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HIGHER HEATING VALUE CALCULATION OF NEEM, MANGO, AVOCADO, BANANA TREE AND CAROB TREE IN GUAYAS (ECUADOR) FROM ELEMENTAL ANALYSIS

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Highlights

• It has become the elemental analysis of five fruit biomass of Ecuador.

• Models for predicting higher calorific have been evaluated.

• Three are statistically significant has been selected.

Abstract

The use of biomass in rural areas is starting to have interest for farmers in Ecuador. Its use is recognized as clean energy respectful with the environment, but knowledge about their raw materials to be used as bioenergy is very low yet. The objective of this research was to characterize five species located in the province of Guayas: avocado (*Persea americana* L.), carob (*Prosopis spp*.), mango (*Mangifera indica* L.), neem (*Azadiractha indica* L.), bananas (*Musa acuminata* L.). The elemental composition and high heat value were analyzed following harmonized standards. These species had not significant differences in CHN composition, being about 33.012% C, 6.232% H, 0.610% N, and their heat high value 14.322 MJ kg^{-1}. However, significant differences exit respect on Cl and S: Banana wood had the highest Cl and S content 1.162% and 0.134% respectively, and Avocado had the lowest Cl and S content, 0.032% and 0.063% respectively. Fifteen mathematical models to predict the heat high values from elemental analysis were performed. Three from them were selected by better conditions to be used. They are based primarily on carbon with an R2 greater than 0.829 and mean percentage absolute error (MAPE) less than 3.38%.

Keywords: bioenergy, renewable energy, biomass, plant remains

1. Introduction

Fossil sources for energy are being extinguished, and nuclear has a high risk to the population in case of accident [1]. Thus, the new global frame points to renewable energy sources as alternative to local necessities [2]. The most important role in the new energy frame is given to the biomass [3]. Biomass is defined as biodegradable products, waste and residues from biological origin, such as agriculture (including vegetal and animal materials), forestry and related industries, including fisheries and aquaculture, as well as the biodegradable fraction of industry and municipal wastes [4]. All biomass raw materials can be converted into biofuels and biomaterials through biorefineries. This conversion is done using technologies as liquefaction, hydrolysis, pyrolysis, gasification, fermentation and catalysis, among others [5, 6]. For the use of one technology or another, proximate analyzes (moisture, volatile matter, fixed carbon and ash), elementary analyzes (carbon [C] hydrogen [H], nitrogen [N], sulfur [S], oxygen [O] and chlorine [Cl]), and structural analyzes (lignin, cellulose, hemicellulose and extractive) are necessary, besides knowing the high heat value (HHV). The realization of such analysis, especially the calorific value, depends on as the resources of each laboratory as analytical instruments, and reagents are usually very expensive [7]. For this reason, many authors have performed mathematical models for predicting the calorific value of different biomass from the parameters of each type of analysis [8].

Carbon, hydrogen and oxygen are the principal components in the biomass. Of these, carbon usually has a direct correlation with HHV [9], which justifies the higher HHV of woody biomass from crops to herbaceous biomass [10]. The concentration of N and S in biomass is important because they are involved in the generation of NO_x, SO_2 gas, SO_3. Cl produces acidic emissions with corrosive effect during the combustion. This makes that these elements are undesired in the composition of the biomass [11].

C contents in biomass can be ranged 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% [12]. Similarly, HHV (dry basis) ranges between 17 and 21 MJ kg^{-1}, being very different from forest wood (pine with 21 MJ kg^{-1}) and fruit (19 MJ kg^{-1}). In wet biomass, the obtained values decrease depending on moisture content [13]. The determination of the elemental components is performed by standardized analysis (Table 1).

Table 1. Biomass analysis methods.

Property	Analytical method
Standard test meted for analysis	ASTM E870 - 82(2006) [14]
Elemental analysis	
Carbon (C)	UNE-CEN/TS 15104:2008 EX [15] ASTM E777 – 08 [16]
Hydrogen (H)	UNE-CEN/TS 15104:2008 EX [15] ASTM E777 – 08 [16]
Nitrogen (N)	UNE-CEN/TS 15104:2008 EX [15] ASTM E778 – 08 [17]
Sulphur (S)	ASTM E775 - 87(2008)e1 [18]
Oxygen (O)	By difference
Chlorine (Cl)	ASTM E776 - 87(2009) [19]
Higher heating value	UNE 164001:2005 EX [20]; UNE 164001:2005 EX ERRATUM:2008 [21] ASTM D5865 - 10ae1 [22] ASTM E711 - 87(2004) [23]
Sample preparation	UNE-CEN/TS 14780:2008 EX [24]

Of total bioenergy produced worldwide, wood from forests raises for 87%, vegetable residues from agriculture, 9% and municipal and industrial waste 4% [25]. It is expected that by 2050 these three sources of bioenergy provide between 50 and 150 EJ $year^{-1}$ [26]. The use of biomass is starting to have interest for farmers in rural areas in Ecuador. However, knowledge about their raw materials to be used as bioenergy is very low yet. Biomass from tropical crops, such as avocado, carob, mango, neem, bananas can be an important source of renewable energy [27]. Its amount could be estimated by image analysis and ultrasound, determining the canopy volume, number of fruits, fruit quality, volume pruning, etc. [28]. Plant remains from the carob and mango can be harnessed to produce bioethanol, favoring a reduction in fossil fuel use and CO_2 emissions [29, 35]. Besides, from mango it can be obtained biogas [36] and briquettes [37, 38]. They are also used as animal feed supplements [39, 40]. The banana biomass is also useful for producing bioethanol [33, 41-42], biogas [43], textiles, and power generated by direct combustion [44]. The neem, especially its seeds, is used to produce oils and their subsequent use as biofuel [45, 47]. Structural composition analysis (cellulose and lignin) of biomass from avocado leaves were conducted by Murovhi et al. [48] with the aim to use as mulch. Other authors have made analysis of the components

of avocado fruit [49, 50], components of the fruit pulp to extract oil [51] and starch content from seed [52].

On the other hand, it is also known that all these plants (neem, avocado, carob, mango and banana) used as organic mulch can improve agricultural soils favoring their fertility [53, 56]. Either as compost or as bioenergy resource, using this biomass can improve economic conditions in rural areas of South America [57].

