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PREDICTING HIGHER HEATING VALUE OF AGRO-INDUSTRIAL WASTE: CLASSIFICATION AND MODELING BASED ON PROXIMATE AND ULTIMATE ANALYSIS

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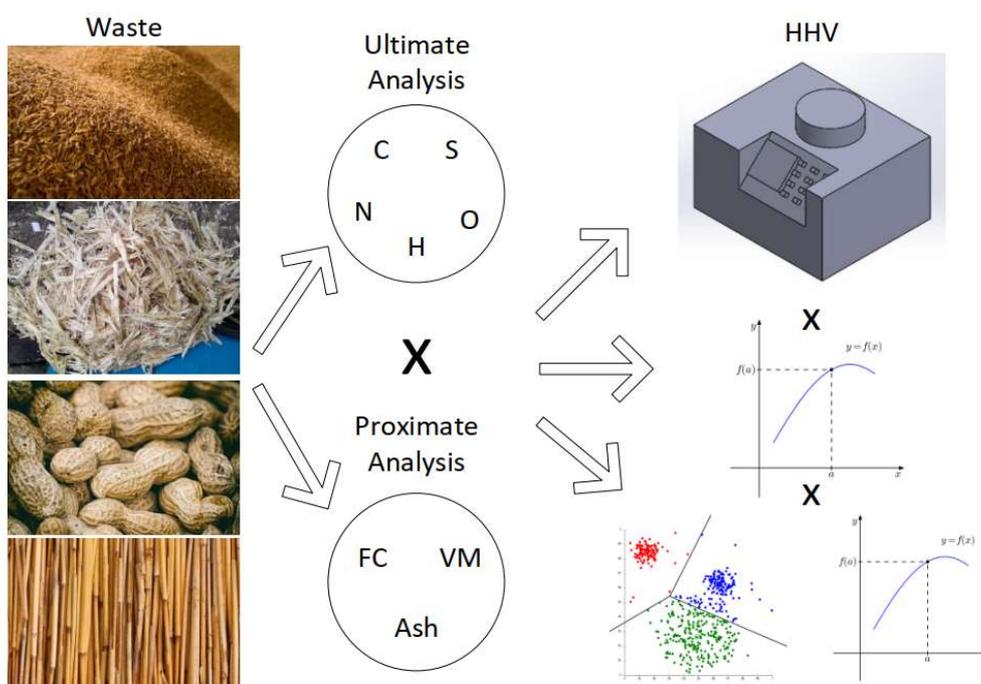
KEYWORDS

biomass energy, higher heating value, proximate analysis, ultimate analysis.

ABSTRACT

Bioenergy production relies on resources such as agricultural waste, which has prompted extensive research on biofuels. The heating value is a crucial parameter for evaluating energy sources. This study aims to analyze and propose formulations for estimating the higher heating value (HHV) based on proximate and ultimate chemical analysis of biomass. A database consisting of 142 samples was created, and 14 formulas available in the literature were initially tested. The datasets for each composition type were classified using the k-means algorithm, and the new sample spaces were validated. For proximate analysis data, specific multiple linear regression models were developed for two classes, one with an average R^2 of 0.697 and SE of 1.05 MJ kg^{-1} , and the other with an average R^2 of 0.678 and SE of 1.27 MJ kg^{-1} . For samples with ultimate analysis, a general model was formulated with an average R^2 of 0.701 and SE of 1.11 MJ kg^{-1} . Sample classification for proximate analysis did not significantly affect the fit of models. Considering that proximate analysis is less expensive than ultimate analysis, the proposed method shows promise in optimizing and reducing costs for determining the HHV of biomass for energy production.

Graphical Abstract



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INTRODUCTION

The world has experienced significant economic development in recent decades, driven by rapid industrialization and urbanization. Concurrently, the global population has increased from 5.3 billion in 1990 to 7.3 billion in 2014, reflecting an average annual growth rate of 1.3% (Dong et al., 2018). The scarcity of natural resources has become a critical concern when considering future perspectives, particularly from energy and environmental standpoints. Developing countries are projected to experience a 33% increase in energy demand by 2040 (Nepal & Pajja, 2019). Notably, the world's energy matrix heavily relies on non-renewable fossil fuel sources, which accounted for 90% of global primary energy consumption in 2017 (Chen et al., 2019). Thus, it is crucial to promote the utilization of alternative renewable energy sources such as biomass to diversify the energy matrix and ensure energy security. Biomass, being reproducible, accounted for 18.1% of global energy consumption in 2017 and is considered renewable (Wang et al., 2020).

