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To cite this article: Mahmut Daskin, Ahmet Erdoğan, Fatih Güleç & Jude A. Okolie (2024) Generalizability of empirical correlations for predicting higher heating values of biomass, Energy Sources, Part A: Recovery, Utilization, and Environmental Effects, 46:1, 5434-5450, DOI: 10.1080/15567036.2024.2332472

To link to this article: <https://doi.org/10.1080/15567036.2024.2332472>



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# Generalizability of empirical correlations for predicting higher heating values of biomass

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## ABSTRACT

Designing efficient biomass energy systems requires a thorough understanding of the physicochemical, thermodynamic, and physical properties of biomass. One crucial parameter in assessing biomass energy potential is the higher heating value (HHV), which quantifies its energy content. Conventionally, HHV is determined through bomb calorimetry, but this method is limited by factors such as time, accessibility, and cost. To overcome these limitations, researchers have proposed a diverse range of empirical correlations and machine-learning approaches to predict the HHV of biomass based on proximate and ultimate analysis results. The novelty of this research is to explore the universal applicability of the developed empirical correlations for predicting the Higher Heating Value (HHV) of biomass. To identify the best empirical correlations, nearly 400 different biomass feedstocks were comprehensively tested with 45 different empirical correlations developed to use ultimate analysis (21 different empirical correlations), proximate analysis (16 different empirical correlations) and combined ultimate-proximate analysis (8 different empirical correlations) data of these biomass feedstocks. A quantitative and statistical analysis was conducted to assess the performance of these empirical correlations and their applicability to diverse biomass types. The results demonstrated that the empirical correlations utilizing ultimate analysis data provided more accurate predictions of HHV compared to those based on proximate analysis or combined data. Two specific empirical correlations including coefficients for each element (C, H, N) and their interactions (C\*H) demonstrate the best HHV prediction with the lowest MAE (~0.49), RMSE (~0.64), and MAPE (~2.70%). Furthermore, some other empirical correlations with carbon content being the major determinant also provide good HHV prediction from a statistical point of view; MAE (~0.5–0.8), RMSE (~0.6–0.9), and MAPE (~2.8–3.8%).

## ARTICLE HISTORY

Received 21 July 2023  
Revised 6 March 2024  
Accepted 11 March 2024


## KEYWORDS

Biomass; higher heating value; ultimate analysis; proximate analysis; HHV prediction

## Introduction

Recent decades have seen a worldwide energy and climate crisis (Erdogan and Canbazoglu 0000) mainly caused by the fast depletion of fossil fuel reserves and political conflicts between countries. To mitigate both crises, many countries have attempted to handle this issue by promoting the use of biomass as a source of energy production (Güleç et al. 2022). Biomass/bioenergy has the potential to replace fossil fuels in various applications as a sustainable and renewable energy source (Rahib et al. 2021). In biomass processes, organic compounds in biomass can be utilized/valorized through various

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 Supplemental data for this article can be accessed online at <https://doi.org/10.1080/15567036.2024.2332472>

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processes including combustion, gasification, and pyrolysis to produce bioenergy (Aziz et al. 2024). Biomass has, therefore, gained substantial attention owing to its lower carbon footprint and availability in recent years (Wei, Cheng, and Shen 2024). The physicochemical, thermodynamic, and physical properties of biomass resources play a crucial role in the design of energy systems (Ma et al. 2024). A significant parameter in determining the value of biomass is the higher heating value (HHV) (Nhuchhen and Afzal 2017; Nhuchhen and Salam 2012). HHV of a biomass can be determined by a bomb calorimeter, which is an experimental method, but this method has limitations in terms of time, accessibility, and cost (Güleç, Şimşek, and Tanıker Sarı 2022). Moreover, the small sample size typically used in bomb calorimetry (usually 1.0 g) may not adequately represent bulky feedstocks. To obtain a homogeneous HHV value, a significantly larger number of experiments would be required, posing practical challenges. These limitations have therefore led to developing the prediction methods using the physicochemical characteristics of biomass feedstocks (Li et al. 2024).

In addition to HHV, the bioenergy potential of biomass can be assessed using different characterization methods. The elemental composition of biomass is analyzed by the ultimate analysis (UA) (Ozyuguran, Akturk, and Yaman 2018), which determines the composition of carbon (C), hydrogen (H), nitrogen (N), oxygen (O), and sulfur (S) (Lyons, Lunny, and Pollock 1985). Once C and H are oxidized, an exothermic reaction occurs, generating  $\text{CO}_2$  and  $\text{H}_2\text{O}$  (Oberberger, Brunner, and Bärnthaler 2006). C and H have a positive impact on HHV since C is an essential component of solid biomass and H plays an important role in combustion (Demirbas 2002). It is seen that the concentration of N in biomass is an important parameter if the environmental effect of  $\text{NO}_x$  is considered (Golgiyaz et al. 2022; Telmo, Lousada, and Moreira 2010). Proximate analysis (PA) reveals the contents of biomass such as volatile matter (VM), fixed carbon (FC), and ash content (Nunes, Matias, and Catalao 2017). The percentages of these contents have effects on the combustion of biomass. Unless nonvolatile matter is formed from noncombustible gases such as  $\text{CO}_2$  and  $\text{H}_2\text{O}$  (Özyuğuran and Yaman 2017), the HHV increases with FC and VM (Vargas-Moreno et al. 2012). Biomass comprises a different amount of cellulose, hemicellulose, and lignin (Zhang, Xu, and Champagne 2010) in addition to lipids, proteins, simple sugars, and starches albeit in various quantities. Detecting the components through structural analysis not only helps in predicting HHV but also plays a vital role in the production of derivative fuels and chemicals, as well as in analyzing combustion (Saidur et al. 2011).

The HHV value of biomass can be estimated using either PA or UA alone or together. Based on only UA analysis, several studies have been conducted to estimate the HHV of biomass (Huang and Lo 2020; Qian et al. 2021). Empirical equations have demonstrated how the rate of C, H, N, O, and S in biomass elementally affect HHV value, depending on the type of biomass. The major determinant of HHV in all empirical correlations based on UA is C content of biomass. A few empirical correlations consider only C (Channiwala and Parikh 2002) as the variable predicting HHV, while others take into account C, H, O, and N together (Demirbas et al. 1997). In addition to elemental composition, some studies have been conducted to predict the HHV level of biomass utilizing the results of the PA (Dashti et al. 2019). The empirical equations obtained with PA include one (Kathiravale et al. 2003), two (Callejón-Ferre et al. 2011), or all (Ahmaruzzaman 2008) of the proximate analysis results of FC, VM, and ash with various correlations. In addition to estimating HHV using the UA and PA analyses separately, there are also studies in which the estimation of HHV is carried out by using these two analyses together (Nhuchhen and Afzal 2017). It is the rapidly developing field of machine learning that provides a variety of approaches for optimizing biomass HHV predictions. Artificial neural networks decision trees, random forests, support vector machines, and deep learning are among these approaches. However, the limitations of machine learning are its inability to design proper models due to its lack of interpretability, the risk of overfitting or underfitting the data, the challenge of determining the optimal number of training epochs, the need for high-quality and diverse training data, systematic errors and outliers in the data, and the need for curated datasets that are accurate and accessible to machine learning (Dobbelaere et al. 2021). Despite the existence of a wide range of empirical correlations developed to predict the HHV of different types of fuels, there is a limitation on

their applicability to a wide range of biomass feedstocks. Moreover, the existing literature does not sufficiently show a comprehensive understanding of how parameters derived from both ultimate and proximate analyses impact HHV prediction. Consequently, there is a need for a thorough investigation that explores the universal applicability and reliability of these empirical correlations across an extensive array of biomass feedstocks.