Because of high cost to obtain directly high heat value by calorimeter, respect on elemental analysis [58], the objective of this research was to perform mathematical prediction models for calorific power based on elemental analysis of the species of avocado, banana, mango, neem and carob located in the province of Guayas (Ecuador).

2. Material and Methods

Biomass of avocado (*Persea americana* L.), carob (*Prosopis spp*. L.), banana (*Musa acuminata* L.), mango (*Mangifera indica* L.) and neem (*Azadiractha indica* L.) was studied. These fruit trees are among the most important in the Province of Guayas (Ecuador) (Figure. 1). Samples were taken from commercial plantations. Four plots were sampled in each species. Five samples were randomly taken from each plot immediately after pruning residues. All sampled plantations were between 8 and 12 years, all of them in Guayas province (Ecuador) under tropical growing conditions. Carob, mango and avocado trees were separated 10 x 10 m^2. They were pruned after harvest. Banana plants were spaced 5 x 5 m^2. They were pruned regularly. Neem plants were separated 7 x 7 m^2.

Figure 1. Location of the study area.

After pruning the branches and leaves of each species were carried to the laboratory. Then wood and leaves were separated. The wooden parts were reduced by a saw, making cross sections to facilitate subsequent crushing. The leaves were dried in an oven at 105 degrees Celsius for 4 hours. Both the leaves and wood were crushed separately (Figure 2).

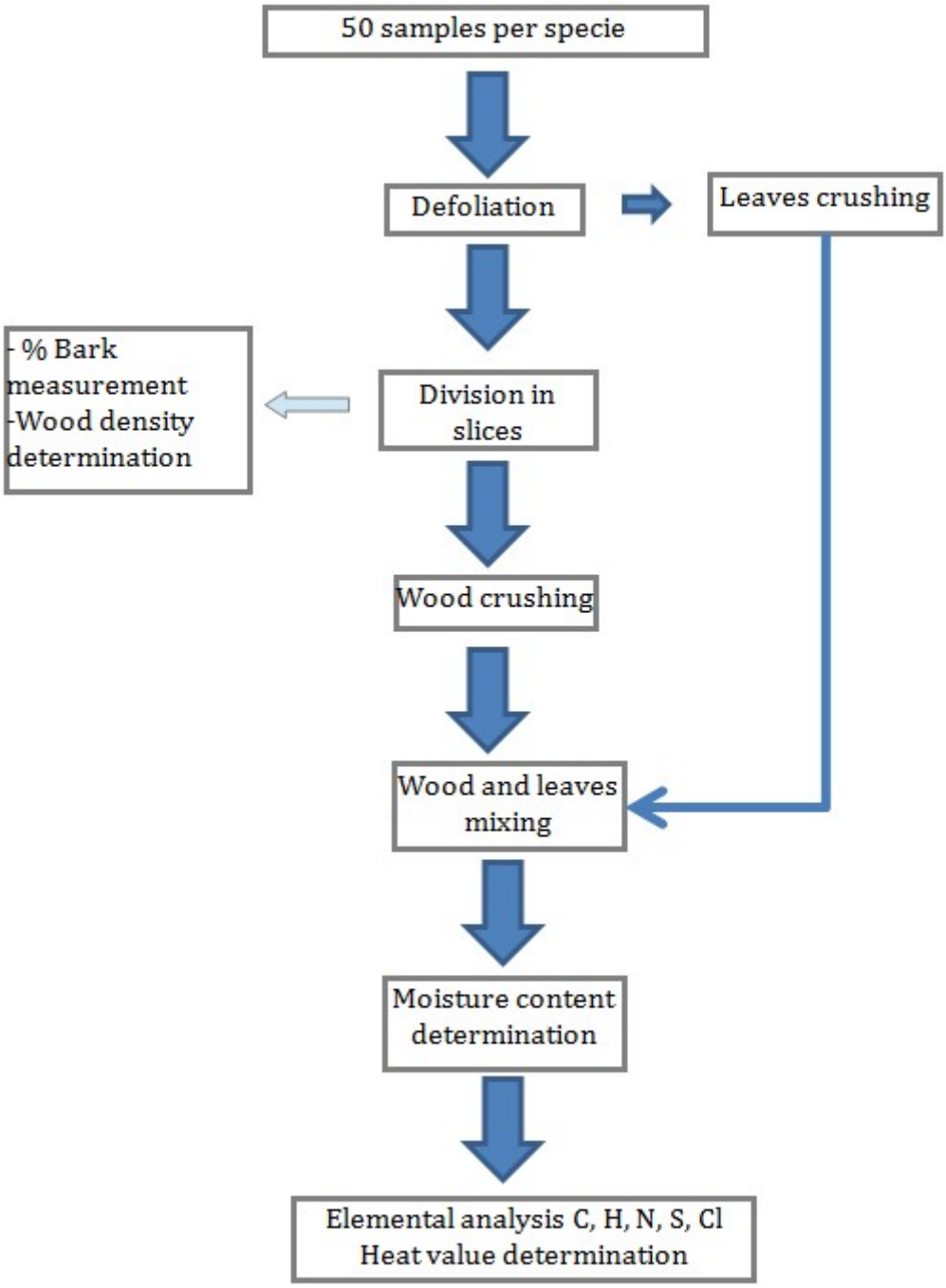

Figure 2. Process of preparation and analysis of samples

Subsequently, 10 mixtures of wood and leaves of each species were made according to Table 2. These mixtures allowed simulate actual situations where the leaves are dried but the wood is wet yet. These situations produce variability in the elemental composition of biomass.

Table 2. Data combined samples of wood and leaves of the species.

