Near infrared spectra features of cocoa pod husk used for feedstuff

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Abstract. This presented study aimed to study the near infrared spectroscopic features of cocoa pod husk samples used as raw materials for animal feedstuff. Spectral data of organic material samples contains chemical properties information that can be revealed through modelling. Thus, the study of this features is essential to assess and reveal buried respective information. Cocoa pod husk samples were obtained from several districts in Aceh Province, grinded and prepared as bulk samples. Diffuse reflectance spectral data for a total of 30 bulk cocoa pod husk samples were acquired and recorded in wavelength range from 1000 to 2500 nm. Spectral data were firstly projected onto principal component analysis to observe similarities among samples. Spectra correction, namely mean normalization was employed to enhance spectra features. The results showed that several chemical information related to cocoa properties can be revealed such as dry matter, crude protein, crude fibre, ether extract, nitrogen-free extract and ash content due to the second and third overtones of combination bands O-H, C=O-H and N-H. Optimum wavelength for estimating cocoa pod husk attributes are in 1217, 1405-1474 nm, 1629 nm, 1906-1979 nm, and 2283 nm. Based on obtained study, it may conclude that several quality attributes of animal feed samples further can be determined by means of near infrared spectroscopy approach.

1. Introduction

Agricultural activities, like harvesting, post-harvest handling and processing may lead to agricultural waste or residues. Cocoa pod husk is one of the agricultural residues found in cocoa plantations with the amount 67% as waste by products, whereas 33% constitutes as cocoa bean from a total of cocoa fruit weights [1,2]. In other words, if ten tons of wet cocoa pod husk are obtained from a ton of dry cocoa beans, thus, causing a big matter of disposal problem and an un-exploited resources. Moreover, they allow environmental pollution and host pests [3,4]. Cocoa pod husk contains high energy but low in protein contents when they lie as they state without further processing. Therefore, farmers need to find a way to dispose these agricultural residues, among others as animal feedstuff [5].

The utilization cocoa pod husk as animal feed has been investigated mainly for ruminant animal rather than for monogastric ones [6]. Indonesia is known as agricultural country with abundant agricultural waste resulted from agricultural activities [7,8]. The cocoa pod is defined as a natural
laminated raw material consisting of three distinctly different layers namely epicarp, mesocarp and endocarp [9,10]. The endocarp is a layer with soft and whitish tissue used to protect the delicate cocoa beans in a well lubricated inner chamber; while mesocarp represents a hard composite structure which can be able to maintain the cocoa beans in its states even under high impact or outermost relatively soft layer is the yellow cover that is directly exposed to sunshine, after which it turns black indicating rot due to degradation [11].

Cocoa pod husk vary in color from green to red depends on its maturity stages. The cocoa pod color is a reflection of the exocarp or the outer layer fruit tissue around 1-3 mm of pods harvested 18 weeks after pollination. The three layers of cocoa pod husk have been analyzed for their chemical composition and compared to the whole waste product when incorporated as feed component. They contributed almost 67% of the whole cocoa fruit by weight [3,12]. Cocoa pod husk has been extensively investigated as poultry or livestock feed because of its protein content around 5.9 to 9.1%, fiber content approximately 22.6 to 35.7%, crude fat with the amount of 1.2 to 10% and mineral contents [13,14].

To determine several chemical compositions of the cocoa pod husk or other agricultural residues products, standard laboratory procedures were employed. However, most of these procedures are time consuming, required complicated sample preparations, involved chemical materials and may cause other environmental pollutions [15]. Therefore, an alternative fast, pollution free and non-invasive approach is needed to analyze the chemical properties of those materials. Among others is near infrared spectroscopy or NIRS. This method has been widely applied since the first development to determine chemical properties of foods and agricultural products [16–18]. The advantage of the NIRS is rapid, require only 10 seconds to analyze several chemical constituents simultaneously, with no or minimum sample preparation and without involving additional chemical materials [15,19].

In order to be optimally utilized, the spectra properties of studied raw materials need to be revealed like stretching, bending and overtone bands of the reflected spectrum in the near infrared region which mainly from 1000 to 2500 nm. Therefore, the main aim of this present study is to study the near infrared spectroscopic features of cocoa pod husk samples used as raw materials for animal feedstuff.

2. Materials and methods

2.1. Cocoa pod husk samples
A total of 30 bulk cocoa pod husk samples from different cocoa plantations in Aceh Province were used as studied samples. They were sun-dried to reduce the theobromine content and then grounded using a Hammer-mill.

2.2. Spectra acquisition of cocoa pod husk
Spectral data in form of absorbance or diffuse reflectance spectrum were acquired and recorded in wavelength range from 1000 to 2500 nm with 4x optical gain and co-added of 64 number of scans [20,21].

