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Published by the Faculty of Engineering, Khon Kaen University, Thailand

Evaluating limit of detection and quantification for higher heating value and ultimate analysis of fast-growing trees and agricultural residues biomass using NIRS

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Received 31 July 2023
Revised 8 October 2023
Accepted 12 October 2023

Abstract

Accurate non-destructive assessment of biomass energy properties is essential for optimizing its use as an alternative fuel. In this study, 200 biomass samples were used to determine higher heating value (HHV) and 120 biomass samples for analyzing ultimate analysis parameters using near-infrared spectroscopy within the full wavenumber range of 12489.48 – 3594.87 cm^{-1}. The samples were grounded, and five different types of partial least squares regression (PLSR) models were developed using traditional preprocessing, multi-preprocessing (MP) with 5 range, MP with 3 range, genetic algorithm, and successive projection algorithm. Limit of detection (LOD) and quantification (LOQ) were calculated using the best-performing model among five different PLSR models for HHV in kJ/kg, as well as the weight percentage (wt.%) of carbon (C), oxygen (O), hydrogen (H), and nitrogen (N). The LOD and LOQ for HHV were calculated as 622.42 kJ/kg and 1886.13 kJ/kg, respectively. Additionally, LOD and LOQ for ultimate analysis parameters, including C, O, H, and N were calculated as: 3.24 weight percentage (wt.%) and 9.81 wt.% for C, 2.04 wt.% and 6.18 wt.% for O, 0.35 wt.% and 1.05 wt.% for H, and 0.22 wt.% and 0.68 wt.% for N. The LOD and LOQ values for HHV, C, O, and H were lower than the minimum reference values used for model development, demonstrating the models' high sensitivity and potential to reliably detect and precisely quantify these parameters. However, the LOD and LOQ values exceeded the minimum reference value used during model development for the N, indicating that the selected models have certain limitations in assessing the N content in biomass. The sample range should be expanded for wt.% of N to enhance the model's performance, surpassing the LOD and LOQ values. This will improve the overall sensitivity of the model for reliable detection and quantification of N content in biomass samples.

Keywords: Biomass, Near-infrared spectroscopy, Partial least squares regression, Limit of detection, Limit of quantification

Abbreviations

%	Percentage	O	Oxygen
A	Ash content	PLSR	Partial least squares regression
C	Carbon	R^2_C	Coefficient of determination of training set
FT	Fourier transform	R^2_P	Coefficient of determination of testing set
GA	Genetic algorithm	RPD	Ratio of prediction to deviation
H	Hydrogen	S	Sulfur
HHV	Higher heating value	SD	Standard deviation
LOD	Limit of detection	S_c	Slope of the regression line from training set
LOQ	Limit of quantification	RMSEC	Root mean square error of training set
LVs	Number of latent variables	RMSEP	Root mean square error of testing set
Mean	Average	SNV	Standard normal variate
MSC	Multiplicative scatter correction	SPA	Successive projection algorithm
MP	Multi-preprocessing	sd_1	First derivative
N	Nitrogen	sd_2	Second derivative
N_c	Number of sample in training set	σ_C	Standard deviation of residual of training set
NIRS	Near infrared spectroscopy	wt.%	Weight percentage

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doi: 10.14456/easr.2023.63

1. Introduction

Biomass, derived from organic matter such as wood, crops, and waste, is a renewable energy source with the potential to mitigate greenhouse gas emissions and enhance energy security [1]. Due to its ability to be replenished relatively quickly, biomass is considered a sustainable energy source [2]. In recent years, biomass has gained significant attention as a renewable energy option, offering extensive applications in cooking, heating, electricity generation, transportation, agriculture waste management, and industrial processes [3, 4]. However, biomass can be challenging to handle due to its energy properties, including HHV, proximate analysis parameters (moisture content, volatile matter, fixed carbon, ash content), and ultimate analysis parameters C, H, N, S and O [5], which can vary based on factors such as biomass type, harvesting conditions, storage conditions, and during transportation [6]. The fluctuating quality of biomass feedstocks can significantly affect their suitability for efficient energy conversion [7].