Bioenergy production is closely associated with various resources, with agricultural waste being a prominent alternative. These residues are directly linked to crop yields, meaning that increased agricultural production leads to a higher volume of waste. The biomass generated primarily stems from post-harvest activities in agriculture, involving the cutting and pruning of stems, removal of straw, bark, leaves, and branches. Previously, such residues were disposed of in fields, but today, there is a focus on researching their energy reuse, particularly in the biofuel sector (Avcioglu et al., 2019).

Biofuels, as defined by the National Agency of Petroleum, Natural Gas, and Biofuels (ANP), are derived from renewable biomass, and can partially or completely replace fuels derived from oil and natural gas in combustion engines or other forms of power generation (ANP, 2020). Apart from being a viable alternative, biofuels offer environmental and economic advantages, including reduced carbon emissions, decreased reliance on imported oil, as well as job and income generation (Martins Pereira, 2018). The US government has supported the biofuels industry through various subsidy policies and programs, with the goal of achieving a production volume of 36 billion gallons by 2022. However, concerns arise regarding the competition between energy crops and the food industry, as diverting agricultural land for biofuel production may impact food supply (Wang et al., 2017).

Nevertheless, the dilemma of "energy crops for biofuel or food productions" can be mitigated by using agro-industrial waste. The production of energy from such waste aligns with the circular economy concept, providing a superior alternative energy source (Sonu et al. 2023). Various biomass systems, production techniques, operational practices, pre-processing methods, conversion technologies, and transportation systems are being implemented worldwide for energy production from agro-industrial waste (Ramos et al. 2022).

Anaerobic digestion process, coupled with chemical pretreatment, has been explored as a method to break down cellulose, hemicellulose, and lignin molecules for biogas

production (Keerthana Devi et al., 2022). Additionally, the dark dry fermentation method with autoclaving as a pre-processing step has demonstrated potential for biohydrogen production from agro-waste, yielding a maximum hydrogen content of 41% (Abubackar et al., 2019). Biodiesel production using solvents and the transesterification method has resulted in yields of 58.8-62.2 wt.% from coffee grounds (Caetano et al., 2012; Nair et al., 2022).

One crucial parameter for evaluating promising biofuel sources is the heating value, which measures the amount of energy released as heat per kilogram of matter during the combustion process (Roviero et al., 2018). In the case of biomass, this parameter varies depending on its constituent elements. Materials with higher carbon and hydrogen content tend to have a higher calorific value (Miranda et al., 2015).

In addition to determining the heating value, feasibility studies for biomass often involve analyzing the composition of raw materials through proximate and ultimate chemical analysis. Proximate chemical analysis assesses water content, volatile material (VM), fixed carbon (FC), and ash, while ultimate chemical analysis determines percentages of carbon, hydrogen, nitrogen, sulfur, and oxygen (Pari et al., 2018). Since calorimetric pumps, though accurate, are often costly, researchers have used empirical correlations based on the results of these analyses to estimate the heating value. Therefore, ultimate analyzers and muffle furnaces, commonly found in laboratories, can address this limitation (Yin, 2011). Thus, this study aimed to analyze and propose statistical formulations for estimating the higher heating value (HHV) in samples of agricultural residues. The specific objectives were as follows:

- Conducting a comprehensive literature review to compile a biomass database.
- Evaluating the effectiveness of an unsupervised algorithm for sample classification.
- Comparing equations based on proximate and ultimate chemical analysis methods.

MATERIAL AND METHODS

The database used in this study was compiled by consulting the Web of Science and Google Scholar databases. Information was gathered from 142 samples of agro-industrial waste, including husks, bagasse, seeds, and straw, originating from various crops. For each sample, values corresponding to the experimental higher heating value and proximate and/or ultimate chemical analyses were obtained.

Based on this data, the suitability of existing equations (Table 1) from scientific studies (Tillman, 1978; Jenkins & Ebeling, 1985; Jiménez & González, 1991; Cordero et al., 2001; Channiwala & Parikh, 2002; Friedl et al., 2005; Parikh et al., 2005; Sheng & Azevedo, 2005; Yin, 2011) used for predicting the heating value was initially evaluated. Statistical parameters such as the determination coefficient (Equation 15), adjusted determination coefficient (Equation 16), and standard error of estimate (Equation 17) were employed for this evaluation.

TABLE 1. Equations found in the literature for prediction of heating value.

