass of 1g, previously kiln dried at 105 °C for
199 an hour. Once dried, the sample was inserted in the muffle and the temperature was
200 uniformly elevated to 250 °C for a period of 30 to 50 min (meaning a rise between 4.5
201 °C/min y 7.5 °C/min). This temperature was maintained for 60 min to allow evaporation
202 of volatiles before ignition. Subsequently, the temperature was uniformly raised to (550
203 ± 10) °C during a 30 min period, or a rise of 10°C/min, keeping this temperature for a
204 minimum of 120 min.

205

206 Norm EN ISO 18123 specifies the method necessary to determine volatile matter in
207 solid biofuels. Following these specifications, the sample with a minimum mass of 1g
208 was heated in a covered ceramic crucible, out of contact with air, at 900°C ± 10°C for 7
209 min. The percentage of volatile matter was calculated from the loss of mass in the test
210 portion, after deducting mass loss due to moisture content.

211

212 For the standard muffle furnace tests, in accordance with EN ISO 18122 norm, the ash
213 content was calculated using equation (5), where m_1 is the crucible and sample mass in
214 grams before heating; m_2 is the crucible and sample mass in grams after heating; $m_{crucible}$
215 is the mass for the crucible and its lid in grams.

$$\%ash = \frac{m_2 - m_{crucible}}{m_1 - m_{crucible}} \cdot 100 \quad (5)$$

216 For the standard muffle furnace tests, in accordance with EN ISO 18123 norm, the
217 volatile matter content was calculated using equation (6), where m_1 is the crucible and

218 sample mass in grams, before heating; m_2 is the crucible and sample mass is grams,
219 after heating; m_{crucible} is the mass for the crucible and its lid in grams.

$$\%volatiles = \frac{m_1 - m_2}{m_1 - m_{\text{crucible}}} \cdot 100 \quad (6)$$

220

221 The content of fixed carbon is found by difference, using equation (7).

222

$$\%fixed_carbon = 100 - \%volatiles - \%ash \quad (7)$$

223

224 *Thermogravimetric analysis*

225

226 The thermogravimetric analysis evaluates weight loss in the sample as temperature rises
227 in a controlled atmosphere. This analysis was conducted in two different atmospheres:
228 oxidizing (air) and inert (nitrogen). Four different methods were evaluated, with
229 temperature ramps of 25°C/min and 50°C/min reaching 550°C and 900°C. The analysis
230 was performed in a Mettler Toledo TGA-2 thermogravimetric scale.

231

232 *Fermentability*

233

234 The lechero tree is a lignocellulosic material, and so its fermentation requires a
235 microorganism inoculator in order to produce methane. This experiment evaluated
236 methane production resulting from the fermentation of pruning waste from the lechero
237 tree in co-digestion with swine manure obtained from farms in the Guaranda Canton,
238 Bolivar province. The pruning waste was ground to particles smaller than 0.5 mm. A
239 total of 12 repetitions were conducted, with a mixture of 250 g of wood and 100 g of
240 manure diluted to occupy 1 L. Thus, the mixture had a concentration of 0.35 kg of

241 mixture/L. The process was carried out at room temperature varying from 10°C
242 (nighttime) and 25°C (daytime).

243

244 The experimental device is shown in Figure 2. It consisted of a 2000 ml load-operated
245 vacuum flask, prepared with side outlet, a test tube, a beaker, hoses and rubber stoppers.

246 The produced gases were brought via a hose to an inverted test tube immersed in a
247 beaker filled with water, this made it possible to calculate the volume of biogas by using

248 a volumetric method, according to the shift in distilled water. The percentage of
249 methane was measured by an analyzer in the line. One vacuum flask of 1000 ml with an

250 alkaline solution of sodium hydroxide (NaOH) (5% m/v) and a few drops of
251 phenolphthalein was added. Gases exiting the reactor were passed through it before

252 being taken to the inverted test tube. The carbon dioxide present in the biogas was
253 stopped by bubbling of the biogas [18] in the sodium hydroxide solution. A

254 thermometer was introduced into the mixture to control the temperature. Once the
255 reactor was set, the mixture was placed, the rubber stopper was sealed with silicone and

256 controlled according to the conditions. The use of a CO₂ filter in one of the devices
257 allowed to verify the CH₄ concentration in each treatment.