This study provides a comprehensive understanding of the generalizability of the developed empirical correlations to predict the HHV for two different type of biomass feedstocks. The ground-breaking aspect of this research resides in investigating the diverse application possibility of an empirical correlation for forecasting biomass HHV. This research focuses on three main objectives: (i) discerning the paramount empirical correlation for forecasting the HHV of biomass, (ii) probing the applicability of these correlations across varied biomass feedstocks, and (iii) isolating the superior empirical correlation that can uniformly predict the HHV across these two groups of biomass feedstocks. This research covers the comparative quantitative and statistical analysis of 45 different HHV prediction equations using approximately 400 different biomass feedstocks categorized as woods (category-1), herbaceous and agricultural biomasses (category-2) using their characteristics of PA and UA. A quantitative and statistical analysis is conducted to assess the performance of these empirical correlations and their applicability to diverse biomass types. The main objective of this work is to present this analysis more clearly and concisely, emphasizing its significance in advancing our understanding of biomass HHV prediction.

## Materials and methods

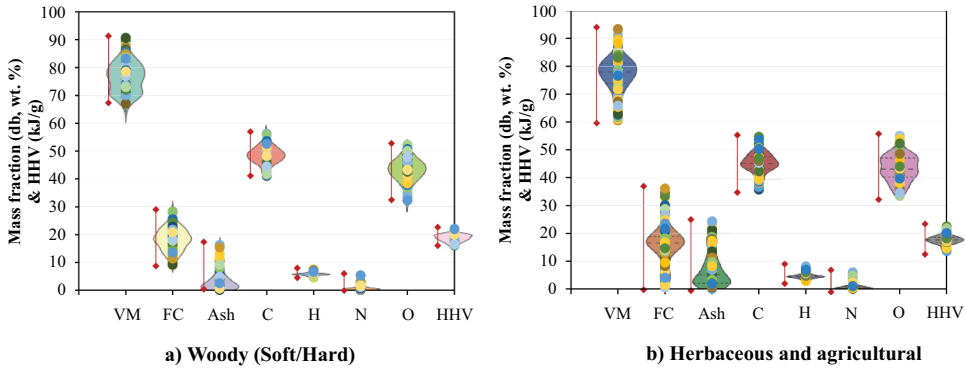
### Dataset collection and analysis

As a data set, 391 different biomass feedstock data of proximate analysis, ultimate analysis, and experimental HHV were collected from the literature (Appendix A, Table A1) and used to investigate the generalizability of 45 different empirical correlations developed for the predicting of HHV. The data set consists of two main biomass feedstocks; 1<sup>st</sup> category is woody biomass consisting of soft and hardwoods with 137 different feedstocks, 2<sup>nd</sup> category is herbaceous and agricultural biomass feedstocks with 254 different feedstocks. The biomass feedstocks are categorized as presented in Table 1. Additionally, the data distribution of proximate analysis, ultimate analysis, and HHV for the woody biomass data and herbaceous-agricultural biomass data are presented in Figure 1.

In this research, we distinguished between “woody biomass” and “herbaceous and agricultural biomass” based on their botanical characteristics and typical usage patterns. Woody biomass,

**Table 1.** Biomass types and categorized collected for the generalizability of the developed equations to predict the HHV.

Biomass types	Details
<b>Woody biomass –</b> <i>Softwood and Hardwood</i> (137 data)	Softwood stems Softwood bark Softwood residues Softwood leaves Softwood seed/fruit Hardwood stems Hardwood bark Hardwood twigs Hardwood leaves Hardwood residues Hardwood seed/fruit/berry
<b>Herbaceous and agricultural biomass</b> (254 data)	Herbaceous and agricultural grasses Herbaceous and agricultural stalks/stems/shrubs Herbaceous and agricultural fibres Herbaceous and agricultural shells/husks/processing residues Herbaceous and agricultural seeds/fruits/grains Herbaceous and agricultural leaf



**Figure 1.** Data distributions of a) woody biomass feedstocks (137 data) and b) herbaceous and agricultural biomass feedstocks (254 data) with proximate analysis, ultimate analysis, and experimental HHV. “db” represents dry basis.

comprising softwood and hardwood, is primarily derived from trees and forests. Although it can be considered a part of agricultural biomass in a broader sense, for the purposes of our study, it is categorized separately due to its distinct physical and chemical properties, which are notably different from those of herbaceous and agricultural biomass. The latter category is typically associated with non-wood plants, including grasses, crops, and residues from agricultural activities. This distinction is crucial for our HHV prediction model as these two categories exhibit different combustion and energy properties.

### Empirical correlations for the HHV prediction

In order to identify the best empirical correlations, about 400 different biomass feedstocks were comprehensively tested with 45 different empirical correlations developed to use ultimate analysis (21 different empirical correlations, Table 2), combined ultimate-proximate analysis (8 different empirical correlations Table 3) and proximate analysis (16 different empirical correlations Table 4) data of these biomass feedstocks.

### Statistical analysis of the empirical models

To assess the performance of developed empirical correlations and their applicability to diverse biomass types (specially the defined two categories), a quantitative and statistical analysis was conducted using the statistical methods including mean absolute error (MAE), mean absolute percentage error (MAPE), correlation coefficient ( $R^2$ ), and root mean square error (RMSE). The statistical analysis of the results obtained from 45 distinct models holds great significance and shows the suitability of these models in the field. MAE, Equation (1), is a widely used standard statistical method to obtain model performance (Chai and Draxler 2014). It can be summarized the average value of sum of absolute errors (Boztepe et al. 2021). It is used to show the distance of the predicted data from the true value. RMSE, Equation (2), is the most widely used statistical method to analyze the prediction performance (Chai and Draxler 2014). The RMSE specifies the square root of the mean of the squares of the differences between the predicted and actual values. Furthermore, the MAPE as defined by Equation (3) and the correlation coefficient ( $R^2$ ) were also employed (Boztepe, Daskin, and Erdogan 2022).

$$MAE = \frac{1}{n} \sum_{i=1}^n |y_i - x_i| = \frac{1}{n} \sum_{i=1}^n |e_i| \quad (46)$$

