Gross calorific value estimation for milled maize cob biomass using near infrared spectroscopy

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Abstract. The maize cob biomass is one of important biomass crops in Thailand. Nowadays, the use of the biomass as renewable resource is increasing, especially residue agriculture waste. As we know that the biomass properties impact combustion, in order to achieve boiler efficiency, its energy characteristics of biomass was required immediately before burning. This work uses the FT-near infrared spectroscopy to estimate gross calorific value (GCV) of maize cob as the rapid method. Each sample was scanned using diffuse reflectance mode at a wavenumber range between 12500-3600 cm^{-1} . The scanning was done with a resolution of 8 cm^{-1} and completed 32 scans per sample, then averaged to be one spectrum. The results showed that this technique could decrease a processing time to 1-2 minutes per sample to determine GCV whereas alternatively the current method used a processing time of 25-30 minutes per sample. The capacity of the model gave root mean square error of cross validation (RMSECV) of 91.1 Jg^{-1} , which was low. Hence, the model was acceptable and could be used for screening.

1 Introduction

Maize cob is a waste from agricultural process after the seed is removed from the cob. Maize cob can then become a habitat of bird and rat and moreover, bad smell could happen as well. This is the important problem of traders. Previously, the maize cob was used as a fertilizer but it was not popular for farmer because it takes a long time for decomposition. Hence, it has been initiated to use the maize cob as a fuel.

Thailand has imported maize cob. It's a waste of agricultural product from one of the economic crops of Thailand as a biomass fuel. When the maize cob is burned, it has calorific value approximately 17,000 kJ/kg , and it takes a long time to burn before becoming the ash. This implies that it has a characteristic of good fuel.

The major aspect of waste residue properties to be renewable energy is the gross calorific value (GCV) which is also known as the higher heating value. GCV is total energy in biomass released during burning process, which takes into account the latent heat of vaporization of water in the combustion products. Normally, GCV can be measured by bomb calorimeter but this method takes a processing time about 25-30 minutes per sample for measuring and is subject to high cost of analysis.

Near infrared (NIR) spectroscopy is a non-destructive and rapid technique for estimating a quality of food and agricultural products. In addition, there have

been some reports that demonstrated the use of NIR spectroscopy for the evaluation of the GCV and other properties of biomass such as the evaluation of heating value of bamboo [1], the evaluation of moisture content and GCV of *Leucaena leucocephala* pellets [2], the prediction of GCV of *Miscanthus* [3], the GCV prediction of straw [4], the evaluation of moisture content and the GCV of oil-extracted residue of *Jatropha curcas* [9] and the analysis of GCV and elemental compositions of sorghum [10]. The results of their studies suggested that NIR spectroscopy had the potential to estimate the calorific value of biomass fuel. Hence, the objective of this research was to assess the potential of NIR spectroscopy to estimate GCV of milled maize cob biomass.

2 Materials and Methods

2.1 Sample

60 maize cob samples were collected from different area. The 60 samples were divided into two groups, 50 samples were used for utilizing calibration model and 10 samples were used as unknown sample for testing the calibration model. After harvest each sample from a plant, they were crushed into 5 cm and then dried to a constant weight by hot air oven (Memmert, model ULM 500, Germany) at 105 °C for 24 h, this process was

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preparing sample for easy milling in next process. Then, all sample were milled by milling machine (FRITSCH, 14.3000/10857, Germany) through a hole sizes of 2.00 mm and kept in an aluminium bag prior to the experiment. Next, each sample was measured the NIR absorbance using FT-NIR spectrometer and then some part of sample was measured the GCV by bomb calorimeter and other part was measured the moisture content for reference data by hot air oven at 105 °C, 24 h. The averaging moisture content of 60 samples were around 9.43% dry basis.

2.2 NIR spectral acquisition

Each milled maize cob sample was poured into a quartz bottom sample cup having dimension of 43 mm in diameter and 50 mm in height. For the reflectance mode, the thickness of sample was confirmed as infinity and must be ensured that there was no light leaked or transmitted through the sample. Fourier-transform infrared spectroscopy (FTNIR) (MPA, Bruker, Germany) was applied for scanning and absorbance was derived in $\log 1/R$ unit. Scanning conditions involved a resolution of 8 cm^{-1} , wavenumber range of 12500-3600 cm^{-1} , and the number of scanning of 32.