The HHV is a crucial characteristic of biomass fuel as it is mainly used to calculate combustion efficiency and the amount of energy that can be generated by the fuel [8]. Carbon, the primary component of biomass, serves as the main energy source during combustion. The carbon content can vary depending on the biomass type, but it typically ranges around 50% [9]. Oxygen, the second most prevalent element in biomass, plays a significant role in the combustion process [10]. The oxygen content in biomass can vary, but it is typically around 40%. Hydrogen, the third most prevalent element in biomass, is an important component of many biofuels. In addition to its clean-burning properties, hydrogen can be utilized for heat and electricity generation. Evaluating the feasibility of hydrogen production from biomass requires determining the hydrogen content within the biomass [11]. The amount of hydrogen in biomass varies depending on the type but is typically around 6%. Nitrogen, despite being a minor component in biomass, has an impact on both combustion efficiency and emissions during combustion. The nitrogen content in biomass can vary, typically ranging between 1% and 2% [12]. Biomass also contains sulfur (S) in quantities less than 1%. Even in small amounts, sulfur can contribute to emissions such as sulfur dioxide [13]. Therefore, the fast and precise prediction of biomass energy properties is crucial for the effective and efficient utilization of biomass resources.

NIRS, a fast, reliable, and non-invasive method, has been widely utilized for quality control purposes in various biomass applications. It enables the rapid and accurate assessment of important parameters such as HHV, proximate and ultimate analysis parameters [14]. This technique offers improved prediction accuracy models, thereby facilitating efficient and precise characterization of biomass properties.

In our prior research, we conducted a thorough evaluation of ground biomass characteristics for energy applications. We employed NIRS and spectral multi-preprocessing methods to enhance the performance of a PLSR model, specifically focusing on predicting HHV and parameters related to ultimate analysis [15]. However, to comprehensively evaluate the sensitivity of the selected NIR-based models, it is essential to assess two key parameters: the LOD and the LOQ [16]. In NIRS, the calculation of LOD and LOQ is influenced by factors such as the type of analyte, the instrument used, and the employed method [17]. These parameters are important in NIR modeling as they determine the minimum detectable and quantifiable concentration of the substance being measured, ensuring reliable predictions. LOD and LOQ play a vital role in regression analysis by ensuring the validity of analysis findings [18]. They enhance the model's reliability by minimizing false positives and negatives, enabling effective comparison of results across various analyses. Additionally, LOD and LOQ ensure data quality by establishing limits for allowable substance concentrations in samples. This further improves the usefulness of these measures in selecting the optimal training range.

To our knowledge, no research has been reported regarding the calculation of LOD and LOQ for HHV and the ultimate analysis parameter of ground biomass. Therefore, the main objectives of this research were to assess the LOD and LOQ based on the performance of the best training model for HHV and the ultimate analysis parameters to improve the model sensitivity.

2. Materials and methods

2.1 Samples

The commonly used biomass samples from fast-growing trees (5) and agricultural residues (5) were collected from various locations in Nepal. The samples included: 1) *Alnus nepalensis*, 2) *Pinux roxiburghii*, 3) *Bombusa vulagris*, 4) *Bombax ceiba*, 5) *Eucalyptus camaldulensis*, 6) *Zea mays* (cob), 7) *Zea mays* (Shell), 8) *Zea mays* (stover), 9) *Oryza sativa*, and 10) *Saccharum officinarun*. In this study, 200 biomass samples were used to develop a PLSR-based models for HHV, while 120 biomass samples were used for the ultimate analysis parameters [15]. Each sample varieties were grounded and scanned using FT-NIRS, and its HHV was measured using bomb calorimeter. Similarly, the ultimate analysis parameters, wt.% of C, H, N, and S, were measured using the CHNS/O analyzer. The wt.% of O was calculate as a difference from wt.% of C, H, N, S and A [19]. Here, the wt.% of A is measured employing a thermogravimetric analyzer (TG 209 F3 Tarsus, Netzsch, Bavaria, Germany).

2.2 Instrument

FT-NIRS (MPA, Bruker, Ettlingen, Germany) was used to log the spectral absorbance data of ground biomass samples in transflectance mode within a wavenumber range of 12489.48 – 3594.87 cm^{-1} [15]. Figure 1 illustrates the representative particle size distribution of the ground biomass, covering a range from 0.01 to 3080 µm. The ground biomass was placed up to a height of 10 mm inside a glass vial with a diameter of 20 mm and a height of 48 mm for scanning the samples in a controlled laboratory environment at 25±2 ^{o}C. Although the amount of ground biomass sample used for scanning in the tranflectance mode is small, the variation of the constituent is less, and light is diffuse in the homogenous ground biomass, allowing for better penetration and diffusion to obtain high-quality spectra. Each sample underwent two scans, and the resulting average value was used for the model development.

