Prediction of elemental components of ground bamboo using micro-NIR spectrometer

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Abstract. The combustion performance depended on heating value of as-received bamboo which involved elemental components (C, H, N, O, S). The experiment using Micro-NIR spectrometer to investigate of 80 ground bamboo samples and partial least squares regression (PLSR) with cross validation technique was used to develop the model. The reference method was performed on the elemental analyser. It was showed that only C (carbon) was efficiently possible to determine with R² approximately of 0.6, RMSECV 0.612%, SECV 0.616% and Bias 0.001%. Important peaks in regression coefficient plot at wavelengths 1174 nm and 1927 nm corresponded to C-H overtone and C=O str. 2nd overtone for lignin. At wavelength 1395 nm and 1728 nm were related to 2C-H str.+C-H def. and C-H str. overtone for hemi-cellulose. At wavelength 1580 nm, 1632 nm, 1779 nm, 1824 nm, and 2023 nm conformed respectively to O-H str.1st overtone, C-H str.1st overtone, C-H str. overtone, O-H str.+2C-O str. and 2O-H def.+ C-O def. for cellulose.

1. Introduction

Bamboo has been considered to be an affective bioenergy as it has capability in good heating value compared with other biomass such as wheat straw, sugar cane bagasse, sugarcane, rice husk, rice straw, corn straw, ply wood and saw dust [1-3]. The heating value of these biomass were in range of 15 -20 MJ/kg while the heating value of bamboo was approximately of 18 MJ/kg. Furthermore, bamboo is a short crop plant and widely cultivated in the tropical country as Thailand. All of these advantages of bamboo promoted to be an alternative and interested biomass as high potential to be use as bamboo gave the characteristics of this bioenergy and it could be used to predict the heating value [1, 4]. The procedure to carry out these values spends processes and times. Recently, NIR spectroscopy has been introduced to reduce these troubles in order to rapidly investigate and to produce prediction models in many aspects of bio-materials such as moisture content, heating value, percentage of ash and chemical contents [5-10].

As mentioned, NIR spectroscopy has been promoted as a method to evaluate agricultural constituents in both chemical and physical characteristics. This technique also provides rapid results with accuracy and reproducibility [11], non-destructive samples, and a nature-friendly technique. Posom and
Sirisomboon [12] reported the evaluation of moisture content and heating value of Jatropha curcas kernels that the NIR could develop the predicting model of both the moisture content and the heating value by partial least squares regression with validation of a test set. It was also stated that vibration bands of fiber and cellulose affected the predictions. Another study of Leucaena leucocephala pellets by using the NIR showed rapid quality analysis of moisture content (MC) and higher heating value (HHV) by implementing partial least squares regression with full cross validation. The model of MC and HHV showed accuracy by $R^2$ of 0.995 and 0.964 respectively [11]. This rapid quality evaluation method could be claimed to use for trading biomass pellets. This research aimed to use near infrared (NIR) technique to predict the chemical contents of ground bamboo as C, H, N, O and S in order to reduce time and find the effective method to evaluate the characteristics of the biomass which in this case was bamboo. The experiment carried out by using the regular method and the NIR technique.

2. Materials and method

Bamboo 80 samples collected from Uttaradit province (Thailand) were used in this study. As-received bamboos were cut of 10 cm above the ground and chopped by the chopping machine (P5508, Patipong, Thailand). The chopped bamboos were dried under the sun until moisture reached 5%. The dried bamboos were ground through sieve diameter of 3 mm (60201, QC, UK) and kept in sealed aluminium bags. The ground samples were placed into a sample cup, diameter of 43 mm with height of 55 mm, which the bottom was made from quartz. Samples were scanned at 25±2 ºC with controlled air conditioner and each sample was repeated by 3 times. Micro-NIR spectrometer (JDSU, USA) was used for scanning of diffuse reflectance mode in range of 1144-2074 nm with integration time of 13.5 ms. The absorption was recorded in log (1/R) unit ($R$ was the reflection intensity). The spectral data were analyzed by implementing the Unscrambler X software version 10.3 (Camo, Norway) to determine chemical compositions and generate models. For laboratory of element analysis, the experiment of element compositions (C, H, N, O, S) was carried out with CHNS analyzer (Vario EL CUBE, Elementar, Germany) duplicately and oxygen content was determined as equation (1).