258

259 Chemical oxygen demand (COD), microbial count, pH, total solids and volatile solids
260 were evaluated every 24 hours, over a period of 30 days. Regular measurement of the

261 chemical demand of soluble oxygen (COD) and solids analysis allowed monitoring the
262 biodegradation process of the organic matter [19], while anaerobic biodegradability was

263 analyzed by COD balance of the substrate before and after the anaerobic treatment
264 performed [20]. The methods used are outlined in Table 3.

265

266 **RESULTS AND DISCUSSION**

267

268 *Dendrometric analysis*

269 The Table 4 shows the statistical summary for each of the variables measured in the
270 dendrometric analysis. $W_{br\ leaves}$ is the biomass in kg per tree of pruned branches with
271 leaves, while W_{br} is the biomass in kg per tree of pruned branches without leaves, Dc is
272 the diameter of the crown in m, Dt is the diameter of the trunk in cm, H is the height of
273 the plant in m and Ht is the height of the trunk

274

275 The statistical summary includes parameters of central tendency, variability and shape.
276 The shape parameters, skewness coefficient and standard kurtosis, are especially
277 relevant due to they can be used to determine if the sample comes from normal
278 distribution. Statistical values out of the -2 to +2 range indicate significant deviation
279 from normality, consequently invalidating many of the statistical procedures typically
280 applied to this data. In this case, all the variables are within range, indicating they all
281 have normal distribution.

282

283 The trees analyzed have a crown diameter ranging between 0.3 and 5 m, and height
284 ranging from 1.1 to 9 m. The average dry pruned biomass obtained per tree is 9.95 kg,
285 with a 1.49 kg standard deviation, while biomass with no leaves had a dry weight of
286 5.28 kg, leaf mass meaning approximately 40% of the weight of the pruning waste.

287

288 Table 5 shows the Pearson correlation coefficients between variables. These correlation
289 coefficients range from -1 to +1, and measure the strength of the linear relationship
290 between variables. A coefficient close to 1 indicates a direct linear relationship, if a

291 variable increases so will the other. A coefficient close to -1 indicates an inverse linear
 292 relationship, when a variable increases the other decreases. A coefficient near 0
 293 indicates there is no relationship between the variables. The asterisk used in the table
 294 indicates the estimated correlations are statistically significant, in other words, the
 295 relationship has a P-Value inferior to 0.05 and the correlations are significantly different
 296 from zero, with a confidence level at 95.0%. It is evident that the dimensions of the
 297 plant all have a direct linear relationship, namely, positive values. A bigger trunk
 298 diameter implies greater crown diameter and height, with coefficients of 0.52 and 0.61.
 299 The weight of the pruning waste increases with crown size as well ($r=0.6$ and $r=0.67$).
 300 However its relationship with trunk diameter is much weaker ($r=0.23$ and $r=0.29$).
 301 While the relationship is positive, the diameter of the trunk is a poor indicator of
 302 potential obtainable pruning waste.

303

304 More than 15 regression models were used to predict waste biomass from dendrometric
 305 variables. The model with the highest coefficient of determination resulted from using
 306 standardized variables. The standardization of the variables used is shown in equations
 307 (8), (9) and (10).

$$H_{nom} = \frac{H - H_{min}}{H_{max} - H_{min}} \quad (8)$$

$$Dc_{nom} = \frac{Dc - Dc_{min}}{Dc_{max} - Dc_{min}} \quad (9)$$

$$Dt_{nom} = \frac{Dt - Dt_{min}}{Dt_{max} - Dt_{min}} \quad (10)$$

308

309 The improvement of predictive models to determine pruning waste based on
 310 standardized dendrometric variables was previously observed by Velazquez et al.,
 311 (2016) [22]. These researcher analyzed quantification models of residual biomass from
 312 the pruning of orange trees in Bolivar province (Ecuador) based on dimensionless

313 dendrometry. However, the majority of these predictive studies used absolute
314 dimensions, Velazquez y Cazco (2017) [23] and their work with plum trees in Ecuador
315 is an example.

316

317 The RMS, 1 kg, is the standard deviation of the difference between the observed values
318 and the ones predicted by the model (Table 6). This value can be used to build limits in
319 further observations. The median absolute error (MAE) of 0.77 kg corresponds to the
320 median value of the deviations mentioned.