**Table 2.** Empirical correlations for the prediction of biomass HHV using UA data.

Equation Number	Developed empirical correlations for HHV prediction (HHV, kJ/g)	Reference
Eq. 1	$0.4373 * C - 1.6701$	Channiwala and Parikh (2002), Sheng and Azevedo (2005)
Eq. 2	$0.4373 * C - 0.3059$	Channiwala and Parikh (2002)
Eq. 3	$(491.2 * C - 911.4 * H + 117.7 * O) / 1000$	Thipkhunthod et al. (2005)
Eq. 4	$(425.9 * C - 69.8 * H + 181.7 * O - 2277) / 1000$	Thipkhunthod et al. (2005)
Eq. 5	$(414.8 * C - 184.1 * H + 178.9 * O - 2159.5) / 1000$	Thipkhunthod et al. (2005)
Eq. 6	$0.3259 * C + 3.4597$	Sheng and Azevedo (2005), Yin (2011)
Eq. 7	$0.34 * C + 1.4 * H - 0.16 * O$	Zanzi, Sjöström, and Björnbom (2002)
Eq. 8	$(416.638 * C - 570.017 * H + 259.031 * O + 598.955 * N + 5829.078) / 1000$	Kathiravale et al. (2003)
Eq. 9	$0.301 * C + 0.525 * H + 0.064 * O - 0.763$	Channiwala and Parikh (2002), Sheng and Azevedo (2005)
Eq. 10	$(3.55 * C^2 - 232 * C - 2230 * H + 51.2 * C * H + 131 * N + 20600) / 1000$	Friedl et al. (2005), Yin (2011)
Eq. 11	$(5.22 * C^2 - 319 * C - 1647 * H + 38.6 * C * H + 133 * N + 21028) / 1000$	Friedl et al. (2005)
Eq. 12	$(1.87 * C^2 - 144 * C - 2820 * H + 68.3 * C * H + 129 * N + 20147) / 1000$	Friedl et al. (2005)
Eq. 13	$4.18 * (103.34 * C - 73) / 1000$	Demirbas (2004)
Eq. 14	$(33.5 * C + 142.3 * H - 15.4 * O - 14.5 * N) / 100$	Demirbaş (1997), Demirbas et al. (1997), Sheng and Azevedo (2005), Thipkhunthod et al. (2005)
Eq. 15	$(33.5 * C + 142.3 * H - 15.4 * O) / 100$	Demirbas et al. (1997)
Eq. 16	$0.2949 * C + 0.825 * H$	Yin (2011)
Eq. 17	$-5.29 + 0.493 * C + 5.052 / H$	Callejón-Ferre et al. (2011)
Eq. 18	$5.736 + 0.006 * C^2$	Callejón-Ferre et al. (2011)
Eq. 19	$-3.393 + 0.507 * C - 0.341 * H + 0.067 * N$	Callejón-Ferre et al. (2011)
Eq. 20	$-2.907 + 0.491 * C - 0.261 * H$	Callejón-Ferre et al. (2011)
Eq. 21	$-3.147 + 0.468 * C$	Callejón-Ferre et al. (2011)

**Table 3.** Empirical correlations for the prediction of biomass HHV using combined PA and UA data.

Equation Number	Developed empirical correlations for HHV prediction (HHV, kJ/g)	Reference
Eq. 22	$-1.3675 + 0.3137 * C + 0.7009 * H + 0.0318 * (100 - C - H - Ash)$	Sheng and Azevedo (2005)
Eq. 23	$23.668 - 7.032 * H - 0.002 * Ash^2 + 0.005 * C^2 + 0.771 * H^2 + 0.019 * N^2$	Callejón-Ferre et al. (2011)
Eq. 24	$4.622 + 7.912 * H^{-1} - 0.001 * Ash^2 + 0.006 * C^2 + 0.018 * N^2$	Callejón-Ferre et al. (2011)
Eq. 25	$9.756 - 309.454 * VM^{-1} + 6.164 * H^{-1} + 0.006 * C^2$	Callejón-Ferre et al. (2011)
Eq. 26	$-0.417 - 0.012 * VM - 0.035 * (Ash + C) + 0.518 * (C + N) - 0.393 * (H + N)$	Callejón-Ferre et al. (2011)
Eq. 27	$-1.642 - 0.024 * Ash * 0.475 * (C + N) - 0.376 * (H + N)$	Callejón-Ferre et al. (2011)
Eq. 28	$-0.465 - 0.0342 * Ash - 0.019 * VM + 0.483 * C - 0.388 * H + 0.124 * N$	Callejón-Ferre et al. (2011)
Eq. 29	$-1.563 - 0.0251 * Ash + 0.475 * C - 0.385 * H + 0.102 * N$	Callejón-Ferre et al. (2011)

$$RMSE = \sqrt{\frac{1}{n} \sum_{i=1}^n (y_i - x_i)^2} = \sqrt{\frac{1}{n} \sum_{i=1}^n (e_i)^2} \quad (47)$$

$$MAPE(\%) = \frac{100\%}{n} \sum_{i=1}^n \left| \frac{y_i - x_i}{y_i} \right| \quad (48)$$

**Table 4.** Empirical correlations for the prediction of biomass HHV using PA data.

Equation Number	Developed empirical correlations for HHV prediction (HHV, kJ/g)	Reference
Eq. 30	$(255.75 * VM + 283.88 * FC - 2386.38) / 1000$	Thipkhunthod et al. (2005)
Eq. 31	$(259.83 * (VM + FC) - 2454.76) / 1000$	Thipkhunthod et al. (2005)
Eq. 32	$19.914 - 0.2324 * Ash$	Sheng and Azevedo (2005)
Eq. 33	$-3.0368 + 0.2218 * VM + 0.2691 * FC$	Sheng and Azevedo (2005)
Eq. 34	$4.183 * 10^{-3} * (8000 + VM * (70 - 1.65 * VM))$	Majumder et al. (2008)
Eq. 35	$0.3536 * FC + 0.1559 * VM - 0.0078 * Ash$	Ahmaruzzaman (2008), Majumder et al. (2008), Sheng and Azevedo (2005), Yin (2011)
E. 36	$(356.047 * VM - 118.035 * FC - 5600.613) / 1000$	Kathiravale et al. (2003)
Eq. 37	$(356.248 * VM - 6998.497) / 1000$	Kathiravale et al. (2003)
Eq. 38	$-10.81408 + 0.3133 * (VM + FC)$	Ahmaruzzaman (2008), Cordero et al. (2001), Jiménez and González (1991), Majumder et al. (2008), Parikh, Channiwala, and Ghosal (2005)
Eq. 39	$0.312 * FC + 0.1534 * VM$	Ahmaruzzaman (2008), Demirbaş (1997), Sheng and Azevedo (2005), Thipkhunthod et al. (2005)
Eq. 40	$0.196 * FC + 14.119$	Demirbaş (1997), Majumder et al. (2008), Parikh, Channiwala, and Ghosal (2005), Thipkhunthod et al. (2005)
Eq. 41	$0.3543 * FC + 0.1708 * VM$	Ahmaruzzaman (2008), Cordero et al. (2001), Majumder et al. (2008), Parikh, Channiwala, and Ghosal (2005), Thipkhunthod et al. (2005)
Eq. 42	$0.1905 * VM + 0.2521 * FC$	Yin (2011)
Eq. 43	$-2.057 - 0.092 * Ash + 0.279 * VM$	Callejón-Ferre et al. (2011)
Eq. 44	$-13.173 + 0.416 * VM$	Callejón-Ferre et al. (2011)
Eq. 45	$20.086 - 0.261 * Ash$	Callejón-Ferre et al. (2011)

Here,  $\bar{X}$  is the mean value of the sample,  $z$  is the value of the confidence level,  $s$  is the standard deviation of the sample,  $n$  is the sample size, and  $i$  is the sample index.  $y_i$  and  $x_i$  are the predicted and measured HHVs for the  $i^{th}$  sample.