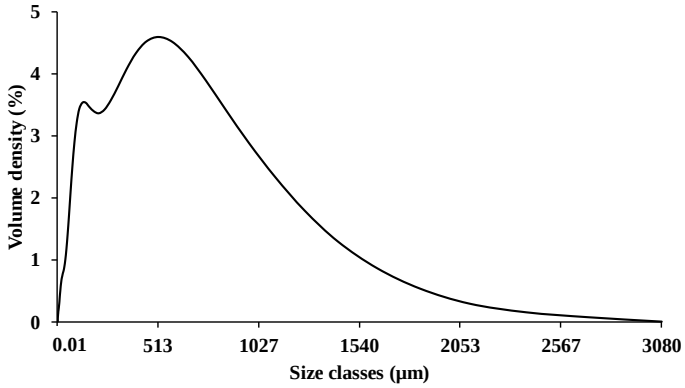

Figure 1 Representative particle size distribution of the ground biomass ranging from 0.01 to 3080 µm.

A bomb calorimeter (IKA C 200, Germany) was used to measure the HHV, and the CHNS/O elemental analyzer (Thermo ScientificTM FLASH 2000) was used to measure wt.% of the ultimate analysis parameters. The HHV was measured in kJ/kg, while the ultimate analysis parameters were measured as wt.%. The reference parameters for each biomass sample were measured twice, and their average were regarded as the reference values for the model development. The CHNS/O elemental analyzer did not detect the S content in the grounded biomass samples. Therefore, the sulfur content has not been taken into account for the calculation of LOD and LOQ in this study.

2.3. Spectral preprocessing and model development

After logging spectral data (independent variable) and their respective reference data (dependent variable), the total data set for each evaluating parameter is prepared to develop a training model. First, outliers were calculated from the entire dataset as follows:

$$\frac{(X_i - \overline{X})}{SD} \geq |\pm 3| \quad (1)$$

Where X_i represents the measured value of sample i, while $\overline{X}$ and SD denote the average and standard deviation of the measured values of all samples [20].

If equation (i) is satisfied, a sample is considered an outlier and is removed from the dataset. After the removal of outliers, the total dataset is manually divided into a training set (80%) and a testing set (20%) to develop a model. The training set includes samples incorporating both the highest and lowest reference values to facilitate model development.

PLSR, recognized as a leading regression technique for NIR data analysis, is highly effective in developing calibration models due to its ability to handle the data's multi-collinearity and high dimensionality [21-25]. Therefore, this study developed five different types of PLSR-based models, which are as follows:

1. Full wavenumber-PLSR
2. MP-PLSR – 3 range method
3. MP-PLSR – 5 range method
4. GA-PLSR
5. SPA-PLSR

Full wavenumber PLSR is a conventional approach for developing PLSR models. It involves preprocessing the spectra using a single preprocessing technique applied across the entire wavelength range. Before model development, the spectral data were pretreated using following preprocessing techniques, and individual models were developed for each technique: 1) sd_1, 2) sd_2, 3) constant offset, 4) SNV, 5) MSC, 6) vector normalization, 7) min-max normalization, 8) mean centering, 9) sd_1 + vector normalization, and 10) sd_1 + MSC. The training model is then developed using raw spectra and each preprocessing technique and is validated using a testing set. In contrast, the MP technique, a new approach [15], divides the full wavelength range into distinct sections. For example, in the five-range method, the full wavenumber range is divided into five segments, and in the three-range method, it is divided into three segments. Each section is subjected to preprocessing using a combination set of 5 for the 5 range method and 3 for the 3 range method from 7 different preprocessing methods (codes: 0 = empty (all the absorbance values = 0), 1 = raw spectra, 2 = SNV, 3= MSC, 4= sd_1, 5= sd_2, and 6 = constant offset). For example, the combination set 3, 0, 1, 0, and 1 which corresponds to MSC, empty, raw, empty, raw for 5 range method, signifies segmenting the entire spectral range into 5 equal segmentations and preprocessing them as follows: MSC from 3625.72–5392.30 cm^{-1}, empty from 5400.02–7166.59 cm^{-1}, raw spectra from 7174.31–8940.89 cm^{-1}, empty from 8948.60–10,715 cm^{-1}, and raw spectra10,722.9–12,489.48 cm^{-1}. Similarly, for 3 range method, if the combination set is 4, 4, and 4 (i.e., sd_1, sd_1, and sd_1), it signifies that the spectral spectrum is segmented into three segments and subjected to preprocessing using the sd_1 for the segments 3594.87–5492.59 cm^{-1}, 7498.31–5500.30 cm^{-1}, and 7506.02–12,489.48 cm^{-1} [15]. Based on this combination set of preprocessing techniques, PLSR model were developed. This approach aims to enhance model performance by incorporating various preprocessing techniques and their combinations across different wavelength regions. By leveraging this diverse preprocessing approach, the MP-PLSR model strives to create a more robust model. GA and SPA are two different optimization techniques that can effectively capture important wavenumbers while avoiding collinearity issues. GA-PLSR leverages the strengths of both GAs (ensuring maximum fitness) and PLSR (maximizing covariance between absorbance values and the target of interest) [26, 27]. On the other hand, SPA-PLSR carefully selects feature variables to mitigate redundancy and address collinearity issues. These optimization techniques are employed to select the important wavenumbers that are then used to develop a PLSR model [15].