%wood	%leaves	Neem	Mango	Banana tree	Carod tree	Avocado
95	5	X	X	X	X	Not data
95	5	X	X	Not data	X	Not data
90	10	X	X	X	X	X
90	10	X	X	X	Not data	Not data
85	15	X	X	X	X	Not data
85	15	X	X	X	Not data	Not data
80	20	X	X	X	X	Not data
80	20	X	X	X	X	Not data
75	25	X	X	X	X	X
75	25	X	X	X	X	Not data
70	30	X	X	X	X	Not data
70	30	X	X	X	X	Not data
65	35	X	X	X	X	X
65	35	X	X	X	X	X
60	40	X	X	X	X	X
60	40	X	X	X	X	X
100	0	X	X	X	X	X
100	0	X	X	X	Not data	X
0	100	X	X	X	X	X
0	100	X	X	X	X	X

Although the energy characteristics of a determined anhydrous material can be considered constant, received materials for combustion in industrial applications have variability in moisture, presence of leaf and even they are mixed with other materials. Under these conditions, the heat properties are no longer constant. For this reason %C, %H, and %N in wet basis were used to develop prediction models to predict high heat value on different biomasses with different content of leaf and wood. Currently there are devices capable of measuring these elements in 5 minutes [58].

For the preparation of samples UNE-CEN/TS 14780: 2008 EX [24] was followed. Elemental components (C, H, N) were obtained using a elemental analyzer LECO Truspec CHN according to UNE-CEN/TS 15104: 2008 EX [15]. For the determination of S and Cl ASTM E775-87 (2008)e1 [18] and ASTM E776-87 (2009) [19] were respectively followed. HHV (MJ kg-1) was obtained using a LECO AC-500 calorimeter

by UNE 164001: 2005 EX [20] and UNE 164001:2005 EX ERRATUM: 2008 [21] (Table 1).

To account the heat from the formation of nitric acid from N_2, O_2 and H_2O (60 J $mmol^{-1}$), or sulfuric acids from SO_2 (302 J $mmol^{-1}$) during combustion inside the vessel they were subtracted of heat values registered by the calorimeter.

To perform predictive models have been used up to three variables (C, H and N). For evaluating the models were obtained the coefficient of determination (R^2), adjusted coefficient of determination (adjusted R^2), sum of the squares of the errors (SSE), mean square of errors (MSE), root mean square of the errors (RMSE), mean absolute percentage error (MAPE), Akaike's AIC and Schwarz's SBC [59].

For all equations, 71 data were used to develop the models, and 15 random data were used for validation. The statistical program used was XLSTAT 2014, even for the calculation of the significance of the variables of the mathematical prediction models by the beta coefficients and Student's t-test.

The validation of the regression models was conducted with independent samples of that were used to make the models. The data observed in the new experiments and predicted by the model were compared with paired-sample test based on the t-student. The validation test takes the differences between the observed and predicted in independent samples and assesses whether the mean is statistically different from zero. Otherwise, the model is valid.

3. Results

The average and standard deviation of high heat value (HHV) and elemental analysis (C, H and N) on wet basis can be seen in Table 3.

Table 3. Data replicates for the regression models and average with standard deviation.

Species	%Carbon				%Hydrogen		%Nitrogen		HHV (kJ kg^{-1})	M±SD (kJ kg^{-1})
	%wood	%leaves	C	M±SD	H	M±SD	N	M±SD		
Neem	95	5	35.0	34.2±1.0	6.8	6.7±0.4	0.7	0.9±0.5	14218.3	13835.7±676.0
	95	5	35.6		6.9		0.6		15449.3	
	90	10	35.0		7.0		0.8		13925.3	
	90	10	35.6		7.0		0.7		14293.9	
	85	15	32.6		7.3		0.8		12535.0	
	85	15	34.4		6.9		0.8		14212.4	
	80	20	34.3		6.8		1.0		14344.5	
	80	20	35.4		6.7		0.5		14110.4	
	75	25	34.2		6.6		1.0		14158.5	
	75	25	34.9		6.7		0.8		14097.1	
	70	30	32.8		6.2		0.9		14483.3	
	70	30	34.7		6.2		0.7		13733.0	
	65	35	33.7		6.7		1.2		13535.7	
	65	35	34.0		6.2		0.8		13264.0	
	60	40	33.1		6.2		0.9		12987.3	
	60	40	32.9		6.9		1.3		12991.4	
	100	0	34.4		5.9		0.4		13417.8	
	100	0	35.0		6.7		0.2		14095.0	
	0	100	33.5		6.8		2.1		13942.8	
	0	100	33.1		6.9		2.2		12919.1	
Mango	95	5	26.3	31.7±4.4	7.6	6.7±0.5	0.3	0.5±0.3	12139.6	13202.7±1189.5
	95	5	26.6		6.7		0.2		11446.5	
	90	10	25.8		7.7		0.3		12504.9	
	90	10	31.6		6.6		0.4		11904.2	
	85	15	32.2		6.7		0.4		13275.7	
	85	15	32.6		6.8		0.4		12352.7	
	80	20	31.1		7.0		0.4		12989.8	
	80	20	32.7		6.6		0.3		12998.5	
	75	25	28.5		7.1		0.5		12879.0	
	75	25	29.4		7.2		0.5		12583.9	
	70	30	36.3		6.1		0.7		13978.8	
	70	30	33.2		6.6		0.6		13368.5	
	65	35	31.3		7.0		0.6		13206.3	
	65	35	32.2		6.6		0.7		13683.6	
	60	40	33.7		6.6		0.7		13371.8	
	60	40	33.8		6.5		0.7		13422.0	
	100	0	27.6		7.0		0.2		12474.4	
	100	0	26.9		7.2		0.2		13125.2	
	0	100	41.5		5.7		1.1		16341.7	
	0	100	41.6		5.6		1.0		16007.7	

C: carbon (% by mass on wet basis); H: hydrogen (% by mass on wet basis); N: nitrogen (% by mass on wet basis); HHV: higher heating value (kJ kg^{-1} on wet basis); M: Mean and SD: Standard deviation.

All species studied (neem, mango, carob tree, banana tree and avocado) had a similar carbon ratio on wet basis (C), between 31.7% (mango) and 36.9% (carob tree). The percentage of hydrogen ranges were from 6.1% (carbob tree) and 6.8% (avocado). Nitrogen ranges were from 0.5% (mango) and 0.9% (neem). These species had not significant differences in CHN and high heat value (HHV), which was between 13202.7 kJ kg^{-1} (mango) and 14697.3 kJ kg^{-1} (carob tree).