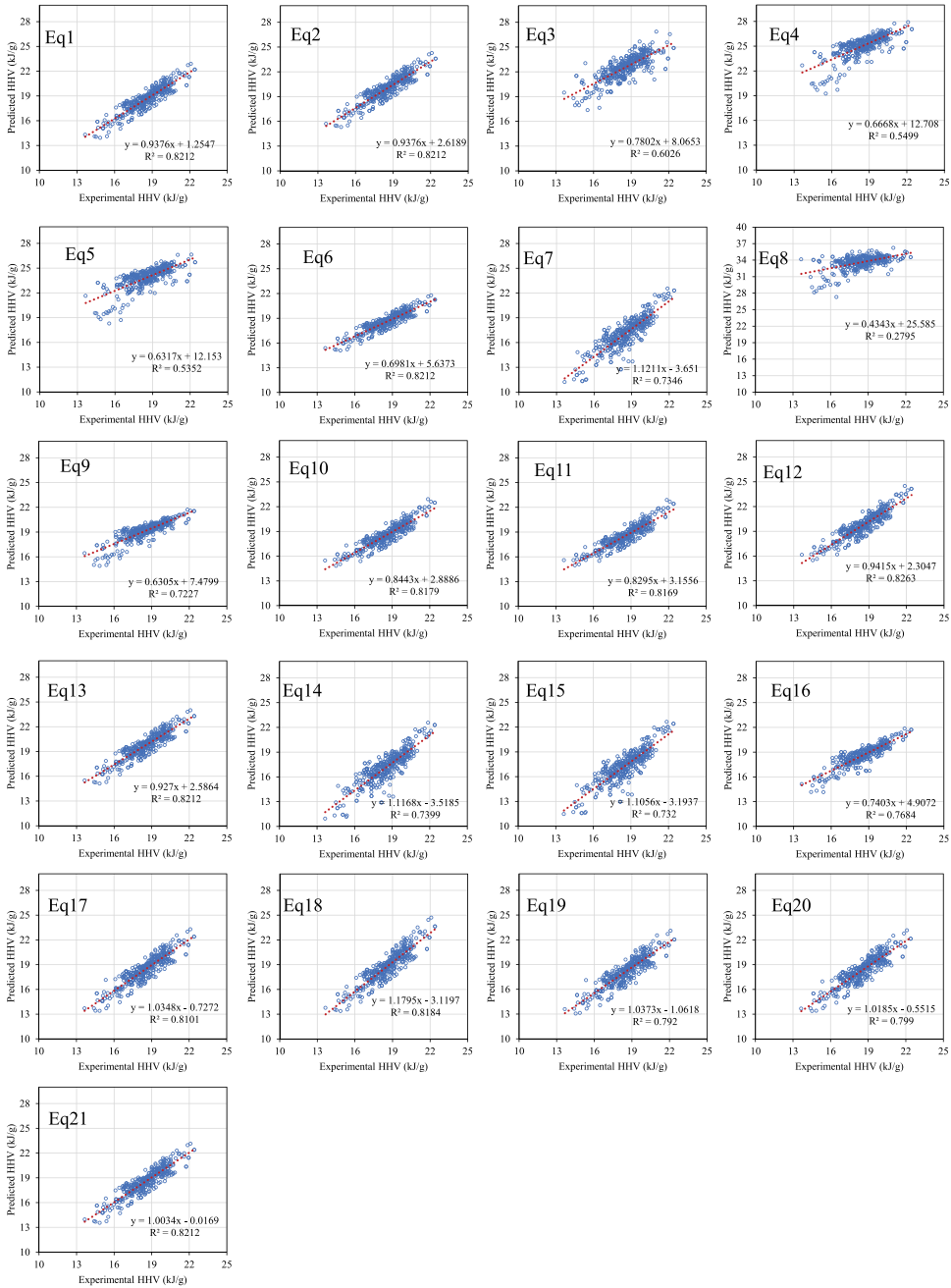
## Results and discussions

### Analysis with a mixed biomass feedstock

Figure 2 presents the HHV prediction results of mixed biomass feedstocks using the empirical correlations based on ultimate analysis data (Eqs. (1)-(21)). Tables 5–8 summarize the results of the statistical analysis aimed at assessing the performance of the developed empirical correlations for HHV prediction of biomass feedstocks. To derive these values, the MAE, RMSE, MAPE, and  $R^2$  were applied as primary statistical tools. Each of these statistical methods offers a different perspective on the accuracy and reliability of our predictive models:

- **MAE** (Equation (46)): This was calculated as the average of the absolute differences between the predicted and measured HHVs. It provides a straightforward measure of prediction accuracy without considering the direction of errors.
- **RMSE** (Equation (47)): This metric was computed as the square root of the average of the squared differences between the predicted and actual HHVs. RMSE is sensitive to larger errors, making it a valuable tool for understanding the variability in prediction performance.
- **MAPE** (Equation (48)): We calculated MAPE as the average of the absolute percentage errors. This metric is particularly useful in contexts where it is important to understand the error relative to the magnitude of the values being predicted.
- **Correlation Coefficient ( $R^2$ )**: This statistical measure was used to determine the strength of the linear relationship between the predicted and actual HHVs.

The data for these calculations were derived from our extensive dataset of biomass feedstocks. For each model, it was applied the aforementioned statistical methods to the entire dataset to evaluate the



**Figure 2.** The HHV prediction results of mixed biomass feedstocks (391 data in total) using the empirical correlations based on ultimate analysis data (eqs. (1)-(21)).

model’s performance across different types of biomass. This comprehensive approach ensured that the results reflected the general applicability of the models to diverse biomass types. The values presented in Tables 5–8 are the culmination of these calculations, reflecting a thorough statistical analysis of the model’s performance. This methodology not only demonstrates the robustness of our approach but also provides a clear and quantifiable way to compare different models.



**Table 5.** Statistical analysis for the prediction of HHV of mixed biomass feedstocks using empirical correlations (eqs. (1)-(21)) based on ultimate analysis.