Figure 2 shows the average raw spectrum of fast-growing trees and agricultural residues of Nepal's ground biomass logged from FT-NIRS within the range of 12489.48 – 3594.87 cm^{-1}.

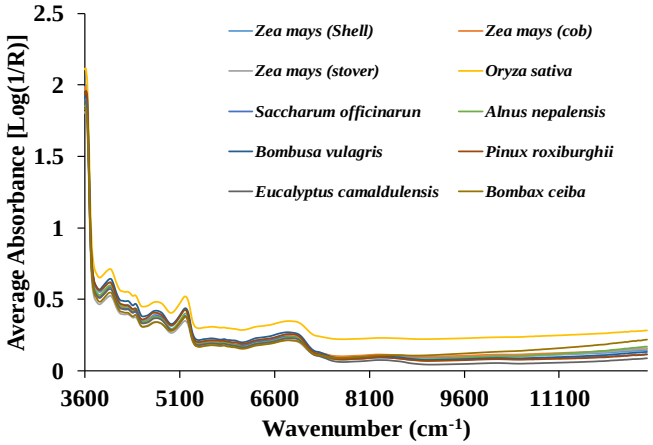

Figure 2 The average raw spectra of the fast-growing trees and agricultural residues of Nepal grounded biomass spanning the range of 12489.48 – 3594.87 cm^{-1} [15].

The accuracy of each model was assessed with the following specific parameters: 1) R^2_C, 2) R^2_P, 3) RMSEC, 4) RMSEP, 5) RPD, and 6) bias. These parameters were employed to evaluated and compare the models' performance. There are several factors that need to be considered to optimize the model's performance. All the instruments used for measuring the reference data should be regularly calibrated to minimize instrumental errors. The laboratory environment, mainly the temperature, should be kept constant throughout the NIR scanning of the biomass. Care should be taken to prevent leakage of NIR radiation as it leads to data loss. The sample should be as homogeneous as possible, and contamination during sample preparation should be avoided to reduce analysis errors as well. Additionally, it is important to properly identify outliers in the data to ensure accurate calibration. Outliers can significantly impact the performance of the model and should be carefully addressed and managed during data analysis.

2.4 Limit of detection and limit of quantification

The LOD refers to the lowest concentration of an analyte in a test sample set that can be reliably distinguished from background noise, but not necessarily quantified accurately. Similarly, the LOQ represents the lowest concentration of the analyte that can be both reliably detected and quantified with an acceptable level of accuracy and precision [28]. In this study, LOD and LOQ are calculated based on the standard deviation of the response to slope [29], as follows:

$$\text{LOD} = 3.3\ \frac{\sigma_C}{S_C} \tag{2}$$

$$\text{LOQ} = 10\ \frac{\sigma_C}{S_C} \tag{3}$$

Where, σ_C is the residual standard deviation i.e., the error obtained from measured and predicted values of the training set and S_C is the slope of the regression line [30].

3. Results and discussion

In our previous study, we developed five different types of PLSR models for ground biomass and compared their performance to select the best model for a comprehensive assessment of HHV and ultimate analysis parameters [15]. In this study, LOD and LOQ values were calculated from the best performance model, based on the standard deviation of the response to slope from the training set.