Table 4 shows the Pearson correlation coefficients of all the variables of elemental analysis. The highest positive correlation was observed between the gross calorific value (HHV) and carbon (C) with a value of 0.905. However hydrogen (H) has a negative influence, with -0.653 Pearson's coefficient. This is due to hydrogen is associated to water content. As it is known, moisture content decreases the high heat value of the biomass, therefore, hydrogen presents inverse proportionality with the heat obtained from combustion. The colineality between moisture content and hydrogen ratio justifies that both rarely were consider in the same model to predict heat value. On the other hand, it should be noted that according to Table 4 an increasing of hydrogen has a parallel decreasing of carbon ratio (C) and nitrogen ratio (N). Nitrogen with 0.578 Pearson's coefficient has low influence in the obtained heat.

Table 4. Correlation matrix with all the variables (Pearson's coefficient).

	HHV	C	H	N
HHV	1	0.905	-0.653	0.578
C	-	1	-0.750	0.627
H	-	-	1	-0.398
N	-	-	-	-

C: carbon (wet basis); H: hydrogen (wet basis); N: nitrogen (wet basis) and HHV: higher heating value (wet basis).

Contents of Cl and S in dry basis are shown on the Table 5. Significant differences were observed: Banana wood had the highest Cl and S content, 1.16% and 0.134% respectively, and avocado had the lowest Cl and S content, 0.032% and 0.063% respectively.

Table 5. Percentage of S and Cl in dry basis in the element composition of each species.

	Neem (M±SD)	Avocado (M±SD)	Carobtree (M±SD)	Banana tree (M±SD)	Mango (M±SD)
S	0.081±0.001	0.063±0.002	0.086±0.021	0.134±0.008	0.064±0.001
Cl	0.057±0.001	0.032±0.001	0.220±0.002	1.160±0.003	0.110±0.001

S: sulphur (% by mass on dry basis); Cl: chlorine (% by mass on dry basis); M: Mean and SD: Standard deviation.

To predict the HHV in kJ kg^{-1} from the elemental analysis (Table 3), we selected 15 prediction equations (models) of a total of 50 performed (Table 6). The models are linear, univariate and multivariate. The explanatory variables used were C, H and N. Also, these transformations have been used: [C^2], [C^3], [C^4], [H^2], [H^3], [H^4], [N^{-1}] [C^{-1}], [H^{-1}], [CH], [CN], [C + N], [H+N], [C+H], [C^2H], [H^2C], [C^2N] and [N^2H]. They are 21 components overall.

Only two models have one component. They depend on of percentage of carbon (Equation 6 [C] and 13 [C^2]). The slope of linear equation 6 coincides with the models obtained for other materials such as wood Sophora japonica or Platanus hispanica [58], some energy crops [65]. Equations 4 and 9 have two components. Equations 3, 7 and 8 have three components. There are also two models with 4 components (equations 1 and 5); one with 5 components (equation 14) and other with 6 components (equation 2). Equations 11, 15, and 12 have respectively 7, 8 and 9 components (Table 6). All equations have been validated with 15 random data of 86 (Table 3) and all R^2 (for univariate models - equations 6 and 13) and ajusted R^2 (for multivariate models) were greater than 0.819 (Table 6 and Figure 3).

Table 6. The 15 equations selected as predictive models.

Nº	Equations	SSE	MSE	RMSE	MAPE	R^2	Adjusted R^2	Akaike AIC	Schwarz SBC
1	HHV = 9580.793-0.122[C^3]+29.556[H^3]+3.433[C^2H]-17.395[H^2C]	22353649.929	338691.666	581.972	3.176	0.830	0.819	908.847	920.161
2	HHV =-215958.730+ 35634.388[H]-63.039[C^2]-1221460.800[C^{-1}]+ 696375.833 [H^{-1}]+16.393[C^2H]-85.922[H^2C]	22378425.026	349662.891	591.323	3.230	0.837	0.822	912.926	928.765
3	HHV = 7998.357+7.001[C^2]+61.806[H^2]-22.698[CH]	25245292.386	376795.409	613.837	3.486	0.831	0.823	915.484	924.535
4	HHV = 11376.781-102.821[N^{-1}]+ 0.002 [C^4]	26273427.704	386373.937	621.590	3.467	0.832	0.828	916.319	923.107
5	HHV = 6302.054+62.354[H^2]-72.981[CH]+1.192[C^2H]+293.389[C+H]	22227525.064	336780.683	580.328	3.251	0.839	0.829	908.446	919.759
6	HHV = 1981.984+348.901[C]	24550838.634	355809.256	596.497	3.380	0.829	0.826	909.504	914.029
7	HHV = 9637.847+11.521[H^3]+1.458[C^2H]-7.014[H^2C]	23960710.661	357622.547	598.016	3.363	0.835	0.832	911.776	920.827
8	HHV = 10473.036+1.527[H^4]+1.576[C^2H]-7.919[H^2C]	24531663.322	366144.229	605.099	3.396	0.850	0.843	913.448	922.499
9	HHV = 6859.254+0.001[C^4] +122.799[C+H]	23190314.853	341034.042	583.981	3.292	0.853	0.849	907.456	914.244
10	HHV = 7444.457+164.720[H^2]-159.747[CH]-0.001[C^4]+2.652[C^2H]+395.047[C+H]	23666652.201	364102.342	603.409	3.280	0.859	0.849	914.900	928.476
11	HHV = -204446.179-1335.186[CN]+548542.415[H^{-1}]-0.708[C^3]+11.531[C^2H]+19.1962[C^2N]-53.764[H^2C] +23378.233[H+N]	19676888.290	312331.560	558.866	2.879	0.869	0.854	905.792	923.893
12	HHV = -240821.134-532.208[C^2]+10430.560[H^2]-3821.831[CH]+0.025[C^4]-39.566[H^4]+59.203[C^2H]-37.753[N^2H]+31313.612[C+N] -30575.354[H+N]	20347328.387	333562.760	577.549	3.077	0.875	0.856	912.170	934.797
13	HHV = 7946.521+5.010[C^2]	21905967.007	317477.783	563.452	3.246	0.860	0.858	911.411	905.936
14	HHV = 55003.537-45.104[C^2]-722568.302[C^{-1}]+100.753[H^3]+12.187[C^2H]-60.697[H^2C]	19370060.755	298000.935	545.895	3.056	0.874	0.864	900.676	914.252
15	HHV = -275260.163-538.962[C^2]+11468.135[H^2]-3911.834[CH]+0.025[C^4]-45.393[H^4]+57.777[C^2H]+32917.297[C+N]-32907.348[H+N]	17029931.633	274676.317	524.096	2.716	0.881	0.866	897.534	917.898

C: carbon (% by mass on wet basis); H: hydrogen (% by mass on wet basis); N: nitrogen (% by mass on wet basis); and HHV: higher heating value (kJ kg^{-1} on wet basis). SSE: sum of the squares of the errors. MSE: mean square of errors, RMSE: root mean square of the errors and MAPE: mean absolute percentage error. The 95% confidence level applied to all equations.