321

322

323 *Elemental, proximate analysis and high heat value*

324

325 The means, standard deviation and analysis of variance of the values obtained from the
326 elemental analysis, proximate analysis and calorific value of the different wood and leaf
327 matter mixtures from the pruning waste of the lechero tree are shown in Table 7. The
328 analysis of variance was carried out with a confidence level of 95%. Since the pruning
329 waste is composed of both wood and leaves in varying proportions, it is very important
330 to analyze the mixture. The nitrogen content in the waste material increases
331 significantly with higher leaf percentage. However sulfur content does not vary
332 substantially according to leaf percentage. The value for both N and S is limited in
333 several biomass norms, such as EN ISO 17225-4 (Table 2). The value of nitrogen is
334 greater than 1% when the percentage of leaf matter exceeds 25%. In order not to go
335 over this value, it is necessary to apply separation techniques to the wood and leaves,
336 such as fans after drying.

337

338 Leaf presence does not influence calorific value significantly. This value is around 18.5

339 MJ/kg. It is similar to that of other woody agricultural waste such as orange trees, olive
340 trees, almond trees and vines [10]. It is also similar to that of the 28 materials presented
341 by Channiwala and Parikh (2002) [24], who worked on unified correlation for
342 estimating HHV of solid, liquid and gaseous fuels. They have similar values to those of
343 pruning waste from urban trees, presented in the work of Velazquez et al., (2014) [25].
344 This means pruning waste from the fig tree, if properly managed, could be introduced to
345 the energy market.

346

347 Ash content increases as well according to leaf content (Figure 3). However, the
348 percentage of volatiles percentage was not affected.

349

350 The best models to predict calorific value based on elemental (equation 11) and
351 proximate analysis (equation 12) are shown in Table 8. Based on determination
352 coefficient, the models that best explain variability of the calorific value are developed
353 from elemental analysis, with a R^2 of 0.81. However, these are lower than those
354 proposed by other researchers. For example, Pérez et al. (2015) [26] presented calorific
355 value predictive models for 5 species in the Guayas province in Ecuador (banana,
356 avocado, neem, mango, carob trees) with a R^2 of 0.85.

357

358 The AIC and BIC statistics make it possible to establish an information criteria based on
359 residual mean square error with a penalty that grows in accordance with the number of
360 coefficients in the model. The aim is to select a model with minimum residual error and
361 as few coefficients as possible.

362

363 The ramp from equation 11 indicates that 1% C increases calorific value by 358 kJ/kg.

364 This value is similar to that obtained by others researchers such as Demirbas y
365 Demirbas (2004) [27] who proposed models for cellulose, hardwood and softwood
366 lignin, beech tree wood and bark, spruce, pine, poplar among many other materials. In
367 all of these, influence of carbon percentage was between 300 and 450 kJ by % C. The
368 same happens in models presented by Sheng and Azevedo (2005) [28], who propose a
369 general biomass model, and Callejón et al. (2011) [29], who introduce models to predict
370 HHV based on the elemental analysis of greenhouse waste.

371

372 The influence of volatiles in the models obtained are consistent with that provided by
373 Kathiravale et al., (2003) [30] in his work with urban residues and that of Sheng and
374 Azevedo (2005) [28] and Yin (2011) [31], who worked with biomass in general.
375 However, calorific value prediction models based on proximal analysis are less precise
376 than those obtained from elemental analysis. Callejón et al. (2011) [28] has made the
377 same observation.

378

379 *Thermogravimetric analysis*

380

381 Figure 4 shows the drop in weight of the 100% wood sample in relative terms (% of
382 weight) as a function of temperature and time both in the air atmosphere test, without
383 air flow and the nitrogen atmosphere test . It is observed that the profiles obtained for 25
384 and 50°C/min temperature ramps are very similar. However, they differ when
385 represented as a function of time. This means the decrease in weight is tied to
386 temperature, regardless of the velocity it is achieved.

387

388

389 As it can be seen, the decrease in weight has got 4 stages. In air atmosphere, first it
 390 slowly diminishes until temperature reaches 250°C. This corresponds at 10 min when
 391 25°C/min ramp is used, or 5 min when 50°C/min ramp is used. Subsequently there is a
 392 rapid decrease in weight, much more pronounced between 250 y 350°C. From here on
 393 the decrease in weight lessens slightly until reaching residual weight at 18 min when
 394 using a 25°C/min ramp. In nitrogen atmosphere, the profiles has also got 4 stages, but
 395 the final mass is higher, due to it corresponds to the char mass and ash mass, while the
 396 final mass obtained in heating under air is simply the ash mass. Residual weight when
 397 the wood is heated in nitrogen atmosphere is in concordance with shown in Table 7,
 398 about 17%. It is reached at 473°C.