Table 1 displays the analysis results of the reference parameters of the grounded biomass [15], providing an assessment of the LOD and LOQ for each parameter. The LOD and LOQ values for HHV from GA-PLSR were calculated as 622.42 kJ/kg and 1886.13 kJ/kg, respectively. Additionally, LOD and LOQ for ultimate analysis parameters, including C from GA-PLSR, O from the MP-PLSR- 5 range method, H from GA-PLSR, and N from the MP-PLSR-5 range method were calculated as follows: 3.24 wt.% and 9.81 wt.% for C, 2.04 wt.% and 6.18 wt.% for O, 0.35 wt.% and 1.05 wt.% for H, and 0.22 wt.% and 0.68 wt.% for N. These values indicate the lowest concentration at which the reference parameters of the biomass can be reliably detected and precisely quantified. It is evident that the LOD and LOQ for all reference parameters, except the wt.% of N, are lower than the minimum value used for developing the models. This suggests that the selected model i.e., GA-PLSR for HHV, C, and H and the MP-PLSR- 5 range method for O has the potential to reliably detect and precisely quantify these parameters based on their corresponding LOD and LOQ values, indicating high sensitivity. However, the model predicting the N content, i.e., the MP-PLSR-5 range method in ground biomass, has limitations due to higher LOD (0.22) and LOQ (0.68) values compared to the minimum reference values used for model development. Hence, to ensure a reliable assessment of wt.% of N, it is essential to incorporate an adequate number of representative samples with predicted wt.% of N values surpassing the LOD and LOQ values. Additionally, considering alternative modeling methods for evaluating N content in the ground biomass would enhance the model sensitivity.

The S_c of the regression line from the training set was found to be 1 for all the measuring parameters. This suggests the accuracy of the prediction of those constituents. A S_c value close to one indicate high accuracy in prediction, while a low σ_c of residual indicate the high precision of the model. A lower value of σ_c and a higher value of S_c result in the smaller values of LOD and LOQ, indicating higher sensitivity of the model.

The coefficient of determination values obtained from the analysis demonstrate a strong correlation between the independent variables and their respective parameters. Specifically, GA-PLSR yielded an R^2_C of 0.95 for HHV, 0.79 for C, and 0.88 for H in the

training set. The 5 range-PLSR model resulted in an R^2_C of 0.89 for O and 0.86 for N in the training set. These findings highlight the high degree of relationships between the variables and their corresponding parameters.

Figure 3 illustrates the comparison between the measured versus predicted values in the training set for various parameters: a) HHV (kJ/kg), b) wt.% of C, c) wt.% of O, d) wt.% of H, and e) wt.% of N.

Table 1 Analysis result of the HHV and ultimate analysis parameters of the ground biomass for assessment of LOD and LOQ

Reference value	HHV	Carbon	Oxygen	Hydrogen	Nitrogen
Unit	kJ/kg	wt.%	wt.%	wt.%	wt.%
Reference value range	14,682 - 18,616	38.4 - 48.0	46.26 - 54.36	4.95 - 6.48	0 - 0.83
Algorithm	GA-PLSR	GA-PLSR	MP-PLSR-5 range	GA-PLSR	MP-PLSR-5 range
Preprocessing technique	sd_1	sd_1	5, 0, 1, 0, 1	SNV	4, 4,4
N_c	157	87	77	74	76
Mean	17005	44.62	44.95	5.72	0.30
SD	842	2.00	2.55	0.30	0.22
LVs	14	9	14	14	10
R^2_C	0.95	0.79	0.67	0.88	0.86
R^2_P	0.96	0.72	0.63	0.77	0.84
RMSEC	188.01	0.98	1.45	0.10	0.07
RMSEP	170.33	0.97	1.53	0.14	0.10
RPD	4.89	1.93	1.71	2.14	2.65
bias	-21.96	0.19	0.45	-0.0	-0.03
σ_C	188.61	0.98	0.62	0.10	0.07
S_C	1.00	1.00	1.00	1.00	1.00
LOD	622.42	3.24	2.04	0.35	0.22
LOQ	1886.13	9.81	6.18	1.05	0.68

