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Free Fatty Acid Assessment of Crude Palm Oil Using a Non-Destructive Approach

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***Abstract*—**Near infrared (NIR) spectroscopy has always been of great interest in the food and agriculture industries. The development of prediction models has facilitated the estimation process in recent years. In this study, 110 crude palm oil (CPO) samples were used to build a free fatty acid (FFA) prediction model. 60% of the collected data were used for training purposes and the remaining 40% used for testing. The visible peaks on the NIR spectrum were at 1725 nm and 1760 nm, indicating the existence of the first overtone of C-H bands. Principal component regression (PCR) was applied to the data in order to build this mathematical prediction model. The optimal number of principal components was 10. The results showed R^2=0.7147 for the training set and R^2=0.6404 for the testing set.

***Keywords*—**Palm oil, fatty acid, NIRS, regression.

I. Introduction

NEAR infrared (NIR) spectroscopy is a well-known technique in agriculture and food engineering. In the mid-1960s, the United States Department of Agriculture (USDA) developed NIR methods assess the internal qualities of apple crops. NIR is a popular method of rapid, non-destructive analyses, especially across in agriculture and food industries [1]. Additionally, this technology has been used to predict the maturity level and sugar content of fruit [2]. The application of NIR in the palm oil industry has been reported in several publications in recent years [3], [4].

The oil palm industry is a very vital industry which contributes tremendously towards the Malaysia's economy. Recently, up until May 2014, Malaysia had produced more than 7milllion tonnes of crude palm oil (CPO) as reported in Malaysia Palm Oil Board (MPOB) website. This amount is about 1million tonnes increased from 2013. In a near future, Malaysia aimed to produce 26-35 tonnes per hectare from the current production of 20.2 tonnes per hectare.

The rapid growth in palm oil production is absolutely a very good thing for our country. Malaysian production of CPO and any other oil palm products based is well known all over the world. In fact, Malaysia is the second world exporter after Indonesia.

Two main oil yields from palm oil fruit are extracted from the mesocarp: CPO and palm kernel oil (PKO). These oils have different characteristic and properties [5]. The properties of CPO make it suitable for food products (e.g. margarine, cooking oil), while PKO is used for non-food products (e.g. cosmetics). In food products, product quality is crucial, more so than with non-food products. In CPO, there is a very high level of β-carotene, which an important source of vitamin A. This substance is very good at preventing exophthalmia, which can cause blindness [6]. Thus, CPO was investigated in this study. Generally, the mean free fatty acid (FFA) composition in standard CPO is 4.3% and ranges between 3.7% to 5.1%;18:0 C-H is the most common chain length [7], [8].

Commonly, the quality of CPO can be measured by five parameters, i.e. the FFA content, the deterioration of bleach ability index (DOBI), the iodine value (IV), the moisture level and the carotene content. Among these parameters, FFA content is the most important as it influences consumer decisions and trading of the commodity [9]. Conventionally, FFA analysis is performed using a wet chemical test employing neutralization of FFA in a standard alkali. However, this test is highly dependent on expertise and is quite time-consuming. Hence, the development of a rapid but reliable technique for FFA determination is needed in order to match the growth of CPO production mentioned earlier. Therefore, this study aimed to develop a novel technique for CPO assessment while the objective of this paper was to develop a reliable system to predict the FFA value from the NIR data from CPO using the principal component regression technique.

II. Materials and Methods

A. Sample Preparation

The experiment took place at Felda Johore Bulkers-Terminal 1, Pasir Gudang, Johor (Malaysia) from 1st December 2012 to 7th December 2012. In total, 110 random samples of CPO were collected in this time period. Sample collection occurred between 9:00 am and approximately 4:30 pm, depending on the arrival of oil tankers. These oil samples originated from various FELDA palm oil mills throughout southern and eastern regions of Malaysia, including Jengka and Keratong in Pahang, Serting in Negeri Sembilan, and Kota Gelanggi and Penggeli in Johor.

B. Free Fatty Acid (FFA) Measurement

The manual procedure to determine the acidity of CPO was conducted based on the Malaysian Standard for Laboratory, MS 817:1989 (Methods of Test for Palm Oil & Palm Oil

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Products). First, as the sample was semi-solid at normal room temperature, it was placed in a water bath and allowed to melt at 60°C to 70°C. Next, 5 g from the sample was weighed in an Erlenmeyer flask. After that, 50 ml of neutralized Isopropanol were added. The flask then placed on a hot plate at 40°C for 3 to 5 min until the solvent reached a temperature of about 40°C in. The sample was then shaken gently while titrating with sodium hydroxide (NaOH) until the first permanent pink color could be seen for 30 seconds. This should take to 2 to 3 minutes. All the measurements of weight and volume were recorded. In order to obtain the FFA value, these recorded measurements were used in the calculation using the following equation:

$$FFA\% = \frac{25.6 \times N \times V}{W} \quad (1)$$

where *25.6* is the weight of palmitic acid (palm oil and fractions), *N* is the normality of NaOH, *V* is the volume (ml), of NaOH used, and *W* is the weight, (g), of the test portion.

