Rapid evaluation of moisture content in bamboo chips using diode array near infrared spectroscopy

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Abstract. Moisture in biomass plays an important role during storage, combustion and pelletization. In order to measure moisture content in bamboo chips, two diode array near-infrared instruments, NIR-Gun (600-1100 nm at 2 nm intervals) and Micro-NIR (1150-2150 nm at 7 nm intervals), were used for scanning bamboo chips. Total number of samples used for developing model after removing outliers was 252. The circumference and moisture content of bamboos used were in the range between 16-39 cm and 39-86% wet basis (wb) respectively. Partial least squares regression technique was used to develop the model to predict the moisture content in bamboo chips. The R², SECV, SEP, bias and RPD of optimum model of NIR-Gun were found to be 0.924, 2.871% wb, 2.385% wb, -0.250% wb and 3.656, while for Micro-NIR model the values were found to be 0.743, 4.349% wb, 4.499% wb, 0.026% wb and 1.972 respectively. In prediction of moisture content in bamboo chip, both models show the effect of different constituents of bamboo more than moisture. This study indicates that the results are suitable for screening the moisture content in bamboo chips. This would be helpful for process controlling using the moisture parameter during drying, pelletization and thermochemical conversion.

1 Introduction

Biomass is multipurpose renewable energy which can be combusted directly for heat or convert into gas or liquid fuel. Bioenergy has always been one of the major sources of energy which contributes 10% in primary energy supply in 2012 where the share of renewable energy was 13.5% [11]. In the last few years, research on biomass has increased tremendously as an alternative energy because of increasing cost of fossil fuels, fossil fuel crisis and global warming problems originated mostly from fossil fuels combustion [2, 3]. The amount of greenhouse gases in atmosphere can be reduced by increasing the contribution of renewable energy for energy purpose [4]. A fast growing energy crops with high environmental benefits can commensurate the fossil fuels. In such case bamboos can be one of them.

Bamboos are a group of perennial evergreens vegetation which belongs to true grass family [5, 6] and are receiving great interest due to their high growth rate and better reduction of carbon footprint compared to an equivalent area of woody plants [6, 7]. Beside combustion and bioenergy application, bamboos can be used as a construction building material, household products, food, pulp and paper and composite boards [8, 9].

Moisture plays a vital role for determining the quality and price of fuel, storage, pellet production and combustion. High moisture results in swelling, disintegration and prone to mold growth. In other hand, moisture acts as a binder during pelletization. In addition, high moisture content will increase the cost of drying and makes the feedstock slippery producing lower quality pellets. Also, too dry material may plug the die holes during pelletization and increases the resistance [10, 11]. A research conducted on four different biomasses, oak, oak bark, pine, and cottonwood in the forms of sawdust, mulches, and chips, by Li and Liu [12] concluded that the necessary moisture for producing good-quality logs ranges from 5 to 12% for all the woody materials studied, and the optimum moisture content is in the neighborhood of 8%. Furthermore, Komilis et al. [13] concluded that both higher heating value and lower heating value decrease with increase in moisture content, whilst the calorific value depends on the individual organic matters. Moreover, Vamuka and Sfakiotakis [14] reported that the combustion rate decreases with increasing moisture content.

In diode array detector, several diodes are arranged in array in which each array measure the portion of incident light and hence increase the speed of measurement. In addition, diode array spectrometers are smaller in size which made possible to carry in a small box for field works. The ASTM hot air oven reference method for the moisture content measurement is time consuming. Near infrared (NIR) spectroscopy is a non-destructive, rapid, simple sample preparation, chemical free-analysis [15] and employs electromagnetic spectrum of wavelength ranging between 750 to 2600 nm which relates with vibration and combination overtones of the fundamental

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O—H, C—H and N—H bonds [16]. Thus, NIR spectroscopy has great potential to measure the moisture of the samples due to presence of O-H in water. NIR spectroscopy was applied for the evaluation of moisture content of rice straw by Jin and Chen [17], Miscanthus x giganteus and short rotational coppice willow by Fagan et al. [18], biomass pellet by Gillespie et al. [19]. NIR spectroscopy has been used not only to measure the moisture content of biomass but also the composition of biomass like cellulose, hemicellulose, lignin [20, 21], ash [18], heating value [22]. However, to this date no study has reported about potential of NIR spectroscopy to predict the moisture content of bamboo wood chips. The aim of this study was to measure the moisture content of bamboo chip by deploying NIR spectroscopy technique in conjugate with chemometric.

2 Experimental

2.1. Samples

The bamboo samples, Dendrocalamus sericeus cl. Phamon, were procured from Uttaradit, Thailand. The bamboo trees were cut about 10 cm from the ground level and about 1 m from the base of bamboo was selected for the study. The bamboo was then chopped by the chopping machine (P5508, Patipong, Thailand). The size of bamboo chips were less than 3 cm. The total number of bamboo trees were 90 consisting of various culm circumference ranging from 16-39 cm.