399

400 *Fermentability*

401

402 The amount of methane produced by volume and time unit is proportional to the
 403 variation of cellular concentration (X). The proportionality constant $Y_{p/x}$ is called
 404 *product-biomass performance*.

$$405 \quad \frac{d[\text{CH}_4]}{dt} = Y_{p/x} \cdot \frac{dX}{dt}$$

406 Given that variation of cellular concentration is proportional to cellular concentration at
 407 any given instant, the following applies:

$$408 \quad \frac{d[\text{CH}_4]}{dt} = Y_{p/s} \cdot \mu X$$

409 The constant μ is the rate of cellular growth. By developing the variation of cellular
 410 concentration over time, it is possible to prove that the amount of product obtained
 411 (methane) has an exponential growth during the exponential growth of the

412 microorganisms. Consequently, when employing Batch type bioreactors it is best to
 413 work during this phase as it has the highest yield. To this end, retention time must be
 414 adjusted to the duration of this phase.

$$415 \quad \frac{dX}{dt} = \mu X \rightarrow \frac{dX}{X} = \mu \cdot dt$$

$$416 \quad \int_{X_0}^X \frac{dX}{X} = \int_{t_{lag}}^t \mu \cdot dt$$

$$417 \quad \ln \frac{X}{X_0} = \mu \cdot (t - t_{lag})$$

$$418 \quad X = X_0 \cdot e^{\mu(t-t_{lag})}$$

419 X_0 is the initial cellular concentration in the reactor; X is the cellular concentration at
 420 time t , t_{lag} is the lag time or cellular adaptation.

$$421 \quad \frac{d[CH_4]}{dt} = Y_{p/s} \cdot \mu X_0 \cdot e^{\mu(t-t_{lag})}$$

$$422 \quad [CH_4] = Y_{p/s} \cdot X_0 \cdot (e^{\mu(t-t_{lag})} - 1)$$

423
 424 Since the value of $Y_{p/s} \cdot X_0$ is negligible compared to the exponential
 425 $Y_{p/s} \cdot X_0 \ll Y_{p/s} \cdot X_0 \cdot e^{\mu(t-t_{lag})}$, it is possible to graph the accumulated volume obtained,
 426 calculating cellular growth rate, substrate productivity, and optimal retention time for
 427 better energy use.

$$428 \quad [CH_4] = Y_{p/s} \cdot X_0 \cdot e^{\mu(t-t_{lag})} \quad (11)$$

429
 430 The model obtained from the experiments (Eq. 11) is shown in Figure 5. The different
 431 point shape allows to differentiate the exponential production of CH_4 and the stationary
 432 phase where the production of methane is very low. Exponential model of first phase
 433 gave determination coefficients (r^2) between 0.85 and 0.99 in every repetition, which
 434 explains variability in methane production per unit between 85 and 99%. The rate of
 435

436 cellular growth has an aggregated mean value of 0.76 6 day^{-1} . The saturation constant
437 K_s was 0.0015 g L^{-1} , and $1/Y$ average was $253 \text{ g COD removal/g SSV}$.

438

439 CONCLUSIONS

440

441 This research has shown it is possible to develop acceptable models to predict pruning
442 waste from the *Euphorbia laurifolia* in Bolivar province weather, Ecuador.

443 The average amount of material obtained per tree is around 10 kg every year. The
444 calorific value of these residues is consistent with that of other tree species, with a mean
445 of 19 MJ/kg.

446 The pruning waste's N content is influenced by leaf content. If leaf content is less than
447 25%, N content will be less than 1%. This means the material is suitable to be used as
448 biofuel.

449 It is demonstrated that leaf matter affects ash content, nevertheless the change in
450 calorific content is small and not measurable with the uncertainty in the method, or it
451 could be the case that the chemical composition of the leaf offsets the displacing effect
452 of the ash.