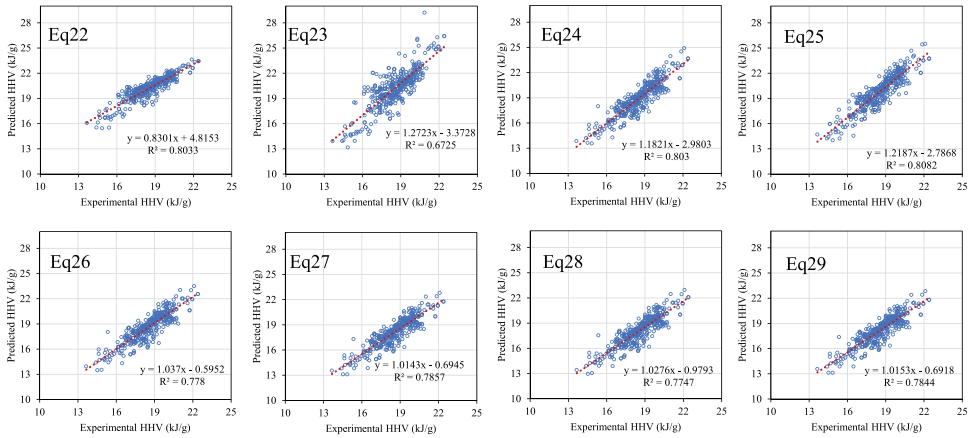
Equation	MAE	STDEV*	RMSE	MAPE (%)	R <sup>2</sup>
Eq-1	0.530	0.40	0.665	2.887	0.821
Eq. 2	1.465	0.65	1.604	8.004	0.821.
Eq. 3	3.995	1.00	4.118	21.865	0.602
Eq. 4	6.539	1.03	6.618	35.765	0.549
Eq. 5	5.334	1.03	5.433	29.241	0.535
Eq. 6	0.517	0.42	0.663	2.849	0.821
Eq. 7	1.453	0.96	1.738	7.969	0.734
Eq. 8	15.110	1.34	15.169	82.532	0.279
Eq. 9	0.801	0.64	1.024	4.525	0.723
Eq. 10	0.490	0.41	0.636	2.693	0.818
Eq. 11	0.491	0.41	0.637	2.699	0.817
Eq. 12	1.244	0.61	1.383	6.808	0.826
Eq. 13	1.253	0.62	1.397	6.860	0.821
Eq. 14	1.402	0.94	1.685	7.697	0.739
Eq. 15	1.307	0.92	1.597	7.166	0.732
Eq. 16	0.548	0.47	0.724	3.038	0.768
Eq. 17	0.590	0.47	0.752	3.213	0.810
Eq. 18	0.714	0.54	0.893	3.842	0.818
Eq. 19	0.670	0.56	0.875	3.650	0.792
Eq. 20	0.611	0.50	0.789	3.324	0.799
Eq. 21	0.553	0.43	0.698	3.013	0.821

\*STDEV of MAE. MAE, STDEV, MMAPE.

Among these 21 different empirical correlations (provided in Table 2), Eq. (10) and Equation (11) demonstrate the lowest MAE (~0.49), RMSE (~0.64), and MAPE (~2.70%) (Table 5). Both these empirical correlations include coefficients for each element (C, H, N) and their interactions (CH) that potentially reflect the energy of the corresponding chemical bonds in the biomass. The empirical correlation Eq. (10) includes a power function, which reflects the non-linear relationship between the HHV and the elemental composition of the biomass. Since the non-linearity may limit the accuracy of the equation for some types of biomasses, especially those with unusual chemical compositions. Equation (11) exhibits distinct leading coefficients for each element (C, H, N, and C\*H) as well as constants within the empirical correlations. Similarly in this study, Eq. (10) has been tested and validated for various types of biomass, including agricultural residues, energy crops, woody biomass, and biochar (torrefied) and has shown reasonable accuracy in predicting their HHV (Friedl et al. 2005; Nhuchhen and Afzal 2017).

In addition to these two equations, eight different empirical correlations (Eq. (1), Equation (6), Eqs. (16)-(21)) also show relatively low MAE (~0.5-0.8), RMSE (~0.6-0.9), and MAPE (~2.8-3.8%) (Table 5). Unlike the best two empirical correlations (Eqs. (10) and (11)), these eight empirical correlations (Eq. (1), Equation (6), Eqs. (16)-(21)) focus on the content of C and H, not N in the biomass. Considering the low N content of biomass resources, the impact of nitrogen in the HHV was evaluated much lower compared to C and H. On the other hand, the empirical correlations include the oxygen (O) content in addition to C, H, and N, which shows higher error for the prediction of biomass HHV. The ultimate analysis of HHV prediction correlations i.e., Eq. (10) and Equation (11), presented in Table 2 can be a useful tool for predicting the HHV of wood, herbaceous, and agricultural solely on their elemental composition. In addition to ultimate analysis, the predictions with Eq. (1) and Equation (6) appear to be reasonably accurate HHV predictions for wood, herbaceous, and agricultural biomasses using only carbon (C) content.

Figure 3 presents the HHV prediction results of mixed biomass feedstocks using the empirical correlations based on combined ultimate and proximate analyses data (Eqs. (22)-(29)). Table 6 also shows the statistical error analysis for the prediction of HHV of mixed biomass feedstocks using combined ultimate-proximate analyses based on empirical correlations. Among these 8 different empirical correlations (provided in Table 3), Eq. (22) is a simple linear regression



**Figure 3.** The HHV prediction results of mixed biomass feedstocks (391 data in total) using the empirical correlations based on combined proximate-ultimate analyses data (eqs. (22)-(29)).

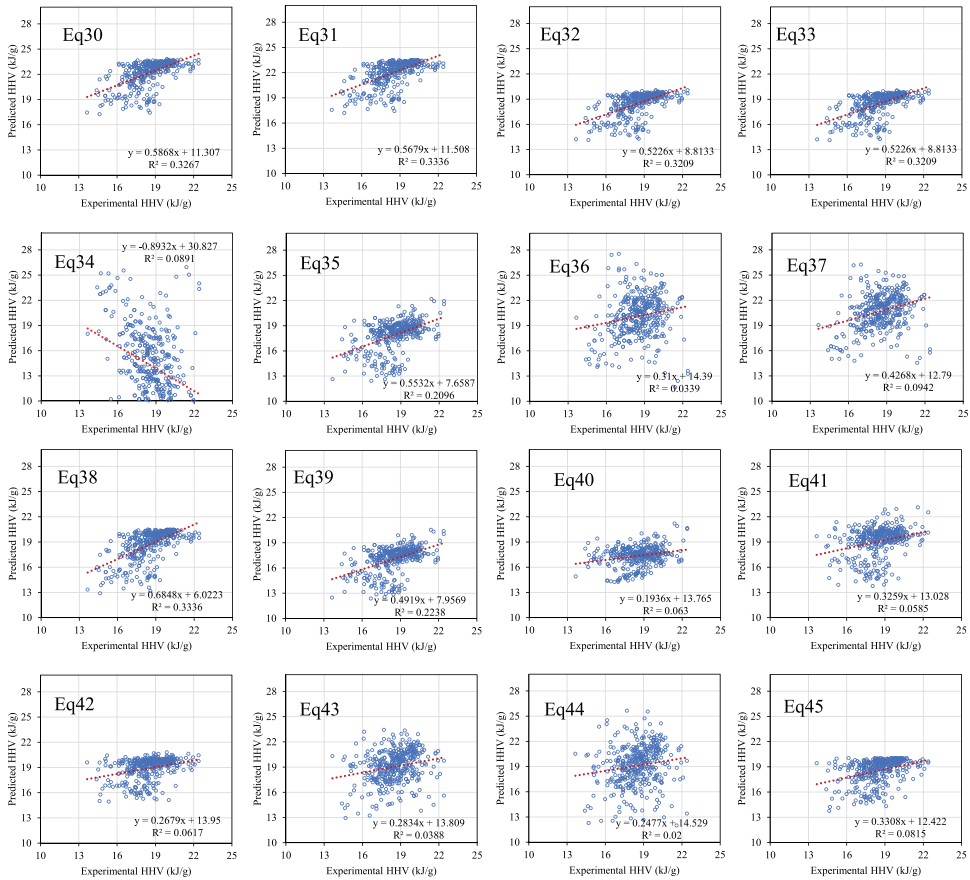
**Table 6.** Statistical analysis for the prediction of HHV of mixed biomass feedstocks using empirical correlations (eqs. (22)-(29)) based on both proximate and ultimate analyses.