2.3. Spectra transformation
In order to reveal more detailed spectra features, the spectra data were transformed onto three spectra form namely spectra smoothing, baseline shift correction and mean normalization.

2.4. Data analysis
Obtained spectra data were analyzed by means of principal component analysis (PCA) to explore similarities among spectra samples of 30 cocoa pod husk. Moreover, spectral data were also projected on Hotelling t² ellipse to detect sample outliers among data. Besides the PCA score plot, explained variance of the PCA result was also being investigated to observe future projection data. Moreover, loading plot was also taken into account to reveal most optimum and relevant wavelength of NIR for chemical composition prediction of cocoa pod husk samples.
3. Results and discussion

The spectra feature of raw cocoa pod husk samples in near infrared region is presented in Figure 1. It corresponds to specific wavebands in the NIR region related to chemical and physical information of the studied samples. The cocoa pod husk spectrum absorption according to the combination of vibrations involving C-H, O-H and N-H which is a chemical structure. Concentrations such as water, protein, fat, and carbohydrates can in principle be determined using these spectral data and spectra derivatives as shown in Figure 2.

![Figure 1](image1.png)

**Figure 1.** Typical spectral data of cocoa pod husk samples in NIR region from 1000 to 2500 nm.

![Figure 2](image2.png)

**Figure 2.** Derivate spectral data of cocoa pod husk samples in NIR region

Whole cocoa pod husk is highly correlated with the temperature used in the cocoa bean fermentation process. The NH3 formed during fermentation also depends on the geographical origin of the cocoa...
bean. In determining the total level of NH3 can use the NIRS instrument. The performance of this method is very efficient, non-destructive and easy to use. NIRS is also able to predict the level of cocoa fermentation by detecting NH3 levels. Chocolate-based food producers can use NIRS to measure the NH3 content of dry cocoa samples based on the quality of their cocoa bean drying container, while cocoa farmers can use NIRS to monitor the fermentation temperature of cocoa beans. Projected spectra data onto principal component analysis is presented in Figure 3.

\[ \text{Figure 3. Score plot of the PCA for cocoa pod husk raw spectra data.} \]

The explained variance of the first 2 principal components accumulated a total of 98% with the PC1 95% and PC2 3% respectively. A total of 100% explained variance data of the raw spectrum can be observed when data is projected onto 3D score plot as shown in Figure 4.

\[ \text{Figure 4. A 3D score plot of the PCA for cocoa pod husk raw spectra data.} \]

A simple and quantitative model is being developed and validated based on color measurements from digital images and using artificial neural tools to predict the total free amino acids in the fermented cocoa bean fermentation index. The analytical test developed includes RGB (red, green and blue) color values
on the cocoa pod husk (CPH). This can apply to food producers and to actors who control the quality and quantity of the level of fermentation of processed cocoa beans. The final result of the research is expected that image acquisition processing and analysis can be further developed and used for the implementation of analytical tools as applications on mobile phone devices. The total explained plot and loading plot for future prediction of chemical composition of cocoa pod husk samples are presented in Figure 5 and Figure 6 respectively.

![Total explained variance plot of the PCA for future projection of CPH spectra data](image1)

**Figure 5.** Total explained variance plot of the PCA for future projection of CPH spectra data

![Loading plot of the PCA for chemical properties determination](image2)

**Figure 6.** Loading plot of the PCA for chemical properties determination

The NIR spectral data involve the response of O-H, C-H, C-O and N-H molecular bonds. The bond refers to the change in vibrational energy when irradiated by NIR frequency, there are two vibration patterns in this bond, namely strain vibration and bending vibration. Energy absorption of organic molecules in the NIR region occurs when the molecules vibrate which is translated into an absorption spectrum in the near infrared spectroscopy. Based on loading plot, the predicted optimum wavelength for estimating cocoa pod husk attributes are in 1217, 1405-1474 nm, 1629 nm, 1906-1979 nm, and 2283 nm. The basic characteristic wavelengths in the NIR region range are 2310 nm for energy as reference, 2230 nm for ash contents, 2180 nm for protein, 2100 nm for carbohydrates, 1940 for moisture content, and 1680 nm for minerals contents.
4. Conclusions

The presented study aimed to study the near infrared spectroscopic features of cocoa pod husk samples used as raw materials for animal feedstuff. Spectral data were projected onto principal component analysis to observe similarities among samples. The results showed that several chemical information related to cocoa properties can be revealed such as dry matter, crude protein, crude fibre, ether extract, nitrogen-free extract and ash content due to the second and third overtones of combination bands O-H, C-O-H and N-H. Optimum wavelength for estimating cocoa pod husk attributes are in 1217, 1405-1474 nm, 1629 nm, 1906-1979 nm, and 2283 nm. Based on obtained study, it may conclude that several quality attributes of animal feed samples further can be determined by means of near infrared spectroscopy approach.

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