Reference	Equation of <i>HHV</i>	N°
R1	$19,914 - 0,2324Ash$	(1)
R1	$-3,0368 + 0,2218VM + 0,2601FC$	(2)
R2	$0,3536FC + 0,1559VM - 0,0078Ash$	(3)
R1	$0,3259C + 3,4597$	(4)
R1	$-1,3675 + 0,3137C + 0,7009H + 0,0318O$	(5)
R3	$0,00355C^2 - 0,232C - 2,23H + 0,0512C \times H + 0,131N + 20,6$	(6)
R4	$0,3491C + 1,1783H + 0,1005S + 0,1034O + 0,0151N + 0,0211Ash$	(7)
R5	$0,3543FC + 0,1708VM$	(8)
R5	$35,43 - 0,1835VM - 0,3543Ash$	(9)
R6	$-10,8141 + 0,3133(VM + FC)$	(10)
R7	$-0,763 + 0,301C + 0,525H + 0,064O$	(11)
R8	$0,4373C - 1,6701$	(12)
R9	$0,1905VM + 0,2521FC$	(13)
R9	$0,2949C + 0,825H$	(14)

In which:

HHV is the higher heating value in MJ kg⁻¹;

VM is the amount of volatile material in %;

Ash is the ash content in %;

FC is the fixed carbon content in %, and

C, *H*, *O*, *N* and *S* are the contents of carbon, hydrogen, oxygen, nitrogen and sulfur in %, respectively.

References: R1 - (Sheng & Azevedo, 2005); R2 - (Parikh et al., 2005); R3 - (Friedl et al., 2005); R4 - (Channiwalwa & Parikh, 2002); R5 - (Cordero et al., 2001); R6 - (Jiménez & González, 1991); R7 - (Jenkins & Ebeling, 1985); R8 - (Tillman, 1978); R9 - (Yin, 2011).

$$R^2 = \frac{\sum_{i=1}^n [y_{mea_i} - \bar{y}_{mea}] \cdot [y_{cal_i} - \bar{y}_{cal}]}{\left[\sum_{i=1}^n (y_{mea_i} - \bar{y}_{mea})^2 \right]^{0,5} \cdot \left[\sum_{i=1}^n (y_{cal_i} - \bar{y}_{cal})^2 \right]^{0,5}} \quad (15)$$

$$\bar{R}^2 = \frac{R^2 \cdot (n - 1) - p}{n - p - 1} \quad (16)$$

$$SE = \sqrt{\frac{\sum_{i=1}^n (y_{mea_i} - y_{cal_i})^2}{n - p}} \quad (17)$$

In which:

y_{mea_i} is the dependent variable observed for each element;

\bar{y}_{mea} is the average of a dependent variable observed;

y_{cal_i} is the dependent variable calculated for each element;

\bar{y}_{cal} is the average of a dependent variable calculated,

n is the number of elements; and p is the number of model parameters.

To enhance the fitting of these equations to the biomass samples under study and determine their efficiency for each case, a methodology involving data segmentation was proposed. The k-means algorithm, implemented in the free software Orange Canvas v. 3.15, was employed for classification.

As described by Castro & Prado (2002), the k-means algorithm minimizes a cost measure by minimizing the internal distance between patterns within a cluster. The cost minimization ensures the identification of a local minimum of the objective function, which depends on the starting

point. This algorithm is classified as "non-convex" since the deviation value decreases with each iteration, and the process concludes when it falls below a pre-established tolerance.

The sample set was divided into at least three classes to eliminate any outliers that could potentially affect the effectiveness of the models and tests. After obtaining the clusters based on the proximate and ultimate analyses criteria, eqs from (1) to (14) were reapplied, and the results were compared with those presented in Tables 2 and 3. Subsequently, new models were developed for each validated class after dividing the database. Additionally, a

new general formula was derived, with the adopted standards outlined in eqs (18) and (19), where β_0 , β_1 , β_2 , and β_3 represent the adjustment constants. Variables N and S were not included in the proposed models, as per [eq. (19)], as most samples either lacked data for these variables or the data was considered insignificant.

$$HHV = \beta_0 + \beta_1 \times VM + \beta_2 \times Ash + \beta_3 \times FC \quad (18)$$

$$HHV = \beta_0 + \beta_1 \times C + \beta_2 \times H + \beta_3 \times O \quad (19)$$

The adjustment constants β_0 , β_1 , β_2 , and β_3 were evaluated using the Student t-test, which tests the null hypothesis (H_0). The t-test statistic, assuming a normal distribution, is employed when the population variance is unknown. In regression, this statistic determines, at a significance level of α , whether the estimated parameters for the model are equal to zero or not. The tested hypotheses

are $H_0: \beta_0, \beta_1, \beta_2, \beta_3 = 0$ and $H_a: \beta_0, \beta_1, \beta_2, \beta_3 \neq 0$, with H_a representing the alternative hypothesis (Tiboni, 2010).