453 It was proved possible to predict calorific value based on elemental and proximate
454 analyses.

455 Weight variation of wood and leaf mixtures of *Euphorbia lancifolia* was analyzed in a
456 thermogravimetric scale (TGA). The results indicate residual weights after using
457 $25^\circ\text{C}/\text{min}$ and $50^\circ\text{C}/\text{min}$ ramps up to 550°C and 900°C do not evidence significant
458 differences from those obtained with standardized methods EN ISO 18122 to obtain ash
459 content and EN ISO 18122 to obtain volatile content. It also seems decrease in weight is

460 tied to temperature, regardless of the rate it is achieved at.

461 The fermentation productivity of lechero wood and swine manure mixtures was proven,
462 determining the kynetic constants.

463

464

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Table 1. Location of cities where samples were collected

Location	X-UTM	Y-UTM	Number of sampled trees
Casipamba	0724310	9823619	40
Cuatro Esquinas	0703282	9831110	40
San Simon	0722484	9820762	40
Las Conchas	0725105	9828657	40
Negroyaco	0722596	9826577	40

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609 Table 2. Biomass characterization analysis norms

Norm Reference	Title
EN ISO 16559	Solid biofuels – Terminology, definitions and descriptions
EN 14778	Solid biofuels – Sampling – Part 1: Sampling methods
EN 14780	Solid biofuels – Methods for sample preparation
EN ISO 18134-2	Solid biofuels – Determination of moisture content – Kiln drying method. Part 2. Simplified method: moisture total.
EN 14918	Solid biofuels – Determination of calorific value
EN ISO 18123	Solid biofuels – Determination of volatile matter content
EN ISO 18122	Solid biofuels – Determination of ash content
EN ISO 16948	Solid biofuels – Determination of total content of carbon, hydrogen and nitrogen – Instrumental methods
EN ISO 16994	Solid biofuels – Determination of total content of sulfur and chlorine.
EN ISO 16993	Solid biofuels – Calculation of the analyses to different bases
EN ISO 17225-1	Solid biofuels – Specifications of biofuel and classes – Parte 1: General requirements
EN ISO 17225-4	Solid Biofuels. Fuel specifications and Classes. Part 4: Wood chips.

610

612 Table 3. Methods used in determining the physico-chemical parameters

Parameters	Standard method / technique *
Total Solids (TS)	Gravimetric method - APHA / SM 2540-B [21]
Volatile solids (VS)	Gravimetric method - APHA / SM 2540-B [21]
COD	5220-C standardized method (Spectrophotometer Hach DR 2800, HACH digester DRB 200)
pH	Potentiometric method, digital pH meter (HACH HQ40d Potentiometer)
Volume of methane	Volumetric method (NaOH 5%)
Volume of biogas	Volumetric method (Distilled Water)

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615 Tabla 4. Statistical summary of variables measured in the dendrometric analysis
616

	Dc (m)	Dt (cm)	H (m)	Ht (cm)	W _{br leaves} (kg/tree)	W _{br} (kg/tree)
Average	1.41	12.86	3.10	12.14	9.95	5.28
Standard deviation	0.69	7.18	1.21	12.55	1.49	1.17
Minimum	0.3	3.5	1.1	0.16	2.24	1.06
Maximum	5.0	48.38	9.0	55.0	10.3	5.15
Standard skewness	1.83	1.77	1.06	1.46	1.02	1.09
Standard kurtosis	1.49	1.17	1.92	-1.01	-1.22	-1.54

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Table 5 Pearson correlation coefficients between the variables measured

	Dc (m)	Dt (cm)	H (m)	Ht (cm)	$W_{br\ leaves}$ (kg/tree)	W_{br} (kg/tree)
Dc (m)		0.5218*	0.7580*	-0.3786	0.6005*	0.6747*
Dt (cm)	0.5218*		0.6186*	-0.1560	0.2303	0.2914
H (m)	0.7580*	0.6186		-0.3535	0.1443	0.2262
Ht (cm)	-0.3786*	-0.1560	-0.3535		0.3474	0.2973
$W_{br\ leaves}$ (kg/tree)	0.6005*	0.2303	0.1443	0.3474		0.9723*
$W_{br\ leaves}$ (kg/tree)	0.6747*	0.2914	0.2262	0.2973	0.9723*	

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623

624 Table 6. Regression model to determine pruning waste biomass from plant
625 measurements

Regression model	R ²	R ² _{adjusted}	RMS	MAE
$W_{br} \text{ (kg/tree)} = 2.50 + 6.31 * D_{cnom} - 14.99 * H_{nom} * D_{cnom} + 6.78 * D_{tnom}$	0.70	0.68	0.99	0.77