$$O\% = 100\% - (C\% + H\% + N\% + S\% + A\%)$$

Where A is percentage of ash content approximated from thermogravimetric (TGA). The repeatability of this experiment was the standard deviation of the difference of duplication. The NIR instrument used absorbance value at wavelength of 1609 nm to determine the repeatability which was the standard deviation of absorbance values of 10 scanning at the same sample position. The selected wavelength for determination of the repeatability was randomly chosen; however, it was recommended should be the wavelength of the important peak of the material. The carbon element was used as a representative of this process. The precision of reference procedure could be shown by repeatability of reference data which was the standard deviation of the different of duplicate.

Analysis of spectral data were carried out with the Unscrambler X software by trail both pretreatment and non-pretreatment to determine the best fitting model of compositions (CHNOS) in Bamboo. The tasks for pre-treatment were Savitzky–Golay, Savitzky–Golay normalisation, mean normalisation, maximum normalisation, range normalisation, first derivatives, second derivatives, baseline, standard normal variate (SNV), detrending, SNV+detrending, and multiplicative scatter correction (MSC). The model was implemented using partial least squares regression (PLSR) and cross validation. Each of composition analyses was carried out at the same procedure. The best model for each composition was investigated from the best value of determination coefficient ($R^2$). The regression coefficient was calculated by the program and plotted. The best model was selected with the lowest root mean square error of cross validation (RMSECV) and the highest value of coefficient of determination ($R^2$). The $R^2$, RMSECV, RPD and bias could be calculated by equation (2)-(5) (adapted from William, [13]). Where $Y_i$ is the measurement value of sample $i$; $\bar{Y}_i$ is the average value of $Y_i$; $Y_{pre}$ is the value of sample $i$ estimated by cross validation; SD is standard deviation of the measurement value; $m$ is the number of samples. SEP is standard error of prediction.
\[
R^2 = 1 - \frac{\sum_{i=1}^{m}(Y_i - Y_{pre})^2}{\sum_{i=1}^{m}(Y_i - \bar{Y})^2}
\]

(2)

\[
RMSECV = \left(\frac{\sum_{i=1}^{m}(Y_i - Y_{pre})^2}{m}\right)^{1/2}
\]

(3)

\[
RPD = \frac{SD}{SEP}
\]

(4)

\[
Bias = \frac{\sum_{i=1}^{m}(Y_i - Y_{pre})}{m}
\]

(5)

Commonly, the usable and accuracy model in any application should provide \(R^2\) value over 0.98. William [13] gave the guideline of \(R^2\) value: lower 0.50 could not be used, 0.50-0.64 could be used for rough screening, 0.66-0.81 could be used for screening and some other approximate calibration, 0.92-0.96 could be used with caution for most application, over 0.98 could be used in any application. Zornoza [10] suggested for the \(R^2\) values: as excellent evaluation with \(R^2 > 0.90\), \(RPD > 3\), as good prediction for \(0.81 < R^2 < 0.90\), \(2.5 < RPD < 3\), and as poor prediction with \(R^2 < 0.66\), \(RPD < 2\). Furthermore, it was also the determination of wavelengths which possibly conformed to bond vibration affected prediction of compositions in Bamboo.