RESULTS AND DISCUSSION

Preliminary assessment

The results of the adjustments to the equations presented in Table 1 are summarized in Tables 2 and 3. It is observed that the equations relying on proximate analysis exhibited a low level of adjustment and a high standard error (Table 2), with data obtained from 117 samples. On the other hand, the equations based on ultimate chemical analysis demonstrated more consistent adjustments and an average standard error (Table 3). Notably, the higher heating value of the 93 samples assessed in this analysis is approximately 20 MJ kg⁻¹ in magnitude.

TABLE 2. Comparative analysis of heating value forecast equations using proximate biomass analysis for the entire proposed database.

Equation	R^2	$\overline{R^2}$	SE (MJ kg ⁻¹)
(1)	0.319	0.314	1.853
(2)	0.117	0.102	2.757
(3)	0.120	0.097	3.262
(8)	0.121	0.106	3.319
(9)	0.134	0.119	3.263
(10)	0.099	0.083	3.455
(13)	0.127	0.111	2.641

TABLE 3. Comparative analysis of heating value forecast equations using ultimate biomass analysis for the entire proposed database.

Equation	R^2	$\overline{R^2}$	SE (MJ kg ⁻¹)
(4)	0.428	0.421	1.621
(5)	0.675	0.664	1.208
(6)	0.201	0.155	2.758
(7)	0.643	0.623	1.689
(11)	0.610	0.597	1.406
(12)	0.428	0.421	1.907
(14)	0.698	0.695	1.142

Database grouping and class evaluation

Figures 1, 2, and 3 display the database clustering focusing on proximate biomass analysis information. The figures reveal that class C2 comprises six outliers, which were subsequently excluded from further procedures. By

examining Figure 1, the division of classes C1 (58 samples) and C3 (53 samples) was primarily determined by the strong volatile material (VM) content. Biomasses with $VM < 78\%$ are classified as part of class C1, whereas those with $VM \geq 78\%$ belong to class C3.

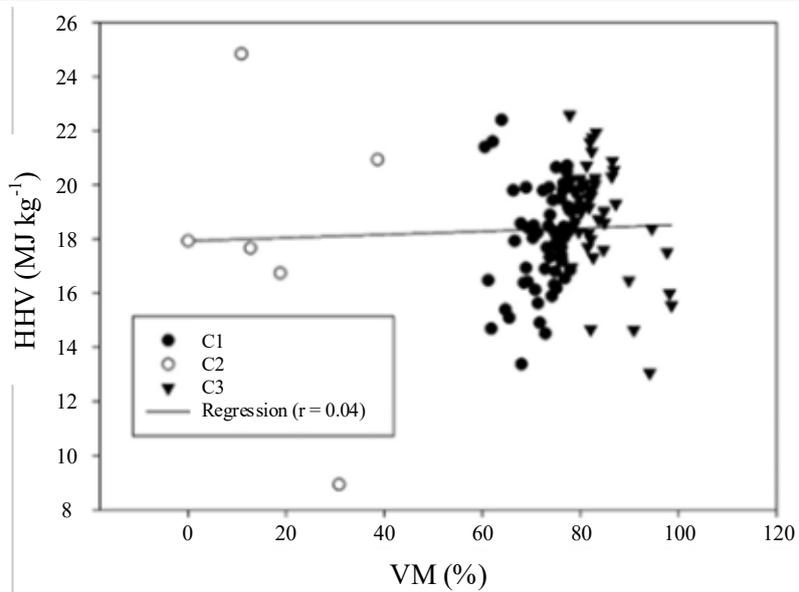


FIGURE 1. Clusters following the criteria of proximate analysis ($VM \times HHV$).

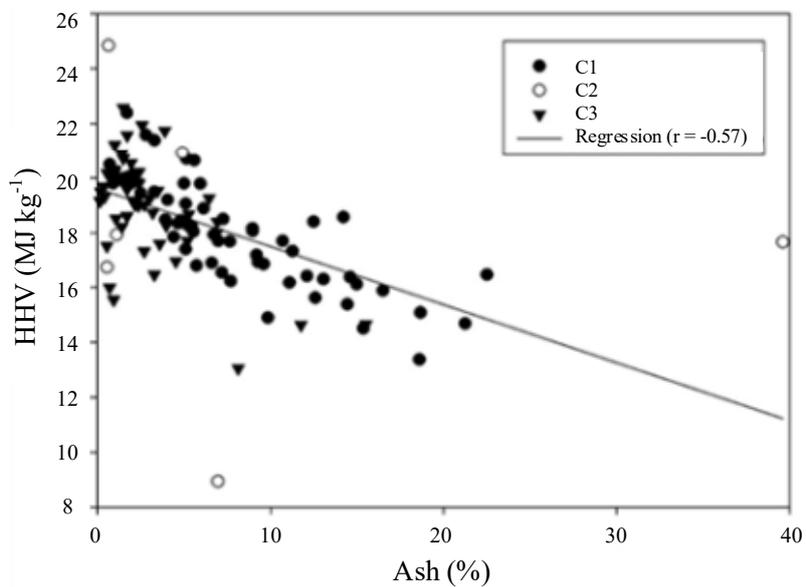


FIGURE 2. Clusters following the criteria of proximate analysis ($Ash \times HHV$).