2.3 Reference data

After the milled maize cob samples had been scanned, the milled maize cob was sampled from the bottom of cup due to direct absorption by NIR radiation. About 0.5 g of sample was pelletized and the GCV was determined using a bomb calorimeter (C200, IKA, Germany) in isoperibol mode. The bomb calorimeter was calibrated by pelletized benzoic acid (IKA C 723, IKA, Germany).

After the GCV had been measured, the outliers were then checked by $((x_i - \bar{x})/SD) \geq \pm 3$, where x_i is the reference data of sample i . $\bar{x}$ and SD are the average and standard deviation of the reference data. If it was found, it was then rejected from the data set and was not used for modelling.

2.4 Data processing and NIR spectroscopy modelling

The NIR spectra and its corresponding reference data of GCV of fifty samples were used for modelling. The NIR models for predicting the GCV were constructed by PLS regression and validated by full cross validation. The spectral pre-treatment and modelling were carried on by OPUS software, version 7.0.129, Germany. Before the model development, the NIR spectra were pre-processed by constant offset elimination, straight line subtraction, vector normalization, min-max normalization, MSC (multiplicative scatter correction), first derivatives, second derivatives, the combination between first derivatives and straight line subtraction, the combination between first derivatives and vector normalization and the combination between first derivatives and MSC.

The effective model was obtained by lowest root mean squares error of cross validation (RMSECV), from

which the number of PLS factor, spectral pre-treatment technique, and wavenumber range were listed. After that, the regression coefficient versus optimal wavenumber range was plotted. After modelling, the external sample of ten were used for tested the PLS model.

The performance of the GCV predicting model was stated by determination of the coefficient of determination (R^2), bias, root mean square error of cross validation (RMSECV) and ratio of standard error of cross-validation to deviation (RPD).

3 Results and discussions

3.1 Ground maize cob spectra

The raw spectra of 60 milled maize cob biomass samples in a range of 12500-3600 cm^{-1} were illustrated in Fig. 1. In the raw spectra of milled maize cob sample, the main absorption bands were observed at 5820 (1718 nm), 5180 (1930nm), 4408 (2268 nm), and 4266 cm^{-1} (2344 nm), corresponding to C-H stretching first overtone of hydrocarbon [5], O-H stretching/HOH deformation combination of starch [6], O-H stretching C-O stretch combination of cellulose [6], and C-H methylene of hydrocarbon [5].

Fig. 1. The raw spectra of 60 milled maize cob biomass samples across the wavenumber of 12500 to 3600 cm^{-1}

3.2 Reference data of the GCV

Statistical data of calibration set, and external sample set for GCV of rice husk was demonstrated in Table 1 which shows the maximum, minimum, average, and standard deviation (SD). The maximum and minimum value of calibration set was higher and lower than external sample set, respectively, which covering the external sample. Then the calibration set can be representative sample for future prediction.

Table 1. Statistical values of gross calorific value data of maize cob milled samples used in model development.

	Calibration set	External sample
Max Jg^{-1}	17800.5	17431.0
Min (Jg^{-1})	17005.0	17253.0
Mean (Jg^{-1})	17405.0	17351.2
SD (Jg^{-1})	178.2	62.9

3.3 Near infrared spectroscopy models for GCV of milled maize cob sample

The effective calibration model was optimized using the wavenumber range of 5450.2-4246.7 cm^{-1} . The spectral pre-treatment of second derivative and the number of PLS factor listed from 1 to 3 was used. The PLS factor of optimal model was selected which gave the lowest RMSECV. Fig. 2a. displays the RMSEE versus PLS factor for calibration set whereas RMSECV versus PLS factor for validation set is shown in Fig. 2b. The PLS factor of three gave the lowest RMSECV which was then used for modelling.