In this standard technique, the acid value is defined as the amount (in mg) of sodium hydroxide (NaOH) necessary to neutralize the free acids in 1 g of sample. In other words, the FFA value is expressed as the number of mg NaOH needed to change 1 g of palmitic acid (FFA) into a neutral substance [3]. For an FFA content below 0.15%, FFA is expressed to three decimal places, while for an FFA content above 0.15%, two decimal places are used. The entire process was performed by qualified laboratory personnel.

C. Near Infrared Spectroscopy

The Near Infrared Spectrsocopy instrument used for this work was the FOSS Microsystem run by Vision Software. The 0.5nm interval wavelengths were measured from the range of 400 nm to 2500 nm in absorbance form. The entire spectrum consisted of 4,201 data points.

D. Pre-Processing

In the present work, the wavelengths used for determining the FFA content were taken from 1600 nm to 1900 nm and consisted of 601 data points.

E. Pre-Processing

After pre-processing the raw spectrum, samples were divided into two sets, namely the training set for calibration and the testing set for validation. For each sample, the FFA values from chemical analysis were noted. A 60% - 40% division yielded 66 samples for calibration and 44 samples for validation. Samples for calibration were used to generate the model while the samples for validation were to verify the reliability of the model. Both paired training and testing datasets were loaded into the MATLAB workspace (version 7.14.0.739 R2012a). The details of the FFA data were simplified, as shown in Table I. In the present work, the wavelengths used for determining the FFA content were taken from 1600 nm to 1900 nm and consisted of 601 data points.

Fig. 1 describes the whole procedure to create the prediction model using NIR spectral data associate with PCR method.

TABLE I
FFA DATA DISTRIBUTION

Data Set	No. of sample	Mean	Range	SD
Calibration	66	4.23	3.16 – 5.26	0.5718
Validation	44	4.27	3.20 – 5.12	0.5498

SD – Standard Deviation

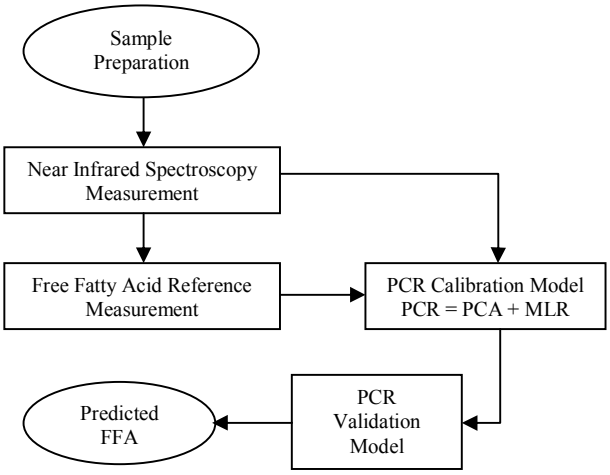

Fig. 1 Summary of the procedures to build PCR Prediction Model

III. RESULTS AND DISCUSSION

This section will present the finding of this work. Fig. 2 shows the 110 raw overlaid spectra of CPO from 1600 nm to 1900 nm.

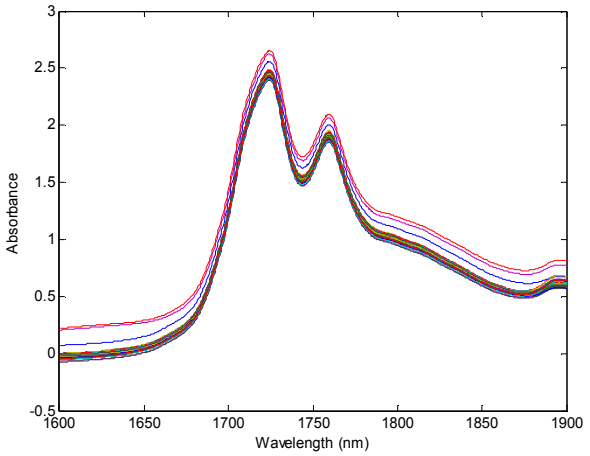

Fig. 2 Raw absorbance spectrums for 110 samples

Two significant peaks were found at 1725 nm and 1760 nm. Based on previous reports, the peaks at 1720 nm and 1760 nm represent the first overtone of the C-H stretching band [10]. The same peak can be found in most agriculture products such as grains, sesame seeds, sunflower seeds, wheat, barley and oats [11]. As in palm oil, all these products contain water, protein, oil, fiber, minerals and carbohydrates.

The related bands associated with these elements are overtones and combinations of the C-H [12], N-H [13], O-H [14] and C=O bands [15]. On the other hand, it has been

reported that the bands at 1725–1730 nm and 1755–1765 nm represent asymmetric methylene C-H stretching [16].