2.2 Near infrared scanning of bamboo chips, Dendrocalamus sericeus cl. Phamon

The chopped bamboo were transferred in aluminum cup (50 mm in diameter and 30 mm in height) and scanned by two NIR instrument: NIR-Gun (FQA, Fantec, Japan) in reflectance mode (over the short wavelength range from 600-1100 nm at 2 nm intervals and the reference material was polystyrene and Micro-NIR (JDSU, USA) in reflectance mode (operating in the long wavelength range between 1150-2150 nm) at 7 nm intervals and the reference material was spectalon. Each sample was divided into three sub-samples and each sub-sample was scanned two times. Hence, the total numbers of samples available for making NIR-model were 270. The samples were scanned on site in atmospheric condition of Thailand. The reflectance (R) spectra was transformed into absorbance, log (1/R), spectra using CA maker software (Fantec, Japan) and The Unscrambler X 10.3 (Camo, Norway) for spectra obtained by NIR-Gun and Micro-NIR respectively. The part of spectra that contain noise or unusual characteristics was erased and was not used for model development.

2.3 Determination of moisture content of bamboo chips, Dendrocalamus sericeus cl. Phamon

Moisture content on bamboo chips was determined according to the procedure described in ASTM International D4442 - 07 — Method A—Primary Oven-Drying Method. About 3g of the chopped bamboo chips, after NIR scanning, was taken in a dried aluminum cup and oven dried in a preheated oven for 3 hours at 103±2°C (ULM 500, Memmert, Germany) in a room relative humidity of less than 70%. The sensitivity of the balance (AR2140 Adventure, Ohaus,) was 0.1 mg. The temperature of the oven was calibrated by the thermocouple (51/52 II, Fluke, USA). The weight of the sample was measured in a 3 h drying interval until the weight was constant and moisture content, wet basis, in a sample was calculated as follows:

\[ MC = \frac{m_i - m_f}{m_i} \times 100 \]  

where, \( MC \) is moisture content in % wb, \( m_i \) and \( m_f \) are initial and final dried mass respectively.

2.4 Determination of outlier of reference data

The outliers of reference data were checked by standard normal distribution for the Z-score greater than as given by equation 2.

\[ \frac{X_i - \bar{X}}{SD} \geq 3 \]  

where, \( X_i \) is the measured value of sample i, \( \bar{X} \) is the average value of all measured samples; \( SD \) is standard deviation of all measured samples.

2.5 Spectra pre-treatment and mathematical modelling

The spectra pre-treatments and model development were performed on The Unscrambler X 10.3 software (Camo, Norway). After the wet-test, the reference data were merged corresponding spectral data. The data were then arranged in descending order, and data were separated into calibration and prediction set. The highest and lowest reference values were used in calibration set. Various pre-treatments on calibration data set were performed before model development which includes no pre-treatment, Savitzky-Golay (S-G) smoothing, area normalization, unit vector normalization, mean normalization, maximum normalization, range normalization, peak normalization, first derivative (second order polynomial with 11 and 21 points), second derivative (second order polynomial with 11 and 21 points), baseline offset, linear baseline correction, standard normal variate, de-trending, standard normal variate plus de-trending and multiple scatter correction. Partial least squares (PLS) regression technique was used to develop the NIR models and confirmed using full cross validation. The model was checked by test set, and the optimum model was selected for lowest number of factor, highest coefficient of determination of
prediction, lower value of standard error of cross validation (SECV), standard error of prediction (SEP) and bias.

3 Results and discussion

The average pretreatment spectrum of bamboo chip scanned from two diode array instruments i.e. NIR-Gun and Micro-NIR of different moisture content is shown in Fig. 1 (a-b). On the spectrum of NIR-Gun, the peaks are seen around 657 nm and 959 nm. The bands vibration between 613-645 nm is associated with visible spectrum which represents the chlorophyll absorption [20, 23] and 950-1040 nm represents the second overtone of O-H stretch [16]. For Micro-NIR spectrum, small rise is seen in the range of 1400-1500 nm and sharp peaks at 1876 nm which corresponds to first overtone of O-H bond (O-H stretch, internal OH bonds, single bridge and/or polymeric) and third overtone O-H deformation (primary and secondary alcohol) [16].

The circumference of bamboos used in this research to measure moisture content were in between 16-39 cm and the moisture content were in range of 39-86% wet basis. The descriptive statistics of calibration and prediction set for the measurement of moisture content are shown in Table 1. The outliers of reference data were removed by standard normal distribution for the Z-score greater than 3, while principal component analysis was used to find the spectral outlier using Hotelling’s T-squared statistic which are isolated from the cluster. The total number of outlier was found to be eighteen, 7 from reference test and 11 from spectrum, in both cases. The model was created from remaining 252 sub-samples.