Equation	MAE	STDEV*	RMSE	MAPE (%)	R <sup>2</sup>
Eq. 22	1.674	0.65	1.795	9.213	0.803
Eq. 23	1.815	1.19	2.167	9.759	0.672
Eq. 24	0.807	0.58	0.992	4.324	0.803
Eq. 25	1.360	0.80	1.574	7.277	0.808
Eq. 26	0.655	0.51	0.831	3.550	0.778
Eq. 27	0.677	0.59	0.898	3.687	0.787
Eq. 28	0.714	0.63	0.949	3.888	0.774
Eq. 29	0.670	0.59	0.891	3.651	0.784

\*STDEV of MAE.

model that includes variables for C, H, and Ash. It does not include N or VM content. Furthermore, Eqs. (23)-(25) include terms for C, H, Ash, and/or N content, as well as additional terms such as VM or Ash squared. These equations demonstrate higher errors; MAE (~0.81–1.82), RMSE (~0.99–2.17), and MAPE (~4.3–9.7%), in the prediction of HHV. The complexity of these equations may be more prone to overfitting and not generalize as well to new data. On the other hand, Eqs. (26)-(29) include terms for multiple variables, such as Ash, C, H, N, and/or VM content, and appear to be more complex than Equation (22) but less complex than Eqs. (23)-(25). These equations show a good balance between complexity and generalizability and provide better HHV prediction with lower errors. Eq. (26) shows the best prediction with the lowest MAE (~0.65), RMSE (~0.83), and MAPE (~3.5%). However, the correlation developed for the combined ultimate-proximate analyses demonstrated higher errors (Table 6) for the prediction of HHV compared to the eight different empirical correlations developed for ultimate analysis data sets (Table 5).

Figure 4 shows the experimental and predicted HHV of mixed biomass feedstocks using the empirical correlations developed for proximate analyses data (Eqs. (30)-(45)). The statistical errors are shown in Table 7 for the prediction of HHV of mixed biomass feedstocks using proximate analyses based on empirical correlations. Among these 16 empirical correlations, none of them shows better prediction (lower errors) compared to the promising empirical correlations developed for ultimate analysis and combined ultimate analysis. The lowest errors (MAE ~0.96, RMSE ~1.27, and MAPE ~5.27%) were observed with Eq. (32) (Table 7), while these errors are much higher than those of many other correlations developed for ultimate analysis (Table 5) and combined ultimate-proximate analyses (Table 6). Although these empirical show better predictions in (Sheng and Azevedo 2005) and



**Figure 4.** The best four empirical correlations based on average confidence intervals to predict the HHV of mixed biomass feedstocks using proximate analysis data; a)Eq. (32), b) equation (33), c) equation (42), d)Equation (45).

**Table 7.** Statistical analysis for the prediction of HHV of mixed biomass feedstocks using empirical correlations (eqs. (30)-(45)) based on proximate analysis.

Equation	MAE	STDEV*	RMSE	MAPE (%)	R <sup>2</sup>
Eq. 30	3.673	1.35	3.913	20.236	0.326
Eq. 31	3.522	1.32	3.761	19.430	0.336
Eq. 32	0.961	0.83	1.272	5.278	0.321
Eq. 33	0.995	0.89	1.336	5.464	0.320
Eq. 34	5.514	3.67	6.622	29.591	0.089
Eq. 35	1.368	1.23	1.837	7.451	0.209
Eq. 36	2.420	1.97	3.119	13.253	0.034
Eq. 37	2.541	1.70	3.057	13.972	0.094
Eq. 38	1.153	1.00	1.526	6.366	0.336
Eq. 39	1.681	1.31	2.129	8.959	0.224
Eq. 40	1.664	1.13	2.009	8.892	0.063
Eq. 41	1.422	1.09	1.791	7.932	0.059
Eq. 42	1.094	0.87	1.400	6.111	0.062
Eq. 43	1.506	1.26	1.960	8.212	0.088
Eq. 44	1.879	1.66	2.503	10.223*	0.020
Eq. 45	0.998	0.88	1.332	5.487	0.082

\*STDEV of MAE.

**Table 8.** Statistical analysis of the best two empirical correlations for the prediction of HHV of herbaceous and agricultural biomass feedstocks (254 data set) and woody biomass feedstocks (137 data set) using either ultimate analysis or combined ultimate-proximate analyses data.

Biomass Feedstocks	Equation	MAE	STDEV	RMSE	MAPE (%)	R <sup>2</sup>
Herbaceous and Agricultural (254 data set)	<i>Ultimate analysis</i>					
	Eq-10	0.501	0.43	0.661	2.806	0.811
	Eq-11	0.500	0.43	0.660	2.804	0.811
	<i>Combined proximate-ultimate analysis</i>					
	Eq-26	0.684	0.55	0.877	3.763	0.760
	Eq-29	0.743	0.65	0.986	4.102	0.765
Woody biomass (137 data set)	<i>Ultimate analysis</i>					
	Eq-10	0.469	0.35	0.587	2.482	0.805
	Eq-11	0.474	0.36	0.593	2.506	0.800
	<i>Combined proximate-ultimate analysis</i>					
	Eq-26	0.541	0.43	0.690	2.839	0.799
	Eq-29	0.536	0.43	0.683	2.813	0.799

\*STDEV of MAE. The statistical analysis for other empirical correlations is presented in the appendix (Table B1 and Table B2).

(Callejón-Ferre et al. 2011), they are not well-suited to the specific data being used in this study and do not capture the full range of variability in the data.