Fig. 2. RMSEE/RMSECV vs rank (PLS factor) for calibration set, and validation set

The PLS model was tested using leave-one-out cross-validation providing R^2 , RMSEE, r^2 , RMSECV, RPD, and bias of 0.83, 75 Jg^{-1} , 0.73, 91 Jg^{-1} , 1.94, and 0.293 Jg^{-1} , respectively. Zornoza et al. [7] recommended that if R^2 and RPD are between 0.66 to 0.80 and 2.0 to 2.5, respectively, it permitted only approximate prediction and could be used with screening and some other “approximate” calibrations [8]. The R^2 and RPD provided were less than 0.66 and 2, respectively, which meant the A content was poorly predicted [8]. William [8] suggested that R^2 between 0.50 and 0.64 could be used for rough screening. The ratio of bias to its mean of measured value were 0.0165 % ($0.293 \text{ Jg}^{-1} \div 17405.0 \text{ Jg}^{-1}$) for GCV, which was very small. So that, we recommended that the models were suitable for estimation of the GCV of milled maize cob sample.

R^2 stated the percentage of proportion of the variance in GCV that can be explained by variance in absorption value [26]. For example, if R^2 was 0.90, means that 90% of variance in GCV was explained by variance in NIR spectra and 10% cannot be counted by NIR spectra (unexplained variance). Bias mentions the overall accuracy of the GCV model [26]. The low value of RPD means the measured value is not robust. If the model had a high RMSECV, then that modelling should need an increasing number of the sample set or sometimes it is seen that not necessary to develop model [26].

Fig. 3a and b illustrated comparison of the GCV of maize cob milled sample predicted by near infrared spectroscopy and measured by the bomb calorimeter of the calibration model and the validation model. The regression coefficient of GCV was shown in Fig. 4. Shown in Fig.5 was first derivative spectra of maize cob milled sample used for model development. The obvious peaks occurring on regression coefficient plot and second derivative spectra were at 5801 cm^{-1} (1723 nm), 4412 cm^{-1} (2266 nm), and 4293 cm^{-1} (2329 nm), related to C-H methylene (CH_2) of hydrocarbons, O-H stretching/C-O stretching combination of cellulose, and C-H stretching/ CH_2 deformation combination of starch [6].

As reported by Posom and Sirisomboon [9], the band of cellulose and fiber had high impact to the forecast of the HV of the oil extracted residue of *Jatropha curcas* kernels. In addition, Zhang et al. [10] also reported that the important band for estimating HHV of sorghum was the C-H stretching and CH_3 structure.

To confirm whether calibration model can estimate the GCV of future sample, the 10 external samples were tested using calibration model, from which the outcome was shown in Table 2. The performance test had a low RMSEP and bias with 77.3 Jg^{-1} and -13.7 Jg^{-1} , respectively.

Fig. 3. Comparison of the gross calorific of maize cob milled sample predicted by near infrared spectroscopy and measured by the reference laboratory of the calibration model and the validation model.

Fig. 4. PLS model regression coefficient plot for the gross calorific of maize cob milled sample.

Fig. 5. First derivative spectra of maize cob milled sample used for model development.

Table 2. Measured value and predicted value of external sample predicted by calibration model

Sample	TRUE (Jg ⁻¹)	Prediction (Jg ⁻¹)
51	17431.0	17375
52	17305.5	17430
53	17404.0	17387
54	17327.5	17242
55	17387.5	17388
56	17348.5	17403
57	17368.0	17438
58	17422.0	17522
59	17253.0	17141
60	17264.5	17322
RMSEP (Jg ⁻¹)	77.3	
Bias (Jg ⁻¹)	-13.7	

4 Conclusions

The outcome showed that there is quite a possibility to the use of NIR spectroscopy as a rapid technique for classifying maize cob properties with a fair performance. Moreover, the time per sample can be reduced to 2-3 minutes where the current analysis took approximately 25-30 minutes per sample. For robustness, the model was tested by external sample (unknown sample) to confirm its ability again because it is the representative population for future. For model development, the vibrational band of hydrocarbons, cellulose, and starch strongly had an impact to the prediction of GCV. In the further study for improvement of the calibration model performance, the mode development should be done by collecting maize cob from various sources to get wider range of GCV, that way the calibration model may be a robust and global model.

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