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628 Table 7. Means and standard deviations of values obtained in the elemental analysis,
 629 proximate analysis, and high heat value

630

Leaves	% N	% C	% H	% S	% Ash	% Volatiles	% Fixed Carbon	HHV (MJ/kg)
0	0.51±0.065 a	44.97±0.40 a	4.58±0.057 a	0.42±0.310 a	3.70±0.04 a	82.92±2.04 a	13.38±2.00 a	18.64±0.56 a
10	0.80±0.018 b	45.00±0.21 a	4.60±0.051 a	0.16±0.050 a	4.95±0.07 b	84.21±0.58 a	10.84±0.56 a	18.54±0.64 a
20	0.88±0.031 c	44.86±0.32 a	4.54±0.065 a	0.09±0.018 a	5.19±0.11 c	79.48±2.66 a	15.33±2.67 a	18.46±0.42 a
30	1.15±0.045 d	44.96±0.35 a	4.54±0.091 a	0.06±0.015 a	6.17±0.14 d	78.85±0.53 a	14.97±0.39 a	18.31±0.29 a
40	1.28±0.033 e	44.83±0.81 a	4.55±0.091 a	0.06±0.011 a	6.50±0.06 e	85.27±9.42 a	8.23±9.48 a	18.61±0.27 a
50	1.62±0.039 f	44.61±0.51 a	4.44±0.036 a	0.06±0.005 a	7.30±0.07 f	76.27±3.90 a	16.44±3.92 a	18.56±0.34 a
100	2.51±0.017 g	45.46±0.29 a	4.38±0.105 a	0.07±0.016 a	10.37±0.17 g	75.75±0.07 a	13.88±0.22 a	18.68±0.07 a
Total	1.25±0.622 h	44.95±0.48 a	4.52±0.101 a	0.13±0.164 a	6.31±2.03 h	80.39±4.91 a	13.30±4.36 a	18.54±0.36 a

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634 Table 8. Prediction models to calculate calorific value (kJ/kg) based on elemental,
 635 proximate and structural analysis

Eq	Regression models	R^2	R^2_{aj}	RMS	MAE	AIC	BIC
11	$HHV = 2.41181 + 0.358645 * C (\%)$	0.81	0.70	109.07	64.02	9.70	9.67
12	$HHV = -25.8414 + 7.20071 * \%Ash - 0.0679335 * \%Ash^2 + 0.519929 * \%Volatiles - 0.0792363 * \%Volatiles * \%Ash$	0.75	0.62	128.06	97.45	11.07	11.05

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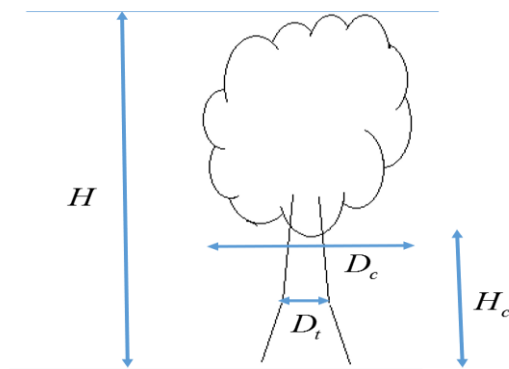
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Figure 1. Geometric measurement of the tree