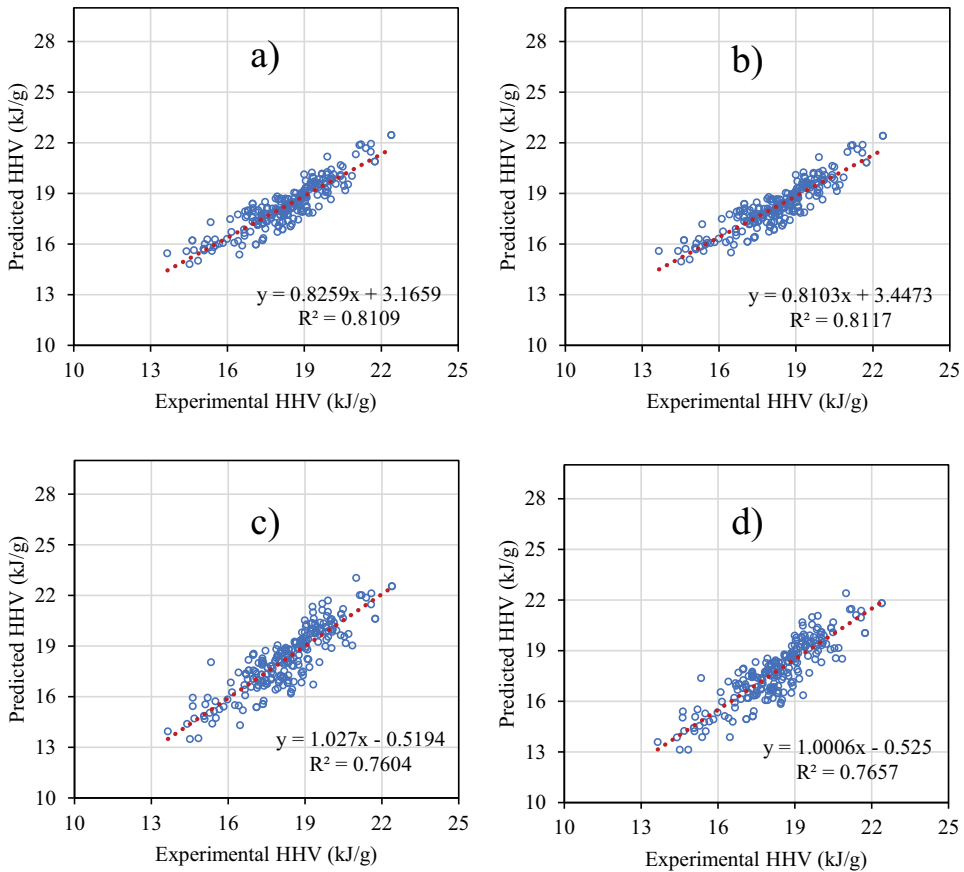
Considering these 45 different empirical correlations, the empirical correlations based on ultimate analysis and combined ultimate-proximate analysis can be useful tools for predicting the HHV of woody, herbaceous and agricultural biomass feedstocks. However, the predictive accuracy may be limited for some other types of biomasses with unusual chemical compositions. Therefore, the next section “3.2 Analysis with categorized biomass feedstocks” will provide the impact of these two groups on different types of biomass feedstocks with the herbaceous and agricultural biomass feedstocks (254 data set) and woody biomass feedstocks (137 data set).

### **Analysis with categorised biomass feedstocks**

In this section dataset was divided into two biomass groups; herbaceous and agricultural biomass feedstocks and woody biomass feedstocks to evaluate the performance of the empirical correlations. Since it is significantly important to understand whether the empirical correlations are good for some specific type of biomass feedstocks or generalizable for any type of biomass feedstocks. Figures 5 and 6 show the best two empirical correlation results for the prediction of HHV of herbaceous and agricultural biomass feedstocks and woody biomass feedstocks using ultimate analysis data and combined ultimate-proximate analyses data, respectively. The HHV prediction results with the correlation developed for only proximate analysis show relatively low prediction as in the previous section (Figure 4) and the results are presented in the Appendix B. In addition, Table 8 and 9 presented the statistical analysis results (MAE, MAPE, STDEV, RMSE, and R<sup>2</sup>) of the best empirical correlations for predicting the HHV of herbaceous and agricultural biomass feedstocks and woody biomass feedstocks with the correlations developed by either ultimate analysis or combination of proximate and ultimate analysis.

The characteristics of these two biomass types (herbaceous and agricultural biomass feedstocks and woody biomass feedstock) show some similarities in terms of ultimate analysis and proximate analysis characteristic distribution (Figure 1). That’s why the results seem to be close to each other. However, herbaceous and agricultural biomass feedstocks biomass have slightly wider characteristic ranges in terms of contents (C, H, O, N, VM, FC, Ash) compared to woody biomass feedstock. Therefore, there is a slight difference in terms of statistical results since woody biomass feedstocks show slightly better performance in terms of prediction using the same empirical correlations.

Both biomass feedstocks (herbaceous and agricultural, woody) demonstrate that the effect of C content is of the utmost importance in the prediction of HHV. Both biomass feedstocks groups provide the same empirical correlations (Eq. (10), Equation (11), Eq. (26), and Equation (29)) as the best candidates for the predicting of HHV. The only differences are

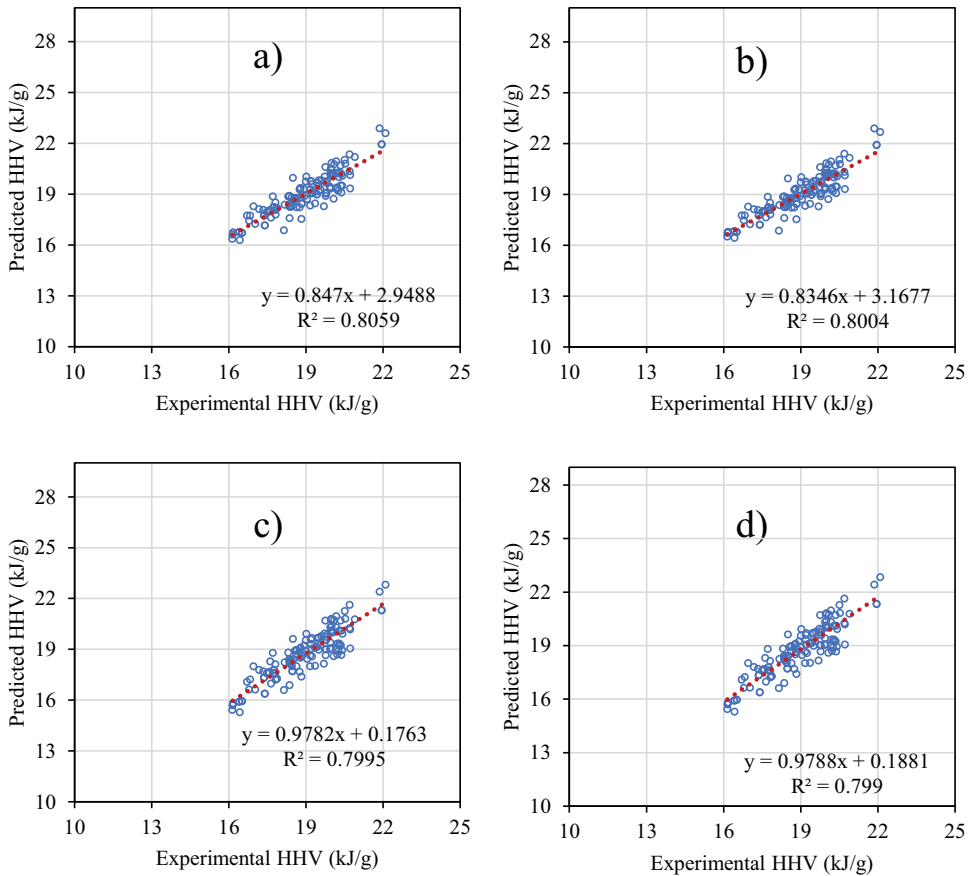


**Figure 5.** The best two empirical correlations for the prediction of HHV of herbaceous and agricultural biomass feedstocks (254 data set) using ultimate analysis data a) equation (10) and b) equation (11) and combined ultimate-proximate analyses data; c) equation (26) and d) equation (29).