3. Results and discussions

The trials of both pre-treatment and non-pretreatment for carbon contents found that pre-treatment tasks showed no improvement of \(R^2\) values compared to non-pre-treatment procedures (Table 1). Similarly, the results of the other components also showed no improvement of the \(R^2\) for every pretreatment processes. As a result, pre-treatment tasks had no requirement to imply for other compositions. The test of repeatability to confirm the precision of the measurement using carbon as a representative showed that the repeatability and maximum \(R^2\) value were 0.436 and 0.792 respectively. The repeatability of Micro-NIR was 78.73 at wavelength of 1609 nm. The results of prediction for carbon content showed in figure 1 with \(R^2\) of 0.601(with standard error of cross validation, SECV 0.616%), the other compositions had less of \(R^2\) which were not applicable for hydrogen, 0.001 for nitrogen, 0.155 for oxygen and 0.120 for sulfur. These results were consistent with a report of Scurlock [14] stating high percentage of carbon in bamboo chip measured from ultimate analysis approximately of 52%. It was also reported that hydrogen, nitrogen and sulfur were slightly traced. This supported why the carbon only showed the highest \(R^2\) while the rest elements showed very low \(R^2\) on trials.

The low \(R^2\) value of N, O, S and H in this experiment may be caused from low amount of these elements in Bamboo and also less of resolution of the Micro-NIR spectrometer. However, the Micro-NIR could be used for rough scanning as Williams [13] stated that for \(R^2\) range 0.50-0.64 could possibly use for preliminary scanning. It could be claimed that this Micro-NIR capably provided rough results for prediction of main element component which was carbon in this case. If we need the good result for prediction, the FT-NIR may be better alternative instrument. It was obviously seen that the resolution of the instrument played a significant role for generating the accuracy model. The another research[4] showed results of composition analysis of ground bamboo using FT-NIR revealed that \(R^2\) value for element C, H, N, O and S were higher compared with this study. The number of samples and condition were the same as using with Micro-NIR spectrometer since they were from the same batch of samples. The \(R^2\) value evaluated from FT-NIR of C, H, N, O and S were 0.803, 0.856, 0.973, 0.522, and 0.785 respectively. These results compared with using Micro-NIR showed dramatically different of \(R^2\) between using of different instrument. Therefore, the Micro-NIR could be claimed to use for preliminary or rough screening with caution of the accuracy of data. It was noticed in the experiment that the homogenous of samples effected to spectra of the Micro–NIR. The solid sample certainly has less homogenous than the liquid sample so that the spectra rather showed a lot of noise and showed less resolution compared with FT-NIR [15, 16]. Although the Micro-NIR provided less resolution than FT-
NIR, it held advantages of cost, size, weight and mobility. This is why the Micro-NIR has been broadly used in many researches [16-18] and it has been continuously improved performance to response in commercial uses [19, 20].

![Figure 1. Scatter plots between prediction and measurement carbon of bamboo by Micro-NIR spectroscopy using PLS regression.](image)

Table 1 obviously showed \( R^2 \) values of each parameter between calibration and validation set. It was noticed that pre-treatment tasks of the carbon element showed no improvement. This led to implementing non-pretreatment for H, N, O and S for this experiment. The absorption of non-pretreatment spectra in experiments also showed a lot of noise. This revealed that the Micro-NIR may be not enough high resolution to get good spectra for creating the prediction model. Furthermore, it was found that pre-treatment tasks also showed no any improvement; therefore, there is no any plot to be showed in this paper.

### Table 1. Results of partial least squares regression comparing between calibration and validation set of each parameter setting