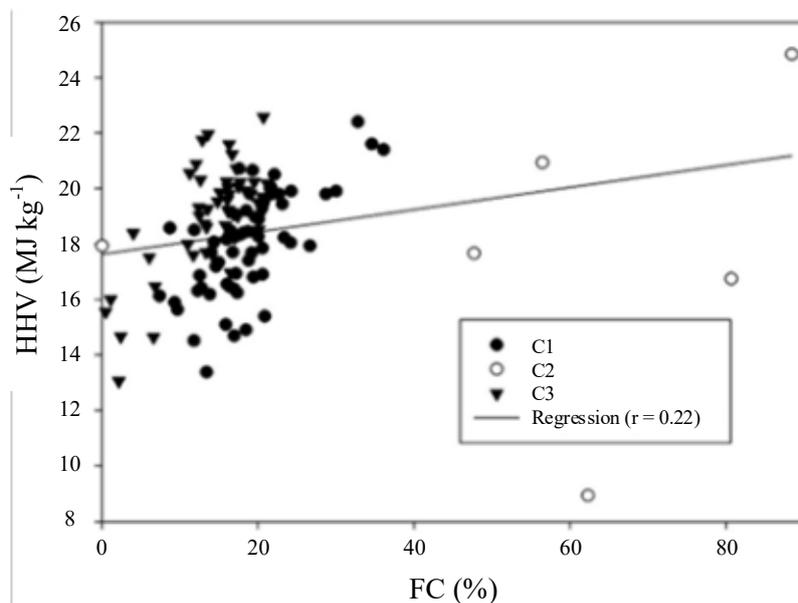


FIGURE 3. Clusters following the criteria of proximate analysis ($FC \times HHV$).

Figures 4, 5, and 6 illustrate the clustering outcomes based on ultimate chemical analysis data. Classes C1 and C3, consisting of 4 and 2 samples, respectively, were deemed as outliers and therefore excluded. However, classes C2 (42 samples) and C4 (45 samples) were identified as valid and were categorized based on the

oxygen content variable. Biomasses with a carbon (C) content of 42% or greater are assigned to class C2, while those with a C content below 42% are allocated to class C4. This threshold is clearly demonstrated in Figure 6, confirming the consistency of the division.

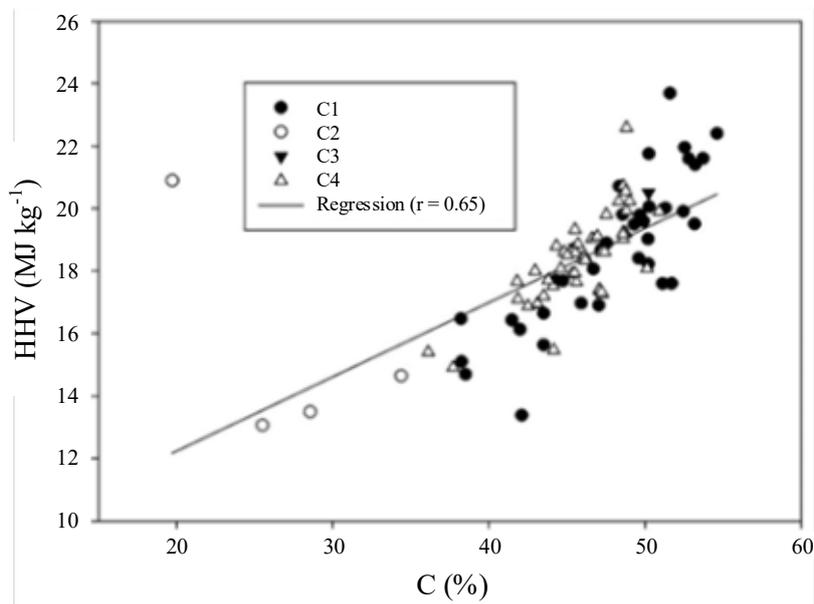


FIGURE 4. Clusters following the criteria of ultimate chemical analysis ($C \times HHV$).