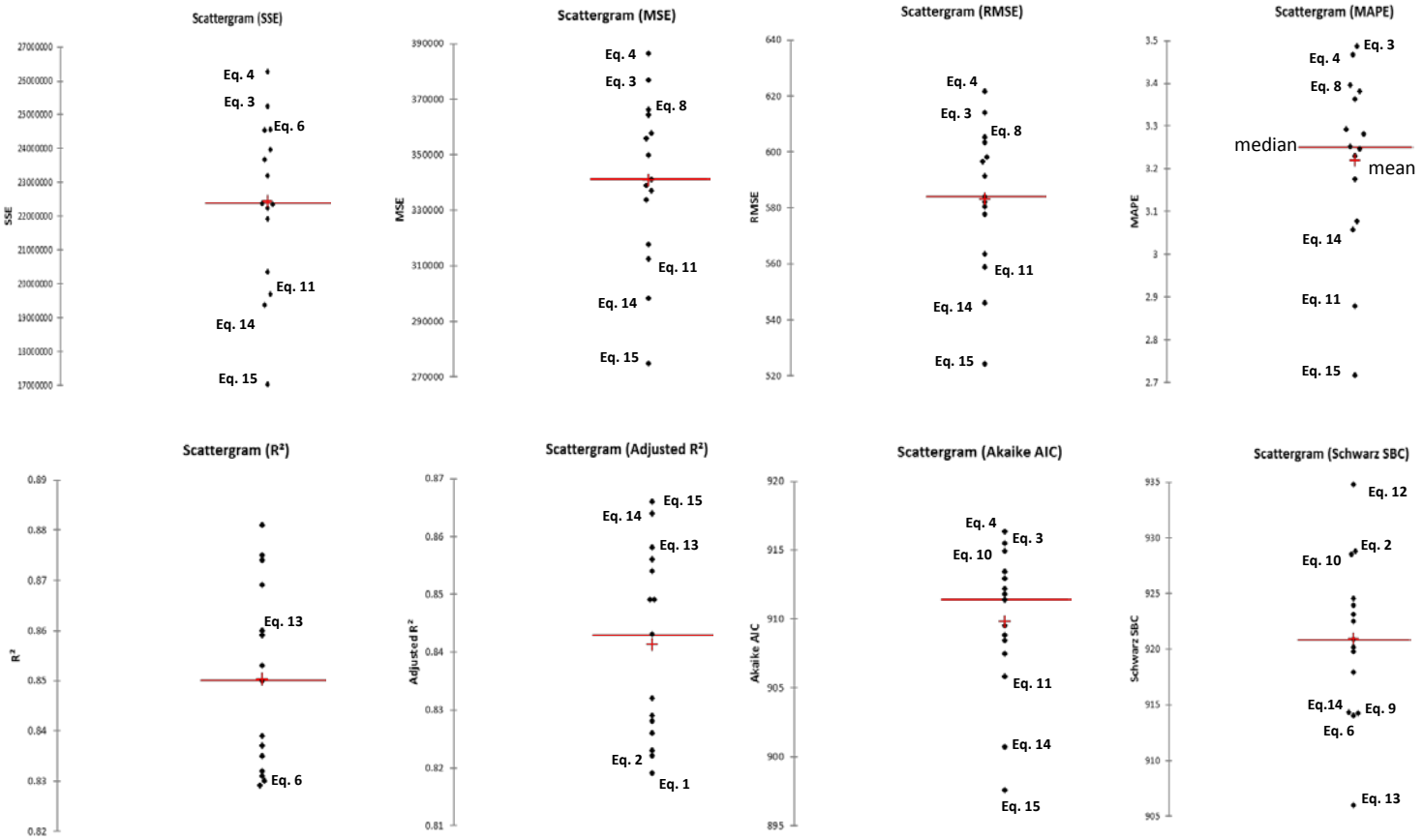

Figure 3. Scatter graphs for the statistical parameters used in the equations, location of the each statistic mean (cross) and median (red line)

Figure 3 shows that the mean and median for all adjusted R2 for all multivariate models were respectively 0.841 and 0.843. The minimum and maximum adjusted R2 for the multivariate equations was 0.819 (Eq. 1) and 0.866 (Eq. 15), respectively. In all the equations (Table 6 and Fig. 3), the mean square of errors (MSE) fluctuated from 0.274 106 (Eq. 15) to 0.386 106 (Eq. 4). The median MSE was 0.341 106, while the mean of the MSE was 0.340 106. Also, the sum of the squares of the errors (SSE) ranged from 17.029 106 (Eq. 15) to 26.273 106 (Eq. 4). The median SSE was 22.378 106, while the mean of the SSE was 22.447 106. The root mean square of the errors (RMSE) varied from 0.524 (Eq. 15) to 621 (Eq. 4) while the median and mean of the RMSE were 0.583 and 0.583, respectively. The mean absolute percentage error (MAPE) reached its minimum at 2.72 (Eq. 15) and its maximum at 3.45 (Eq. 3). The median and mean MAPE were 3.25 and 3.22, respectively.

Meanwhile, Akaike's AIC value varied from 897.53 (Eq. 15) to 916.32 (Eq. 4). The median and mean of Akaike's AIC were 911.41 and 909.78, respectively. Finally, Schwarz's SBC reached its minimum at 905.94 (Eq. 13) and maximum at 934.80 (Eq. 12). The median and mean of Schwarz's SBC were 920.83 and 920.88, respectively (Table 6 and Fig. 3).

Figure 4 lists the prediction values (X axis) of all the models with respect to the values found experimentally (Y axis), as well as the error limits. Dashed lines are the curves fitted by the regression models from black points. Solid lines point to the confidence intervals. The active values for formulating the model appear as a blue circle and the independent values for the validation of the model are identified by a red triangle. All the graphs of equations in general presented good correlations between the observed and predicted data.

