Heating value prediction model of Acacia mangium Willd using near infrared spectroscopy

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Abstract. This study reported the prediction model of heating value for the *Acacia mangium* Willd which is the promoted as energy plant for the farmer to grow in the farm. Its heating value is approximately of 19 kJ/kg which provides high potential using for an alternative energy as biomass. The near infrared spectroscopy technique (NIR) is used to create model to predict the heating value of this biomass in order to reduce the investigated time. The results of model on the validation set were the coefficient of determination (R^2) of 71%, RMSEP of 246 J/g, RPD 1.87 and bias of 33.7 J/g. These results showed the potential and possibility to apply the NIR prediction technique. The robust model was suggested to carried out for more accuracy and may be applied in the online system analysis.

1 Introduction

The fast-growing plants as *Acacia mangium* Willd has been promoted to the farmer to grow in their farms in order to get alternative income over their conventional agricultural plants or horticulture. This *A.mangium* Willd tree has advantages in terms of a short crop cycle, no need fertiliser or watering [1]. The utilization of *Acacia mangium* Willd is for the furniture industrials due to the cheap price and easing for tooling and changing shape. The waste after furniture making process of the *A.mangium* Willd wood, which were in small pieces of wood or sawdust, can be used as biomass for a combustion process. In the way of biomass function, the important concern factor is heating value. The high amount of heating value can indicate the efficiency and quality of biomass.

If biomass has a high value of heating, it means that using a small amount of biomass can get a large amount of heat energy. Therefore, using the quality of biomass to determine the trading price, such as heating values, will make the trading of energy crops fair and have clear standards. The heating value property conventionally determines by using the calorimeter measurement. The process to get the value consumes time approximately of 30 minutes. Recently, there is a new technique to help to reduce this time to get the data consuming less than 1 minute which is known as the near infrared spectroscopy (NIR) [2, 3].

The spectrometer can work with any organic substance which consists of functional group of C-H, O-H, N-H, S-H and P-H. The biomass definitely response to these bonding [4]. Also, this technique can be applied in other properties relevant to the biomass such as

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biomass compositions, proximate and ultimate analysis [5-7]. However, it is still needed to improve on both precision and accuracy of the model for commercial sector.

Currently, Thailand has concerned to utilise the agricultural waste as energy resources essentially biomass. This alternative energy can help to manage waste materials and leftover product from harvesting or processing [8]. In order to prepare for the energy crisis that tends to increase from the continuous consumption fossil fuel, the studying, experimenting, and collecting data related to biomass are important both in the present and for future. Biomass includes agricultural waste, wood chips, wood wastes from the wood industries, animal waste, waste from agricultural processing plants, and waste from communities[9-13]. Moreover, the biomass from trees can be directly collected by cultivation in farms that mainly target plant for fast growing trees as *A.mangium* Willd [14].

The studying for prediction heating value is valuable in terms of reducing the collection time and getting the key property for combustion process. The success model then later can be either applied for on-line analysis for commercial sector or using as a measurement for fair trade of biomass. However, the determination of the heating value for one sample requires approximately 30 minutes of laboratory time and also the testing is a destructive process. Therefore, this research aimed to use the near infrared spectroscopy technique, which is rapid and non-destructive test, to create a prediction model for the heating value of *A.mangium* Willd instead of using the conventional measurement by bomb calorimeter.

2 Materials and methods

2.1 Material preparation

The 120 samples of *A.mangium* Willd were collected from Banna district, Chumphon province, Thailand with different 20 *A.mangium* Willd stems and each of them was separated in three parts (bottom, middle and top) and took each two samples from 60 logs. The number of samples was designed with the recommendation of Phil Williams guideline [4] for small sample set as 100-150 samples. Additionally, the rule of thumb of 40–50 sample's spectra will be a sufficient prediction model. The chopper machine (P5508 Patipong, Thailand) was firstly used for reducing size of the stems as wood chip. The hot air oven was used for drying the samples at 105°C, 24 hr. Then, the samples were put in room temperature for 24 hr to make them had equilibrium with the environment. Next, the sieve size of 4 mesh was used in order to get the particle size of sample approximately of 5 mm. The wood chipped samples for scanning with the spectrometer were put in the quartz cup to collect spectra. The pellet samples were used for heating value measurement by a bomb calorimeter.