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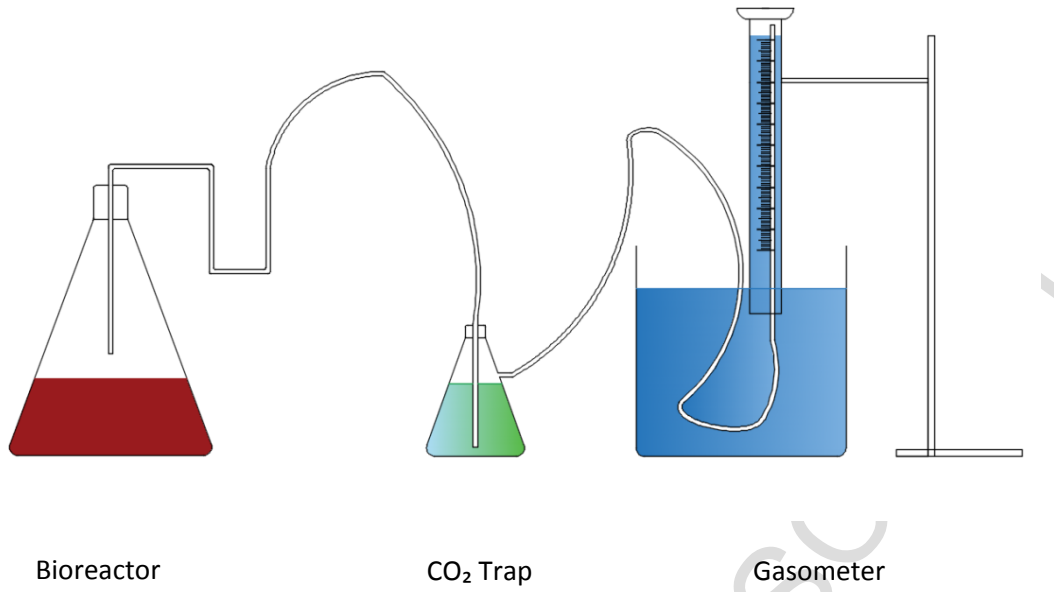
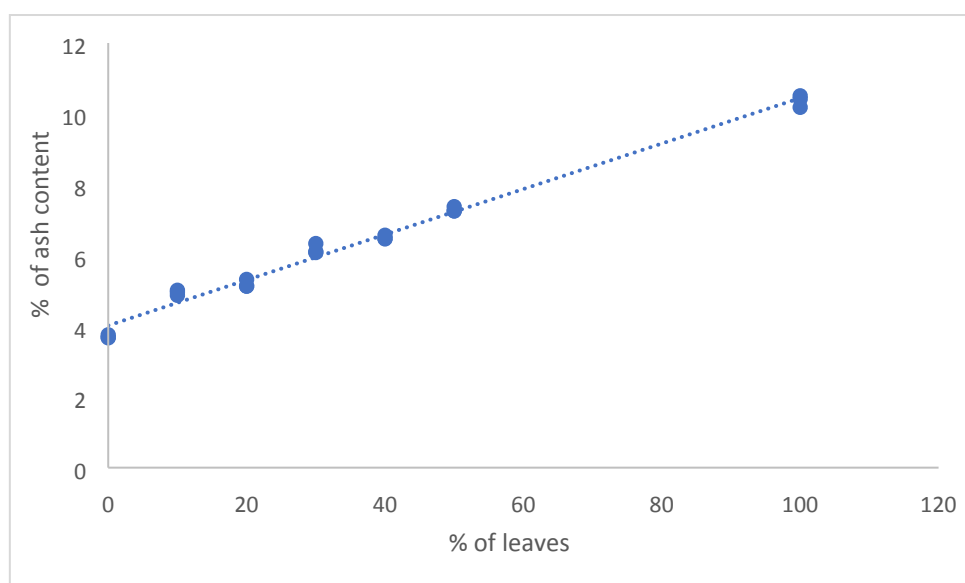


Figure 2. Diagram of the experiment



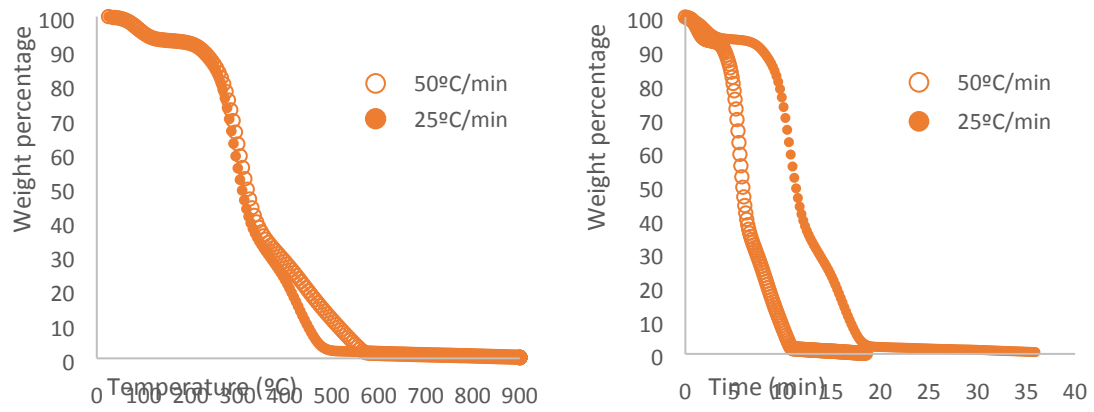
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Figure 3. Ash content according to percentage of leaves