Figure 4. Scatter graphs for the 15 equations showing their reliability as predictors of the higher heating value (active in blue circle and validation in red triangle; Gray line: upper 95% prediction limit and lower 95% prediction limit).

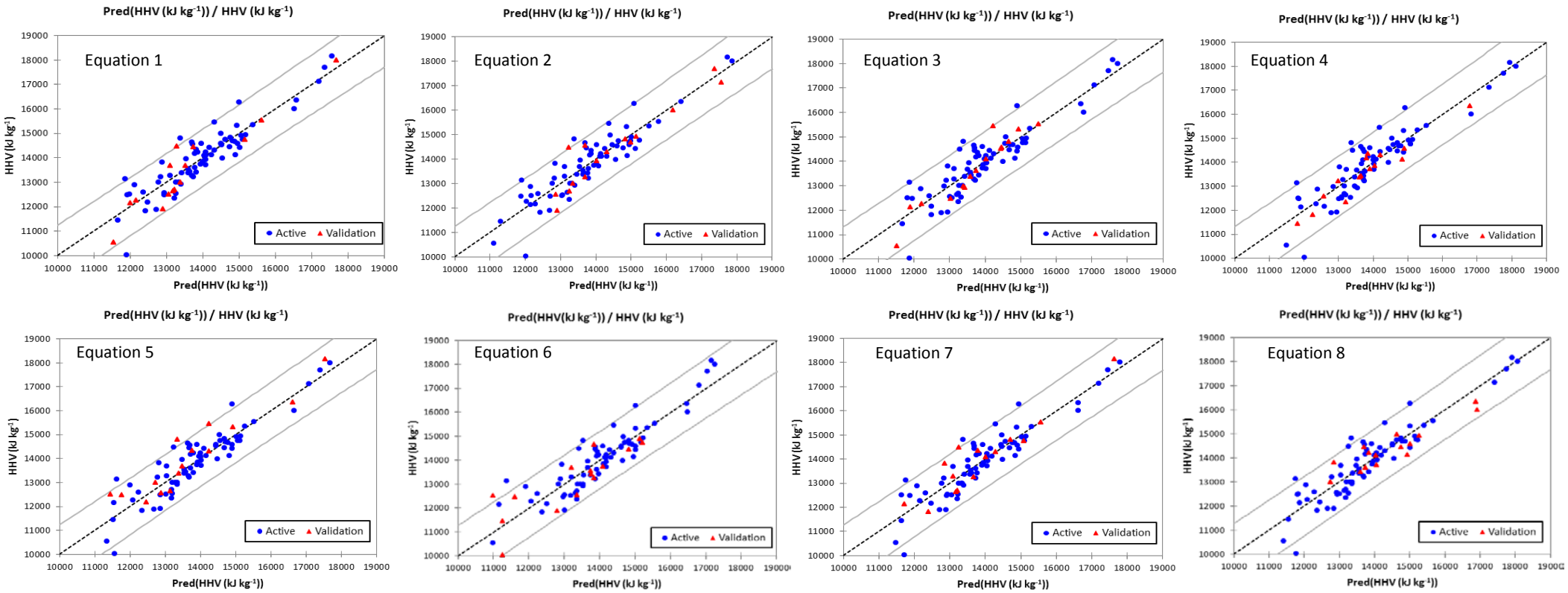

Figure 5. Significance of the variables/components of each equation (see Table 6) by the standardized coefficient.

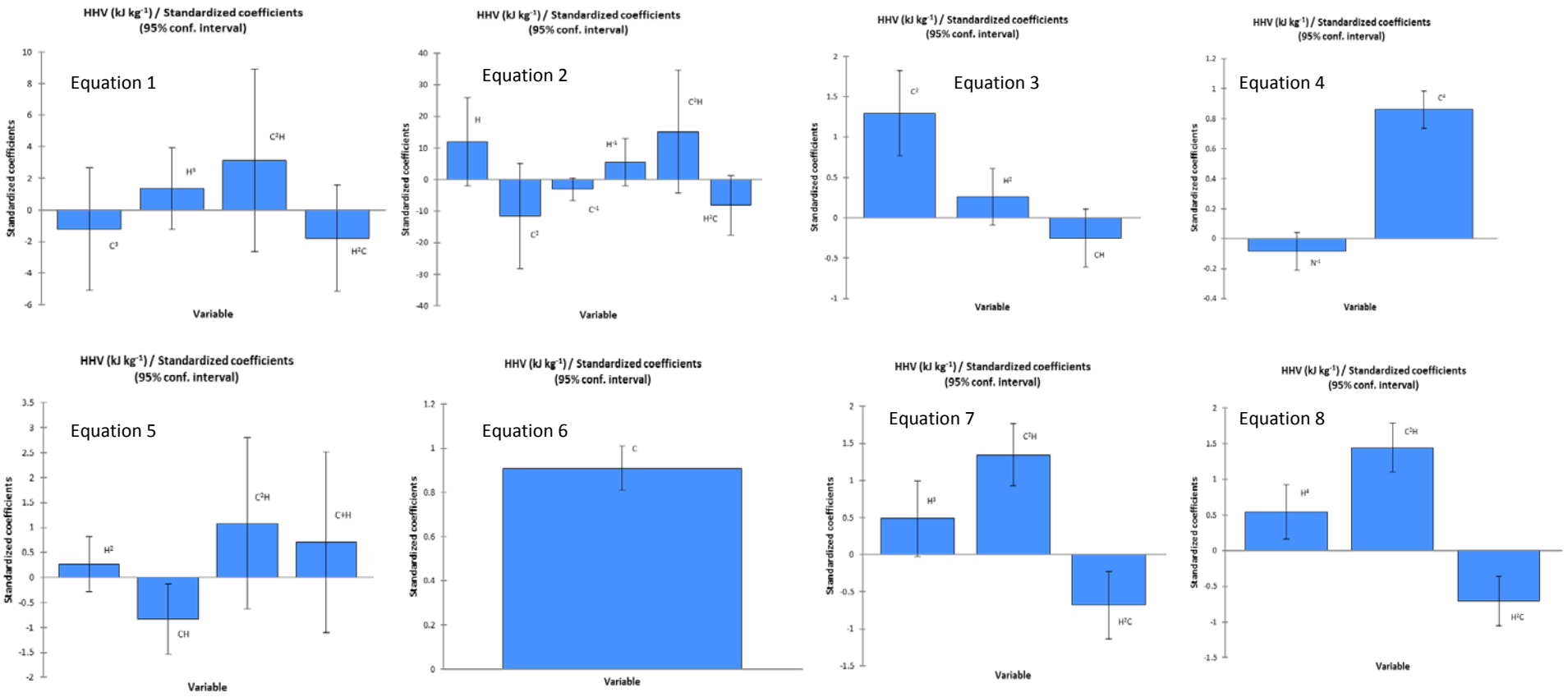

Figure 5 (continued). Significance of the variables/components of each equation (see Table 6) by the standardized coefficient.