The selected wavelength range for creating the model was 615-1068 nm and 1158-2075 nm for short wavelength (NIR-Gun) and long wave length (Micro-NIR) respectively; however, the wavelength range of instruments are 600-1100 nm and 1150-2150 nm respectively. Because of noise at the beginning and end of spectra, some points were skipped. Firstly, the model was developed from the raw spectra without pretreatment and later various pre-treatment on spectra were performed. The second derivative (second order polynomial and 5 points) was found to be the most optimum effective treatment with 7 PLS factors for the NIR-Gun spectra, while SNV+De-trending was found to be the most optimal pretreatment for the spectra scanned by Micro-NIR using 6 PLS factors. The second derivative helps to separate overlapping peaks and baseline shift on spectra caused by the light scattering and particle size into independent peaks of different concentration. After second derivative pretreatment of NIR-Gun spectra, the spectra are arranged in order of increasing moisture content and has common baseline. Higher moisture content depicts higher absorption peak and vice versa. On the other hand, the SNV+De-trending help to reduce multicollinearity, baseline shift and curvature in spectroscopic data.

![Fig. 1. Spectra of bamboo chips of different moisture content (MC) on wet basis scanned by a) NIR-Gun spectrometer, pretreated by 2nd derivative and b) Micro-NIR spectrometer, pretreated by SNV + Detrending.](image)

**Table 1.** Statistical data for the measurement of moisture content (% wb) on bamboo chips sample used for developing PLS model.

| Model     | Calibration | Prediction |
|-----------|-------------|------------|
|           | N  | Max | Min | Mean | SD  | N  | Max | Min | Mean | SD  |
| NIR-Gun   | 232 | 85.5853 | 39.0014 | 56.6868 | 9.0019 | 20 | 75.9423 | 41.3817 | 57.6277 | 8.7190 |
| Micro-NIR | 232 | 85.5853 | 39.0014 | 58.0856 | 9.5470 | 20 | 75.9423 | 41.3817 | 58.8670 | 8.8729 |

N is number of sample, Max is maximum, Min is minimum, SD is standard deviation
Regression coefficient plot of NIR-Gun model is shown in Fig. 2a. The most important variance used in computing the final calibration model can be described by the areas of spectrum for which the regression coefficients are biggest [23]. The highest peaks seen in regression coefficient plot were at 900, 942 and 977 nm which corresponds to the vibration of C—H str. 3rd overtone (CH₃) C—H str. third overtone (CH₂) and O—H str. second overtone (ROH and H₂O), CH₂ (C—H str. third overtone) respectively [24]. Minor peaks were also seen in the visible region between 600-700 nm which are related with hydrocarbon present in environment temperature. The models mostly represent was seen in more common due to the fluctuating moisture and related absorbance peak. Shifting of bands independent moisture peaks were not seen clearly, affected by the different constituent of bamboo. The water molecules [26].

Similarly, Fig. 2b depicts regression coefficient of the Micro-NIR model. The highest peaks seen in regression coefficient are 1366, 1809 nm. The peak at 1366 nm is assigned as the bond vibration of 2×C—O str. + C—H def. of CH₃ whereas the peak at 1809 nm is assigned as the bond vibration of O—H str. + 2×C—O str. of cellulose. In regression coefficient plot, the moisture peak at 1940 nm appears as a small shoulder peak with small peak at 1927 nm which is assign as O—H stretching and H—OH bending combination from water molecules [26].

The models, in both cases, were seen to be mostly affected by the different constituent of bamboo. The independent moisture peaks were not seen clearly, however, strong correlations can be seen between moisture and related absorbance peak. Shifting of bands was seen in more common due to the fluctuating environment temperature. The models mostly represent the bands associated with hydrocarbon present in bamboo rather than moisture in either case. Bamboo is a lignocellulose biomass which is mainly composes of cellulose, hemicellulose and lignin. The major constituent of cellulose is glucose units [27] while hemicellulosis is xylose [28], and lignin is a polymer of aromatic compounds [27].

**Fig. 2.** Regression coefficient plot of optimum PLS model for measurement of moisture content in bamboo chips developed by using spectra scanned from a) NIR-Gun spectrometer and b) Micro-NIR spectrometer.

**Acknowledgements** The authors would like to thank near infrared spectroscopy research center for agricultural product and food (www.nirsresearch.com), King Mongkut’s Institute of Technology Ladkrabang for providing financial support and instruments. Also, the authors would like to acknowledge the plantation owner for providing samples, and all the people who helped to conduct this research.

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