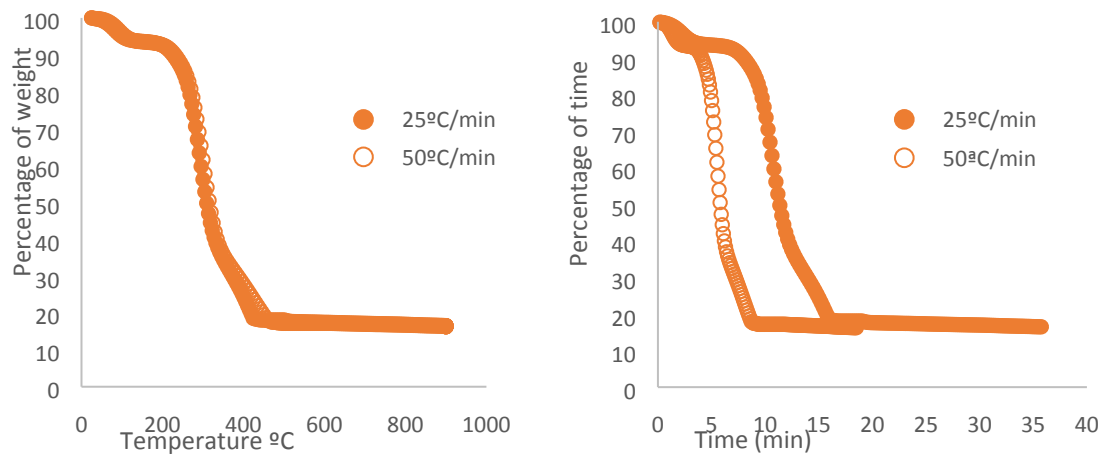
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Air atmosphere



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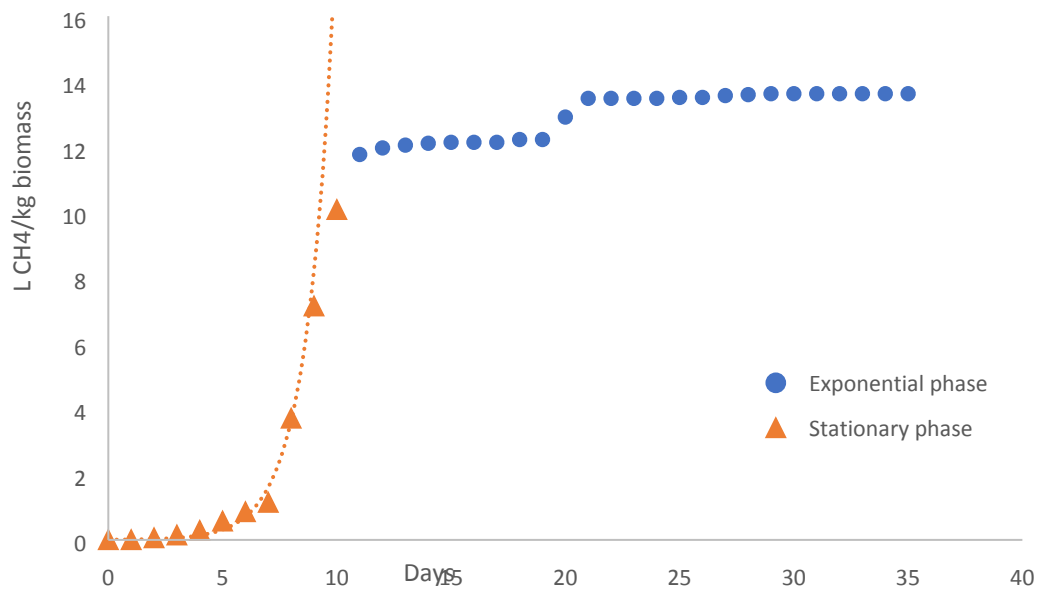
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Nitrogen atmosphere

655 Figure 4. Variation of the weight percentage of the sample versus temperature and time
 656 in different atmospheres.

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661Figure 5. Accumulated CH₄ per kg of substrate

Highlights

- Dendrometric analysis has been carried out of *lechero tree* of Ecuador.
- It has become the elemental, proximate and structural analysis
- Models for predicting higher calorific have been evaluated.