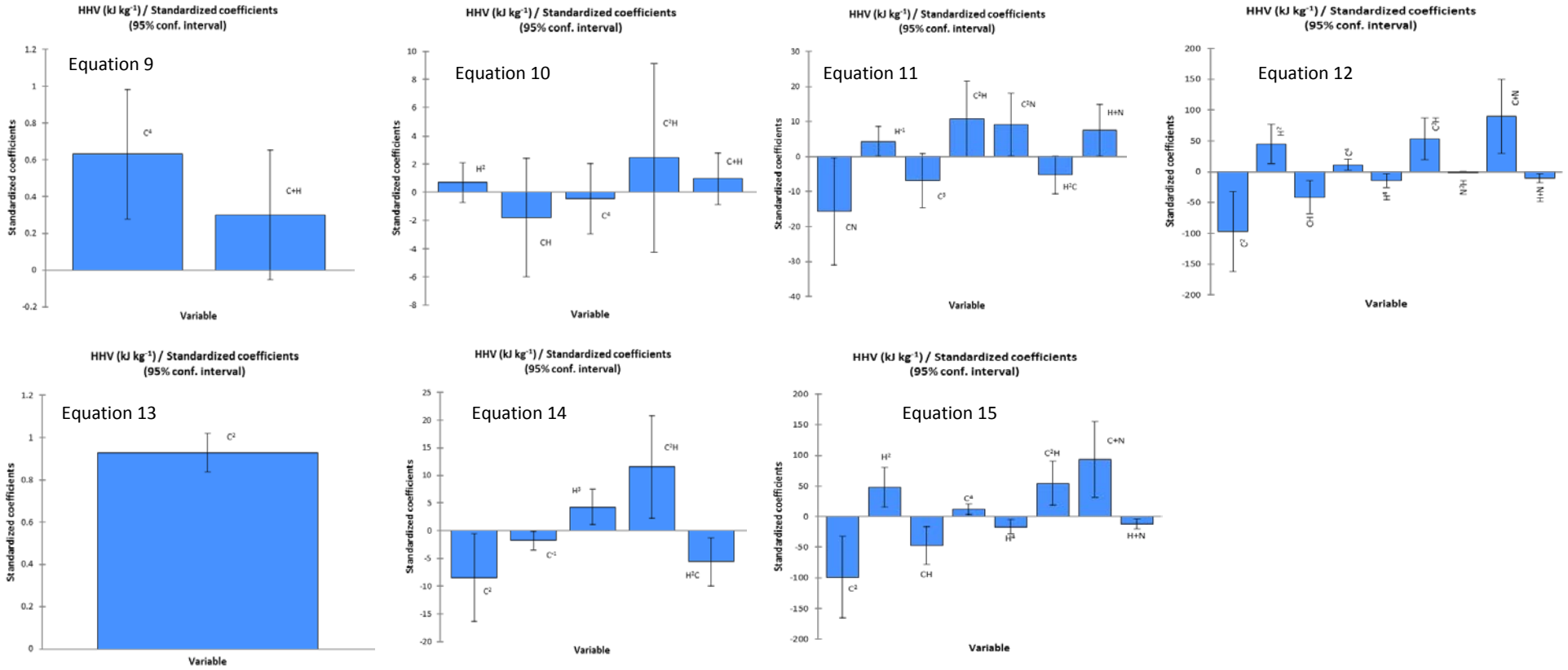

Table 7. Components of each equation whose prediction is higher than the 't' of student and therefore not significant in the model equation.

	Equations																											
	1		2		3		4		5		6		7		8		9		10*		11		12		13		14		15	
Components	t_{pr}	$\lvert t_{cal}\rvert$	t_{pr}	$\lvert t_{cal}\rvert$	t_{pr}	$\lvert t_{cal}\rvert$	t_{pr}	$\lvert t_{cal}\rvert$	t_{pr}	$\lvert t_{cal}\rvert$	t_{pr}	$\lvert t_{cal}\rvert$	t_{pr}	$\lvert t_{cal}\rvert$	t_{pr}	$\lvert t_{cal}\rvert$	t_{pr}	$\lvert t_{cal}\rvert$	t_{pr}	$\lvert t_{cal}\rvert$	t_{pr}	$\lvert t_{cal}\rvert$	t_{pr}	$\lvert t_{cal}\rvert$	t_{pr}	$\lvert t_{cal}\rvert$	t_{pr}	$\lvert t_{cal}\rvert$
C											X	18.284																
C^2			0.171	1.386	X	4.884																	0.004	2.990	X	20.618	0.035	2.149	0.004	2.990
C^3	0.540	0.616																												
C^4*							X	13.971									0.001	3.576	0.708	0.377	0.077	1.797	0.011	2.615					0.007	2.775
H			0.090	1.723																										
H^2					0.141	1.491			0.334	0.972									0.343	0.955			0.006	2.847					0.004	2.964
H^3	0.294	1.058											0.059	1.918													0.011	2.631		
H^4															0.006	2.859							0.011	2.613					0.007	2.813
N^{-1}							0.179	1.358																						
C^{-1}			0.091	1.718																							0.045	2.040		
H^{-1}			0.144	1.479																	0.045	2.041								
CH					0.163	1.411			0.022	2.353									0.395	0.856			0.003	3.079					0.004	3.026
CN																					0.044	2.051								
C+N									0.440	0.776													0.004	2.971					0.004	3.031
H+N																					0.046	2.037	0.005	2.884					0.004	3.030
C+H																	0.093	1.704	0.295	1.056										
C^2H	0.284	1.081	0.123	1.564					0.211	1.262			X	6.411	X	8.401			0.466	0.734	0.050	2.001	0.002	3.166			0.015	2.490	0.004	3.016
H^2C	0.292	1.063	0.089	1.726									0.004	2.999	0.0001	4.051					0.058	1.928					0.013	2.550		
C^2N																					0.046	2.034								
N^2H																							0.451	0.759						
Intercep	X	11.815	0.136	1.509	X	6.572	X	36.969	0.562	0.583	0.004	2.985	X	12.654	X	12.409	0.006	2.863	0.549	0.603	0.053	1.970	0.011	2.625	X	26.722	0.013	2.545	0.006	2.869