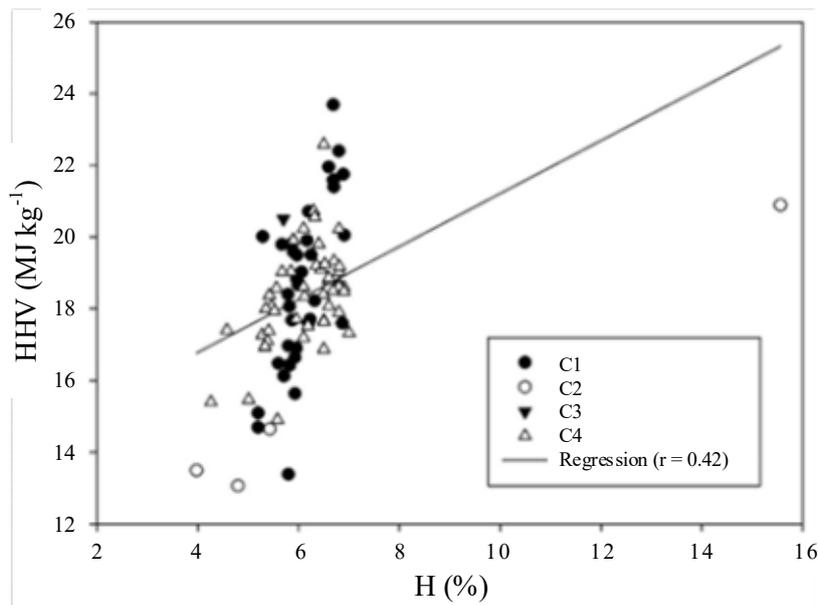
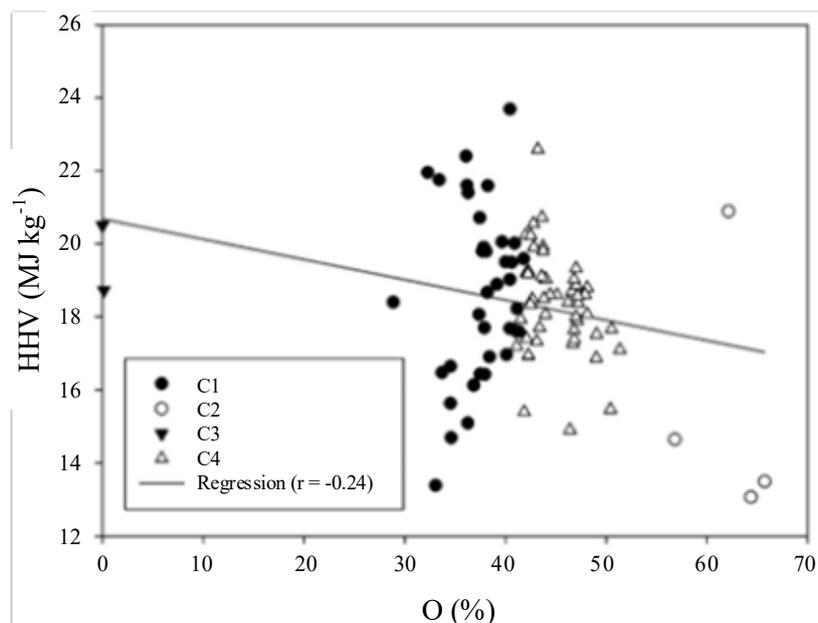


FIGURE 5. Clusters following the criteria of ultimate chemical analysis ($H \times HHV$).


 FIGURE 6. Clusters following the criteria of ultimate chemical analysis ($O \times HHV$).

By applying each class to the models described by eqs (1) to (14), the results shown in Tables 4, 5, 6, and 7 were obtained. It is evident that for the formulas based on proximate analysis, the separation into distinct groups significantly contributed to the improvement of the linear relationship between the estimated higher heating value and the experimental value.

TABLE 4. Comparative analysis of heating value forecast equations based on proximate biomass analysis for class C1 of the proposed database.

Equation	R^2	$\overline{R^2}$	SE (MJ kg ⁻¹)
(1)	0.636	0.630	1.201
(2)	0.538	0.522	1.328
(3)	0.565	0.541	1.423
(8)	0.563	0.547	1.747
(9)	0.691	0.680	1.759
(10)	0.507	0.489	1.502
(13)	0.554	0.538	1.410

TABLE 5. Comparative analysis of heating value forecast equations based on proximate biomass analysis for class C3 of the proposed database.

Equation	R^2	$\overline{R^2}$	SE (MJ kg ⁻¹)
(1)	0.396	0.384	1.632
(2)	0.321	0.293	1.687
(3)	0.541	0.513	1.721
(8)	0.533	0.514	1.399
(9)	0.594	0.578	1.282
(10)	0.186	0.154	1.968
(13)	0.404	0.380	1.688

The majority of the tested models showed a significant improvement in the average determination coefficient (R^2) for both interest classes C1 and C3, with an approximate five-fold increase. Additionally, the standard error (SE) was reduced by half, indicating enhanced accuracy of the formulas. Among the equations evaluated,

[eq. (1)] proposed by Sheng & Azevedo (2005) demonstrated superior performance for class C1, as it yielded a satisfactory average determination coefficient ($\overline{R^2}$) combined with a smaller SE . On the other hand, [eq. (9)] suggested by Cordero et al. (2001) was found to be the best model for class C3.