| Parameters | Processing         | Calibration | Validation |
|------------|--------------------|-------------|------------|
|            |                    | PLS Factors | \( R^2 \)  | RMSEC | SEC  | \( R^2 \) | RMSECV | Bias | RPD |
| C          | Raw                | 9           | 0.745      | 0.483  | 0.486 | 0.601      | 0.612   | 0.001 | 6.00 |
| C          | Savitzky Golay Smooth | 9           | 0.724      | 0.503  | 0.506 | 0.579      | 0.631   | 0.002 | 5.82 |
| C          | Norm Smooth Mean   | 8           | 0.714      | 0.512  | 0.515 | 0.559      | 0.643   | 0.007 | 5.70 |
| C          | Norm Reduced Mean  | 8           | 0.733      | 0.495  | 0.498 | 0.558      | 0.644   | 0.006 | 5.69 |
| C          | Norm Reduced Max   | 7           | 0.721      | 0.505  | 0.508 | 0.597      | 0.615   | 0.005 | 5.97 |
| C          | Norm Reduced Range | 7           | 0.724      | 0.503  | 0.506 | 0.596      | 0.616   | 0.015 | 5.96 |
| C          | 1st derivative     | 7           | 0.717      | 0.509  | 0.512 | 0.602      | 0.611   | 0.013 | 6.01 |
| C          | 2nd derivative     | 6           | 0.725      | 0.502  | 0.505 | 0.632      | 0.587   | -0.005 | 6.25 |
| C          | Baseline           | 9           | 0.745      | 0.483  | 0.486 | 0.603      | 0.611   | 0.001 | 6.01 |
| C          | SNV                | 5           | 0.670      | 0.549  | 0.553 | 0.556      | 0.646   | 0.037 | 5.66 |
| C          | SNV Detrending     | 8           | 0.742      | 0.486  | 0.489 | 0.56       | 0.642   | -0.004 | 5.71 |
| C          | MSC                | 5           | 0.674      | 0.546  | 0.55  | 0.538      | 0.658   | 0.042 | 5.54 |
| C          | Detrending         | 7           | 0.735      | 0.492  | 0.496 | 0.606      | 0.608   | 0.014 | 6.04 |
| H          | Raw                | 1           | 0.021      | 0.094  | 0.094 | NA         | 0.096   | 0.001 | 4.10 |
| N          | Raw                | 1           | 0.021      | 0.123  | 0.124 | 0.001      | 0.126   | -4.8×10^{-5} | 3.20 |
| O          | Raw                | 3           | 0.249      | 1.091  | 1.098 | 0.155      | 1.171   | 0.001 | 3.56 |
| S          | Raw                | 3           | 0.230      | 0.230  | 0.016 | 0.12       | 0.017   | 1.6×10^{-4} | 4.30 |
The result of regression coefficient plot as shown in figure 2 revealed C-H overtone and C=O str. 2nd overtone for lignin at wavelengths 1174 nm and 1927 nm, at wavelength 1395 nm and 1728 nm relating to 2C-H str.+C-H def. and C-H str. overtone for hemi-cellulose, and at wavelength 1580 nm, 1632 nm, 1779 nm, 1824 nm, and 2023 nm respective conforming to O-H str.1st overtone, C-H str.1st overtone, C-H str. overtone, O-H str.+2C-O str. and 2O-H def.+ C-O def. for cellulose. Posom [4] as well as Yang [21] also reported the bond vibration analysis of bamboo samples which were consistent with the analysis of this report.

Figure 2. The regression coefficient plot of samples within wave-length 1100-2100 nm.

4. Conclusions
The trials the Micro-NIR showed capability to predict as rough screening on the ground bamboo because of the resolution of the instrument. The carbon element prediction showed the highest R² value compared with hydrogen, nitrogen and sulfur. The results of carbon prediction were R² value approximately of 0.6, RMSECV 0.612%, SECV 0.616% and Bias 0.001%. The important peaks of analysis revealed compositions of the bamboo at each wavelengths which were lignin, hemi-cellulose, and cellulose. Although the Micro-NIR showed less of resolution compared with the FT-NIR, it holds advantages of cost, size, weight and mobility. That is why the Micro-NIR is still received popularity in research and still developed the performance to response more accuracy and capability.

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Acknowledgement
The authors thank the Near-Infrared Spectroscopy Research Center for Agricultural Products and Food at King Mongkut’s Institute of Technology, Ladkrabang, Bangkok, Thailand, for instruments and helps.