X: <0.0001; If '$t_{prediction}$>$t_{calculated}$' the variable is not significant into equation; *: not significant.

In Figure 5, standardized coefficients (also called beta coefficients) are used to compare the relative weights of the variables. The higher the absolute value of a coefficient, the more important the weight of the corresponding variable. When the confidence interval around standardized coefficients has value 0, the weight of a variable in the model is not significant. It is observed that equations 6, 8 y 13 have all their components with beta coefficients higher than zero at 95% level confidence. Although equations 14 and 15 have also beta coefficients positive, they are very close to zero. This means lower reliability. Some beta coefficients in the other equations are negative at 95% level confidence (Fig. 5).

Finally, it should be indicated that all the significance tests made for each variable using Student's t-test are shown in Table 7. It is observed that the component [C4] is not significant the equation 10.

4. Discussion

Vargas-Moreno et al. [8] conducted a review of models to predict calorific value for different biomass materials based on elemental analyzes. Most of these models reviewed gave determination coefficients between 0.8 and 0.99. For this reason, the correlation coefficients obtained in this work, higher than 0.841, were considered very acceptable. However, on the other hand, Callejon-Ferre et al. [1] proposed models with higher R2 for different materials, but their models were obtained for dry materials and without leaves; whereas the models obtained in this study were obtained from mixtures of wood and leaves, and different moisture content, as received. Therefore, they are more applicable in actual situations in industries; where the material cannot be usually dried completely and they are have different percentage of leaf.

Velázquez-Martí et al. [58] already applied this way to obtain prediction models to predict high heat value on lignincellulosic waste materials from urban tree pruning. In

these works the determination coefficients obtained are similar to those of the present work, between 0.7 and 0.9. This means that the presence of moisture causes decrease in accuracy of prediction models calorific value.

It is observed that species with higher carbon (C) are the highest values of calorific presented (Table 3). This coincides with many other studies [60, 61]. It is also shown in Table 5 with a Pearson correlation coefficient of 0.905 between HHV and C. Because of this, all proposed equations for predicting the gross calorific value (Table 6) are univariate or multivariate present the variable C.

Regarding the content of chlorine (Cl), the banana tree is most content is specifically 11600 mg kg-1 average (Table 4), which could cause long-term problems in boilers of combustion plants. One solution could be the use of banana tree combined with other species with lower chlorine content as Avocado (Table 4). The sulfur (S) is not high in all species studied (Table 4), so it would not be a problem in biomass combustion boilers caused by this element.

In two of the species studied (banana tree and neem) a higher percentage of leaf produces larger carbon content (C) and therefore higher calorific value. Opposite occurs with Carob tree, Avocado and Mango, where higher percentage of wood leads higher content of carbon (C) and calorific value. This discrepancy may be due to the extractive substances of plant biomass (sugars, tannins, sterols, fatty acids, resin acids, oligomeric terpenics, hydrocarbons, etc.) that influence the gross calorific value. Their contents depend on the species, the part of the plant, season, and the growing stage, among other factors [62]. Another explanation could be the botanical family of the studied species, or the character more herbaceous or woody biomasses studied [63].

Not all components of the 15 proposed equations of Table 6 were significant (see Fig. 5). In other words, not all standardized coefficients (also called beta coefficients) were above zero. Something similar happens with the validation of such components using

Student's t-test (Table 7), for example the C4 component of Equation 10 (tprediction> |tcalculated|; 0.708> 0.377). These facts obligate to reject some equations.

The most reliable equations would be five: 6, 8, 13, 14 and 15. Of these, equations 6, 8 and 13 had beta coefficients much higher zero for all components (with 95% confidence). These three equations are based on two variables (C and H), indeed, equation 6 and 13 have only one variable component (C or C^2). Models with high R^2 and few components in the equation are desirable. For this reason, equations 6 and 13 are considered good tools to predict the high heat value in these species. Equation 13 only presents a variable/component (C^2) and the third highest R^2 value, 0.860 (Fig. 3, Table 6). Only two equations, the 14 (5 components and 3 variables - C, H and N) and eq. 15 (with 8 components and 3 variables - C, H and N) had a higher adjusted R^2, 0.864 and 0.866, respectively. The error (MAPE) of the five (6, 8, 13, 14 and 15) equations are quite similar. Although equation 15 had the best MAPE, it has the disadvantage of greater complexity and their beta coefficients very near zero.

All equations, excepting 10, could be considered with acceptable reliability according to beta coefficients. Therefore, they were validated. Figure 4 shows with red triangles the random data selected for validation. It can be observed that they are within the error limits of the proposed models (gray lines Fig. 4). However, due to its reliability and simplicity, the equation number 13 is considered the best model to be applied on these species.

Perhaps prediction models based on proximal and structural analysis could complete this study on the biomass studied.

5. Conclusions

Five tropical species from Ecuador have been characterized: Neem, mango, banana tree, avocado and carobtree species. These species had not significant differences in

CHN composition, being about 33% C, 6.2 % H, 0.6 % N, and their heat high value 14.3 MJ kg^{-1}. However, significant differences exit respect on Cl and S: Banana wood had the highest Cl and S content 1.16% and 0.134% respectively, and Avocado had the lowest Cl and S content, 0.032% and 0.063% respectively. Fifteen models have been proposed and validated for prediction high heat value in wet basis. From these equations the most useful for its reliability and simplicity is number 13 based on a single variable / component: C^2.

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