TABLE 6. Analysis of the heating value forecast equations based on ultimate chemical analysis of biomasses for class C2 of the proposed database.

Equation	R^2	$\overline{R^2}$	SE (MJ kg ⁻¹)
(4)	0.505	0.493	0.970
(5)	0.565	0.530	1.016
(6)	0.536	0.471	0.987
(7)	0.576	0.517	1.088
(11)	0.544	0.508	1.278
(12)	0.505	0.493	0.991
(14)	0.571	0.560	0.927

TABLE 7. Comparative analysis of heating value forecast equations based on ultimate chemical analysis of biomasses for class C4 of the proposed database.

Equation	R^2	$\overline{R^2}$	SE (MJ kg ⁻¹)
(4)	0.699	0.692	1.343
(5)	0.716	0.695	1.317
(6)	0.724	0.688	1.356
(7)	0.711	0.673	1.690
(11)	0.704	0.683	1.409
(12)	0.699	0.692	1.325
(14)	0.720	0.713	1.299

For ultimate chemical analysis-based models, class divisions did not yield satisfactory results except for class C4 (Table 7), where average $\overline{R^2}$ and SE of the evaluated equations improved notably. However, the fluctuations in the class C2 results, depending on the equation, rendered the grouping impractical. As a result, for developing the model correlating higher heating value (HHV) with C , H , and O contents, the complete database (93 samples) was used.

Models proposed to predict higher heating value

Based on the proximate analysis of biomass samples in classes C1 and C3, the models presented in Tables 8 and 9 were developed. Statistical tests at a significance level of 5% were conducted to evaluate the parameters of the

models. The null hypothesis was accepted for the following parameters: (i) β_3 in the model shown in Table 8; and (ii) β_1 and β_3 in the equation discussed in Table 9.

By excluding the variable FC from [eq. (18)] for samples with $VM < 78\%$, a new model was derived, resulting in a $\overline{R^2}$ of 0.697 and SE of 1.05 MJ kg⁻¹, as shown in [eq. (20)]. However, for samples with $VM \geq 78\%$, removing both the variables FC and VM from [eq. (18)] led to a decrease in $\overline{R^2}$ to 0.384 and an increase in SE to 1.54 MJ kg⁻¹, preventing a general change. In this case, only the variable FC , which had a discrepant p-value beyond the 5% limit, was omitted, resulting in [eq. (21)] with a $\overline{R^2}$ of 0.578 and SE of 1.27 MJ kg⁻¹.

TABLE 8. Parameters of the model presented in [eq. (18)] for $VM < 78\%$.

Parameters	Estimate	t -test statistic	p -value
β_0	30.951	5.0866	4.7137×10 ⁻⁶
β_1	-0.13594	-2.1342	0.037386
β_2	-0.3504	-5.1358	3.9554×10 ⁻⁶
β_3	-0.018214	-0.30759	0.75958
Number of observations: 58		Number of degrees of freedom: 54	
SE : 1.06 MJ kg ⁻¹		$\overline{R^2}$: 0.692	

TABLE 9. Parameters of the model presented in [eq. (18)] for $VM \geq 78\%$.

Parameters	Estimate	t -test statistic	p -value
β_0	30.278	2.4943	0.016042
β_1	-0.13202	-1.1055	0.27434
β_2	-0.31373	-2.4982	0.015885
β_3	0.042992	0.31341	0.7553
Number of observations: 53		Number of degrees of freedom: 49	
SE : 1.28 MJ kg ⁻¹		$\overline{R^2}$: 0.571	

Regarding the ultimate chemical analysis of biomasses, a single model was adjusted for the complete dataset obtaining the parameters shown in Table 10. At 5% significance, the null hypothesis is accepted for β_0 and β_3 ; therefore, [eq. (19)] remains with only two plots related to the independent variables C and H . The resulting [eq. (22)] presents a $\overline{R^2}$ of 0.7013 and SE of 1.11 MJ kg⁻¹.

$$HHV = 29,241 - 0,11911VM - 0,33142Ash \tag{20}$$

$$HHV = 33,977 - 0,16787VM - 0,34929Ash \tag{21}$$

$$HHV = 0,27293C + 0,95445H \tag{22}$$

TABLE 10. Parameters of the model presented in [eq. (19)].