2.2 Spectra acquisition and heating value measurements

The FT-NIR spectrometer (MPA, Bruker, Germany) was used for collecting the spectra by scanning in wavenumber range between 12,500-4,000 cm^{-1} at resolution of 8 cm^{-1} with 32 times scanning per one average spectrum. The heating value of all samples were measured with 2 replicates by using the bomb calorimeter (C200, IKA, Germany). The repeatability and reproducibility of both instruments were carried out. The repeatability of the spectrometer was done by scanning the same position of the random sample 10 times and evaluating for the same select 3 different wavenumbers of each sample while the reproducibility was carried out with the same procedure but for each measurement required to reload sample before getting the spectrum [2]. The repeatability of the spectrometer reveals the precision of the measurement while the reproducibility shows how high level of the

homogeneity of the particle size of samples. The repeatability of bomb calorimeter was done by measurement 2 replicates for 10 samples and determine the value of R^2_{max} by Eq.1[15].

$$R^2_{max} = \frac{SD^2_{total} - SD^2_{difference}}{SD^2_{total}} \quad (1)$$

Where R^2_{max} is the maximum coefficient of determination, SD^2_{total} is the standard deviation of measured values of all samples, $SD^2_{difference}$ is the standard deviation of the difference measured value between the same sample of all samples. The evaluation of reproducibility for the bomb calorimeter was done as the repeatability but the measurement was done by the unknow samples with the different user. The reproducibility of the bomb calorimeter shows the precision of the measurement whereas the reproducibility represents how the accuracy of the procedure for measuring the heating value.

2.3 Evaluation of the prediction model

The prediction model was created by the OPUS software version 7.0.129 (Bruker, Germany) with test set validation method using partial least squares regression (PLSR). The PLSR technique has been widely used for creating model which data set of predictor variables and set of response variable are highly correlated. It also showed the success modelling in many research implementing spectra with PLSR[16-19]. The experiment carried out with randomly selected data set of 70% for calibration set and the lest for validation set. The spectrum pretreatment process will be implemented to get the best model. The model performance was evaluated using statistical terms which were coefficient of determination (R^2), root mean square error of prediction (RMSEP), Bias and ratio of prediction to deviation (RPD) as shown in Eq.2, Eq.3, Eq.4 and Eq.5 respectively[4].

$$R^2 = 1 - \frac{\sum_1^m (Y_i - Y_{pre})^2}{\sum_1^m (Y_i - \bar{Y}_i)^2} \quad (2)$$

$$RMSEP = \sqrt{\frac{\sum_1^m (Y_i - Y_{pre})^2}{m}} \quad (3)$$

$$Bias = \frac{\sum_1^m (Y_i - Y_{pre})}{m} \quad (4)$$

$$RPD = \frac{SD_{validation}}{SEP} \quad (5)$$

Where Y_i is the reference value of the validation set, Y_{pre} is the prediction value, m is number of samples, $\overline{Y}_i$ is the average of the reference data of the validation set, Bias is the mean difference between the reference and prediction value to define the overall accuracy of the calibration model, $SD_{validation}$ is the standard deviation of the reference data of the validation set and SEP is the standard error of the prediction.

3 Results and discussion

3.1 Repeatability and reproducibility

The experiment of repeatability and reproducibility for the FT-NIR spectrometer and bomb calorimeter were shown in Table 1.

Table 1. Repeatability and reproducibility of FT-NIR spectrometer and bomb calorimeter.

Instrument	Repeatability	Reproducibility
FT-NIR	Avg. SD of absorbance = 0.0005	Avg. SD absorbance = 0.0219
Bomb calorimeter	SD total = 442.91 (J/g) SD difference= 147.78 (J/g) R^2_{max} = 0.89	SD total = 477.17 (J/g) SD difference = 158.34 (J/g) R^2_{max} = 0.89

The value 0.0005 of SD for the spectrometer was calculated as 0.08% error of the absorbance which showed high precision of the FT-NIR. Also, the value of 0.0219 SD for the reproducibility was equivalent to 4.08% error which showed the high level of the homogeneity of the particle size of the samples. Furthermore, high value of R^2_{max} of both repeatability and reproductivity of the bomb calorimeter revealed high precision of measurement and precision of the procedure respectively. It can be stated that both instruments have very high accuracy and precision of measurement. If there are some errors of the experiment, the analysis may be diagnostic on other factors not from the instruments.

3.2 Heating value and prediction model

The heating value of the *A.mangium* Willd of overall 120 samples which were collected 40 samples from each 3 parts of *A.mangium* Willd tree showed in Table 2.