from a statistical point of view, i.e., MAE was determined to be approximately 0.5 for Herbaceous and Agricultural biomass feedstocks and approximately 0.46–0.47 for Woody biomass feedstocks using Eqs. (10) and (11).

Starting with the best two empirical correlations based on ultimate analysis, Eqs. (10) and (11) have very similar performance across all metrics for both herbaceous and agricultural biomass feedstocks and woody biomass feedstocks. Table 8 shows that Eq. (10) and Equation (11) could potentially be the most reliable correlations for predicting HHV based on ultimate analysis data, with the lowest error and highest accuracy. On the other hand, Eq. (26) and Equation (29) which are obtained from combined proximate analysis, also show good performance for both biomass types with higher error rates compared to Eqs. (10) and (11).

It is possible to achieve better results by using ultimate analysis-based empirical correlations for both biomass feedstocks. Considering the close error rates and the order of the equations that did not change in both groups, the four mentioned equations are applicable to the process of obtaining the HHV. Overall, only ultimate analysis data is sufficient to obtain the best HHV prediction process, even if the dataset includes both proximate and ultimate analysis results.



**Figure 6.** The best two empirical correlations for the prediction of HHV of woody biomass feedstocks (137 data set) using ultimate analysis data a) equation (10) and b) equation (11), and combine ultimate-proximate analyses data; c) equation (26) and d) equation (29).

### Sensitivity analysis

Based on the prediction results for Eqs. 10 and 11, a single variable sensitivity plot was presented to evaluate the relationships between all the independent variables and predicted HHV. The plots can be found in the supplementary materials (Appendix C, Figure C1 and C2). It should be noted that the single variable plots display similar trends across all equations. Furthermore, the C, FC, VM and N contents of biomass shows progressive increase with HHV. A slight increase in C content of biomass from 14 wt.% to 24 wt.% led to an elevation in the HHV from 36 kJ/g to 56 kJ/g. Also, as the FC content of biomass rises from 17 wt.% to 24 wt.% the HHV values also increase up to a value of 40 kJ/g. Other parameters such as ASH and H content did not display a visible trend with HHV values while the O content displays a negative trend. HHV values increase with a decline in O contents. It should be mentioned that the HHV value increases with C content due to the role of carbon in combustion processes (Nhuchhen and Afzal 2017). Carbon atoms react with oxygen to form carbon dioxide, releasing significant amount of energy. The higher the carbon content in the biomass, the more carbon atoms are available to undergo this reaction, thus generating more heat (Maksimuk et al. 2021). Additionally, carbon-rich biomass tends to have lower moisture and oxygen content, which further enhances its combustibility and energy yield. On the contrary, biomass with lower carbon content often has higher proportions of noncombustible elements like oxygen and nitrogen, leading to lower energy release during combustion.

## Conclusions

This study aims to investigate the generalizability of empirical correlations for predicting the HHV of biomass, which is an essential parameter for assessing biomass energy potential. The study comprehensively analyzed 391 different biomass feedstocks, including wood, herbaceous, and agricultural materials, using 45 different empirical correlations. The goal was to identify the best empirical correlations for predicting HHV and assess their performance across diverse biomass types. For this reason, some statistics analysis has been applied using Matlab to real and estimated data to determine the best equation/equations for predicting the HHV of different biomass types.

The results indicated that

- Empirical correlations utilizing ultimate analysis data provided more accurate predictions of HHV (lowest MAE:0.49 and MAPE:2.70% - Equation-10) compared to those based on proximate analysis (lowest MAE:0.96 and MAPE:5.27% - Equation-32) or combined data (lowest MAE:0.65 and MAPE:3.55% - Equation-26).
- Two empirical correlations (Eqs. (10) and (11)), which consider coefficients for each element (C, H, N) and their interactions (C\*H), showed the best HHV prediction with the lowest mean absolute error (MAE) of approximately 0.49, root mean square error (RMSE) of around 0.64, and mean absolute percentage error (MAPE) of approximately 2.70%.

$$HHV = (3.55 * C^2 - 232 * C - 2230 * H + 51.2 * C * H + 131 * N + 20600) / 1000$$

$$HHV = (5.22 * C^2 - 319 * C - 1647 * H + 38.6 * C * H + 133 * N + 21028) / 1000$$

- Other empirical correlations that primarily relied on carbon content as the major determinant also provided good HHV prediction from a statistical perspective, with MAE ranging from approximately 0.5 to 0.8, RMSE ranging from around 0.6 to 0.9, and MAPE ranging from approximately 2.8% to 3.8%.

The advantages of these two empirical correlations are offering high accuracy in predicting HHVs for specific biomass types using their ultimate analysis results (C, H, N), as evidenced by their low MAE, RMSE, and MAPE. They are straightforward to use, requiring only the elemental composition for calculation, making them suitable for quick assessments to predict the HHV in practical applications. However, these models may have limited generalizability beyond the specific types of biomasses tested in this study. Their accuracy heavily depends on precise elemental analysis, and they might oversimplify the complex processes governing HHV. There's also a risk of overfitting to the dataset they were developed from, potentially reducing their applicability to other biomass types or conditions.

Future research endeavors exploring the HHV of various biomass feedstocks should notably focus on the expansion of datasets to improve the robustness and applicability of empirical correlations across a wide array of biomass types. A pivot toward developing novel empirical correlations specifically tailored for unique and outlier biomass types will enhance predictive precision, especially when synthesized with advanced machine learning and deep learning models. This hybrid approach, intertwining empirical and computational methodologies, promises to bolster prediction accuracy by seamlessly navigating through complex, multidimensional biomass characteristic spaces. Lastly, an in-depth study into technological and combustion dynamics will facilitate a practical transition, ensuring that theoretical HHV predictions effectively translate into optimized combustion and sustainable energy generation in real-world contexts. Consequently, these focused strands of exploration stand to fortify the interlink between theoretical predictability and pragmatic energy production efficacy in bioenergy research.

## Disclosure statement

No potential conflict of interest was reported by the author(s).

## Funding

The author(s) reported there is no funding associated with the work featured in this article.

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