Parameters	Estimate	t-test statistic	p-value
β_0	0.12524	0.077918	0.93807
β_1	0.26983	11.53	2.3634×10 ⁻¹⁹
β_2	0.9326	9.1872	1.5388×10 ⁻¹⁹
β_3	0.0037024	0.24838	0.80441
Number of observations: 93		Number of degrees of freedom: 89	
SE: 1.11 MJ kg ⁻¹		R²: 0.698	

It is evident that when existing models from the literature are applied to samples without classification based on percentage values of composition, the use of ultimate chemical analysis to estimate the higher heating value proves to be more efficient compared to proximate chemical analysis. This conclusion is based on the evaluation criteria of average $\overline{R^2}$ and SE . [eq. (1)], which yielded the best prediction using proximate analysis, exhibited an $\overline{R^2}$ of 0.3135 and SE of 1.8537 MJ kg⁻¹. Conversely, [eq. (14)], which provided the most accurate estimation using ultimate analysis, showed an $\overline{R^2}$ of 0.69485 and SE of 1.1425 MJ kg⁻¹. Consequently, [eq. (14)] demonstrated a 122% increase in $\overline{R^2}$ and a 38% reduction in SE when compared to [eq. (1)].

The division of samples obtained through proximate chemical analysis into two classes contributed to the improvement of results for all seven evaluated equations. The results between the two classes were not uniform, indicating that the most effective model for C1 (Equation 1) did not coincide with the most efficient model for C3 (Equation 9). This strengthens the evidence that the results were influenced by the biomass composition rather than the reduction of the sample space. With the introduction of clustering, the statistical parameters of eqs (1) and (9) underwent the following percentage changes, respectively: (i) an increase in $\overline{R^2}$ by 100% and 386%, and a decrease in SE by 35% and 61%.

Clustering the data from ultimate analysis did not yield consistent results. The derived equations showed good performance only for samples in C4 and were more accurate in predicting samples in C2. The evaluated equations showed improvements in $\overline{R^2}$ for C4 ranging from 2.6% to 344%, whereas C2 exhibited improvements between 17% and 204%. In terms of SE , there was a reduction for all equations applied to C2 and only three equations applied to C4. The percentage ranges of variation were: (i) C: 9.1% to 64.2%, and (ii) C4: 17.1% to 51.9%.

Based on the proximate analysis data of C1 and C3, new models (Equations 20 and 21) were developed, which exhibited higher $\overline{R^2}$ values and lower SE compared to eqs

(1), (2), (3), (8), (9), (10), and (13) applied to specific groupings. For C1, the best model, [eq. (1)], resulted in an $\overline{R^2}$ of 0.629 and SE of 1.201 MJ kg⁻¹, while [eq. (20)] yielded an $\overline{R^2}$ of 0.697 and SE of 1.05 MJ kg⁻¹. In C3, the results ranged from an $\overline{R^2}$ of 0.577 and SE of 1.281 MJ kg⁻¹ (Equation 9) to an $\overline{R^2}$ of 0.678 and SE of 1.27 MJ kg⁻¹ (Equation 21). In summary, there was an increase in $\overline{R^2}$ and a decrease in SE of: (i) 10.8% and 12.5% for C1, and (ii) 17.5% and 0.85% for C3, respectively.

Due to the lack of efficiency in classifying ultimate analysis data, eqs (4), (5), (6), (7), (11), (12), and (14) were evaluated using the complete set of samples. Under these circumstances, [eq. (14)] was identified as the most effective model with an $\overline{R^2}$ value of 0.694 and SE of 1.142 MJ kg⁻¹. Additionally, a new model based on [eq. (22)] was formulated, resulting in an $\overline{R^2}$ value of 0.7013 and SE of 1.1090 MJ kg⁻¹, representing a 1% increase in $\overline{R^2}$ and a 3% reduction in SE .

CONCLUSIONS

A database comprising information on proximate and ultimate chemical analysis of 142 samples of agro-industrial waste was compiled. The classification of the dataset led to enhanced efficacy of the formulas employed for estimating the higher heating value (HHV) of biomasses using proximate analysis. However, the equations that relied on ultimate analysis to predict HHV did not exhibit consistent statistical parameters that would justify dividing the sample space into classes in this particular case.

There were no significant disparities in the quality of fit when employing ultimate chemical analysis or proximate chemical analysis as independent variables in multiple linear regression models for HHV predictions. Consequently, considering that proximate chemical analysis is less costly than ultimate analysis, it can be concluded that the clustering methodology, combined with the concentrations of constituent elements in the waste, is a feasible approach for optimizing and reducing costs in obtaining the heating value of biomasses for energy purposes.

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