Table 2. Heating value of *A.mangium* Willd.

Part	Average Heating value ± SD (J/g)
Bottom	19,308.28^{a}±168.68
Middle	19,234.96^{a}±139.11
Top	18,957.48^{b}±164.65

The overall heating value of the *A.mangium* Willd is approximately of 19 kJ/kg which is high potential for using in combustion process. The analysis with One-way ANOVA at 95% confident found that the heating value from the bottom and middle part were not significant different but at the top part showed significantly different. This caused from on the top part of the *A.mangium* Willd consists of more thick bark than wood and also the age of stem is younger. As a result, the amount of the lignin, which affected on heating value, was lower than other parts.

The spectra scanning from the FT-NIR in wavenumber range 12,500-4,000 cm^{-1} showed in the Fig1.

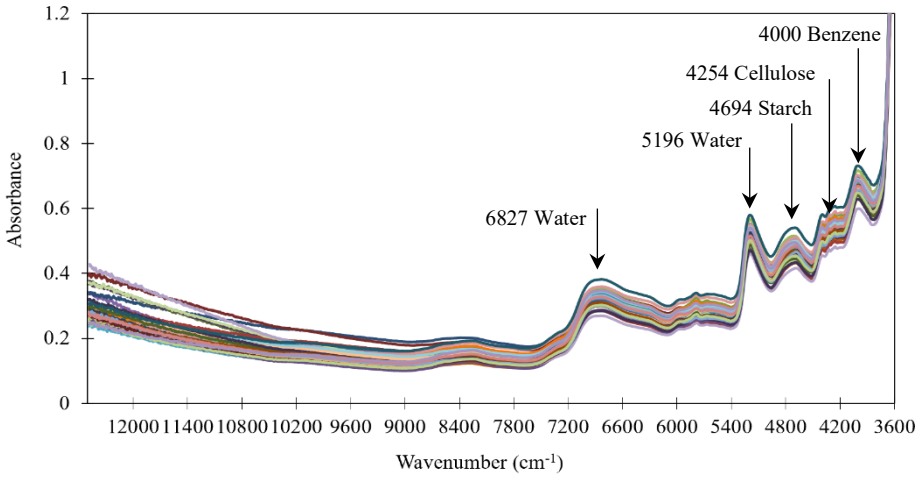

Fig. 1. The *A.mangium* Willd spectra of 120 samples.

The spectra of all samples showed the same trend and peaks. The important peak analysis found the different absorbance i.e. peak at 6827 cm^{-1} and 5196 cm^{-1} for water absorbance, at 4696 cm^{-1} for starch absorbance 4254 cm^{-1} for cellulose absorbance and at 4000 cm^{-1} for benzene absorbance[20]. The implement of statistical technique for spectra of all samples and the heating values with partial least squares regression can create the prediction model of *A.mangium* Willd as shown in Table 3. The calibration and validation plot were shown in Fig. 2 which provided the distribution on both data set comparing with the intercept line at 45 degree (dash line). The regression coefficient plot was shown in the Fig. 3 which revealed the important selected peak used in modelling. The 6 peaks were analysed as two of lignin, cellulose, starch, benzene and hemicellulose respectively.

Table 3. Results of partial least squares regression model for determination of heating value of *A.mangium* Willd.

Parameter	Pre-processing	Rank	Calibration			Validation			
			R^2	RMSEE*	RPD	R^2	RMSEP	RPD	Bias
Heating value (J/g)	First Derivative	6	73.1	219	1.93	71	246	1.87	33.7