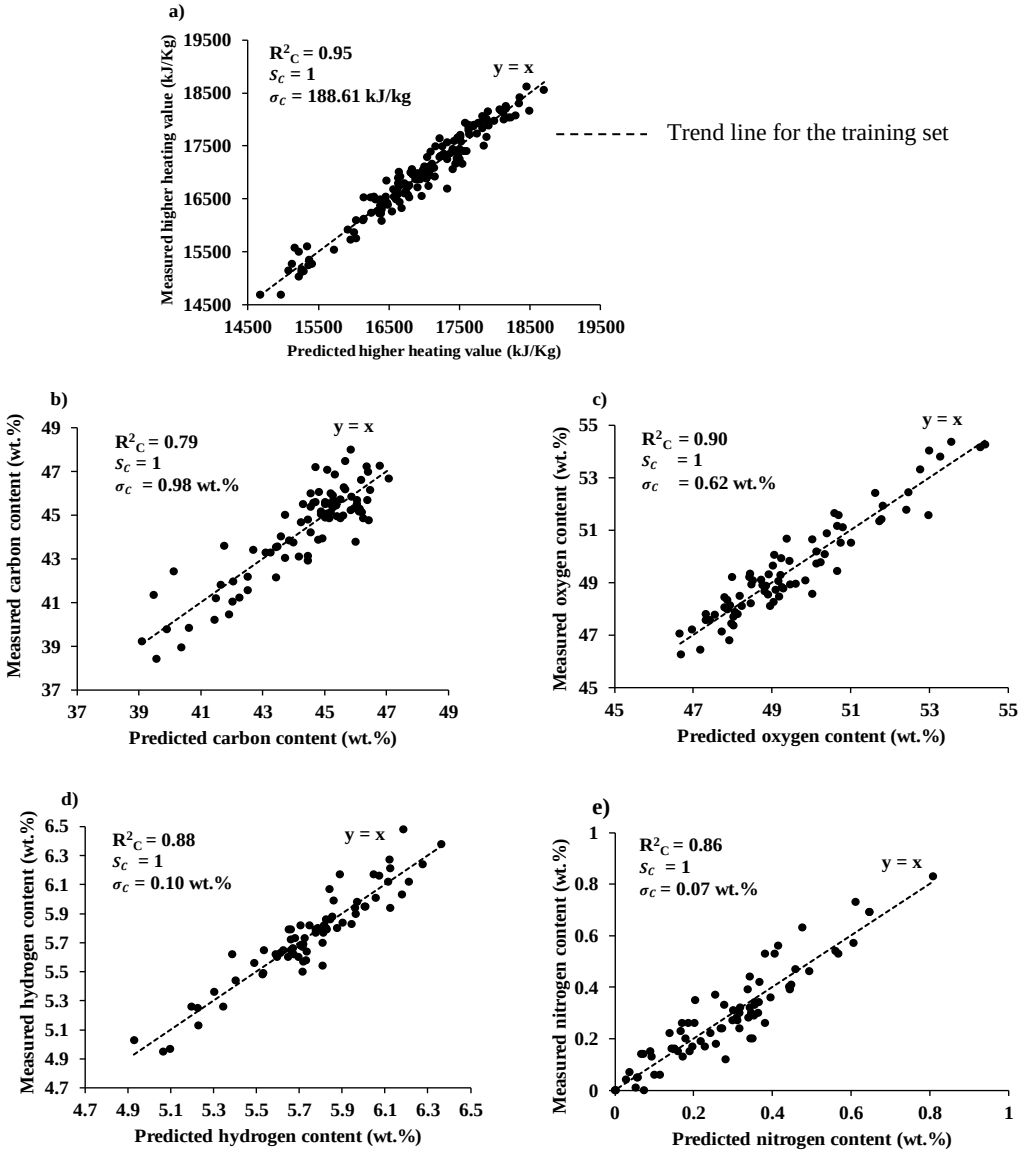

Figure 3 Scatter plot of measured vs predicted values from the training set for: a) HHV, b) wt.% of carbon, c) wt.% of oxygen, d) wt.% of hydrogen, and e) wt.% of nitrogen.

4. Conclusions

The results of this experiment show that the model has high sensitivity in detecting and quantifying parameters such as HHV in kJ/kg, wt.% of C, H, and O in grounded biomass. These results also establish a minimum threshold for detectability and quantifiability of these reference parameters. However, the LOD and LOQ for wt.% of N are higher than the minimum range value used during model development, indicating the necessity for modification to enhance its sensitivity by improving the prediction accuracy and precision. Therefore, to enhance the model's effectiveness, it is advisable to expand the total dataset by including a wide range of representative samples, particularly considering the variations in nitrogen content within the biomass. Additionally, it is crucial to validate the selected models using unknown samples to ensure greater acceptance and reliability. These adjustments will contribute to an overall improvement in the model's sensitivity.

5. Acknowledgements

The authors would like to express sincere gratitude to the Near-Infrared Spectroscopy Research Center for Agriculture Product and Food, Department of Agricultural Engineering, School of Engineering at King Mongkut's Institute of Technology Ladkrabang, Thailand for providing KMITL doctoral scholarship KDS 2020/52 and research fund. Additionally, the authors sincerely acknowledge the Department of Research and Graduate Studies, Khon Kaen University, Thailand, for their valuable research support, which was instrumental in the accomplishment of this study.

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