RMSEE* is the root mean square error of estimation

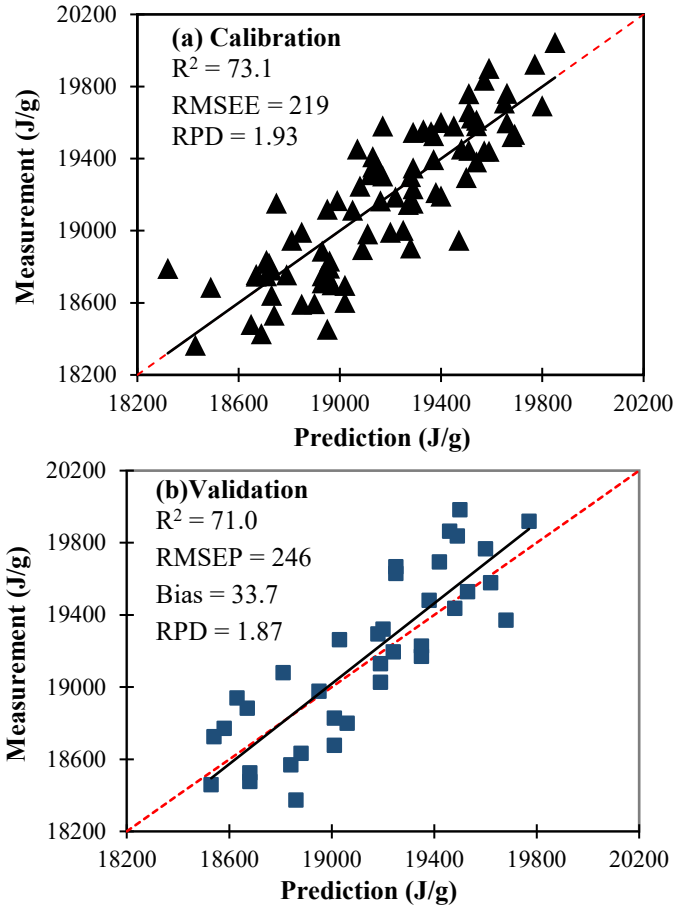

Fig. 2. The scattering plot of measurement vs prediction of (a) calibration set and (b) validation set.

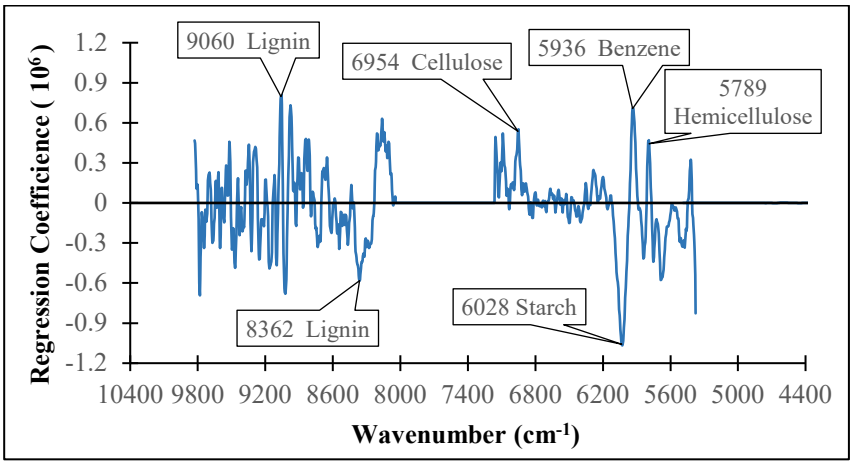

Fig. 3. The regression coefficient of the prediction model.

The selection of the best model had to compare with the highest R^2 and also combined with a smaller number of ranks. In terms of the number of ranks, if possible, should select the rank number not over than 6 with the highest R^2, but some cases it can be chosen with the higher rank than 6 depending on the considering of other important values as RMSEE, RPD and bias. The best model was created with the first derivative pre-processing of spectra using rank of 6 which was shown in Fig3. The R^2 of the calibration model was 73.1% and for the validation was 71%. The low value RMSEP of 246 (lower than 2% error) and bias of 33.7.These can be stated that the model can be used for the roughly group separating [4]. The RPD of 1.87 was not high enough to have accuracy prediction of heating value. Therefore, the model needs to be improved the RPD value which is normally recommended the value above 3 [4]. However, the result discovered the possibility to use this NIR technique for predicting the heating value of the *A.mangium* Willd. To improve the model, the greater number of samples need to be added to cover whole range the heating value data of the different *A.mangium* Willd trees. This consequently will lead to have a robust modelling.

4 Conclusions

The NIR technique showed the possibility to predict the heating value of the *A.mangium* Willd on the validation set with the R^2 of 71%, RMSEP of 246 J/g, RPD 1.87 and bias of 33.7 J/g. However, the more accuracy model is still needed to be improved by adding a greater number of samples. The success and robust model can reduce the time to measure the heating value from 20 minutes to less than 1 minute and also can be applied in commercial sector for the on-line process. Additionally, the model can be used to predict for the other plant species which are normally consist of same major compositions as cellulose, hemicellulose and lignin by adding their heating values and spectra into the database before creating a new model.

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