The Savitzky-Golay first order filter design was applied to the data before proceeding with the analysis. The length of data frames was set to 15. This filter was used to obtain a smoother spectrum, as shown in Fig. 3.

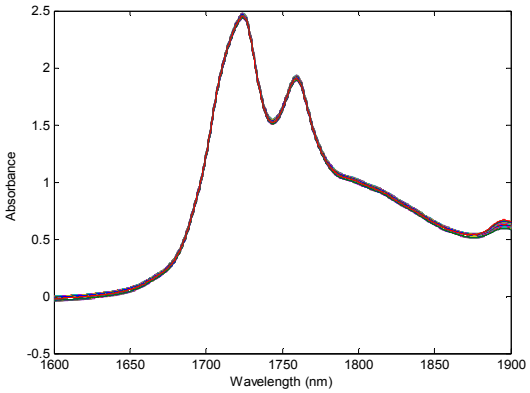

Fig. 3 Smoothed absorbance spectrums for 110 samples

Determination of the optimal principal component number was done by observing the performance of the PCR model. The chosen number of PCs must have a root mean square error of calibration (RMSEC) and root mean square error of prediction (RMSEP) with the smallest difference. The root mean square error (RMSE) of the PCR model against the number of principal components (PCs) is shown in Fig. 4.

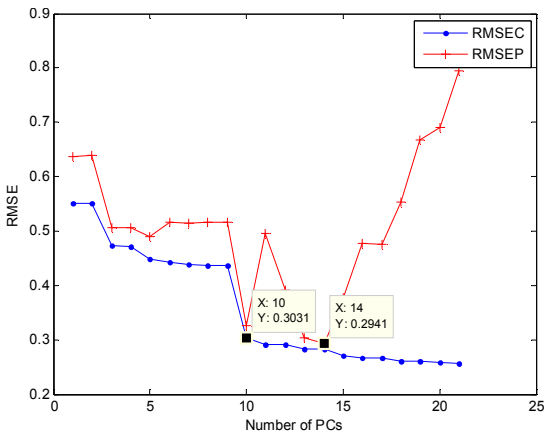

Fig. 4 Performance plot of PCR Model

From the observations, it was found that both RMSEC and RMSEP decreased when the PC number increased. RMSE considerably diverges when the PC number was set to 15 and above, leaving a choice in PC number of either 10 or 14 PCs. Since there was no significant improvement with the additional four PCs, the chosen PC number was 10.

The beta values from this were: β1 = -0.1581, β2 = -0.0031, β3 = 2.3340, β4 = -0.2325, β5 = 5.3119, β6 = -4.3818, β7 = -3.7509, β8 = 3.5002, β9 = 1.1922, β10 = -75.6119. Figs. 5 and 6 show the scatter data points for training set and the testing set, with R^2=0.7147 and R^2=0.6404, respectively.

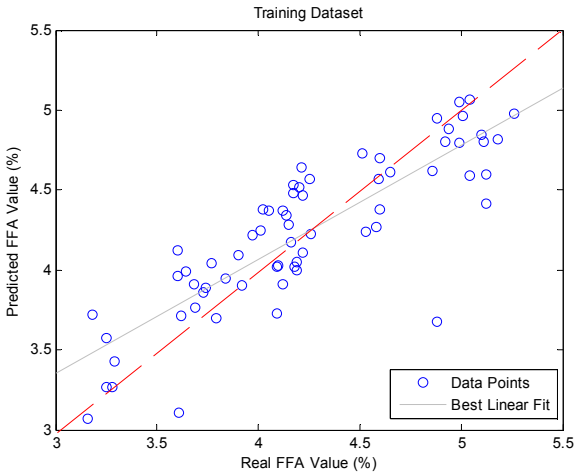

Fig. 5 Scatter plot for training data, R^2 = 0.7147

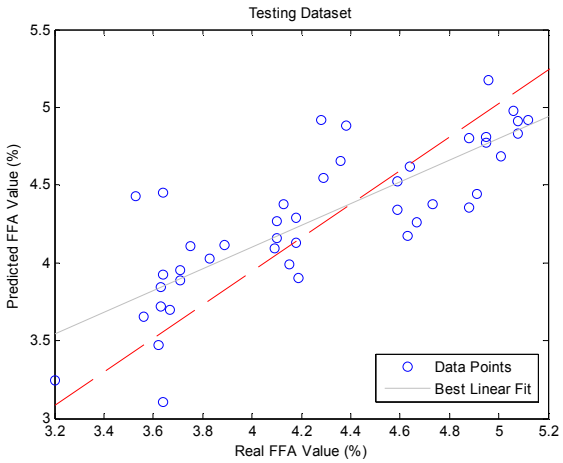

Fig. 6 Scatter plot for testing data, R^2 = 0.6404

IV. Conclusion

The findings of the present study indicate that the wavelength of NIR at 1600 nm to 1900 nm did not provide a great deal of unique relevant information for the assessment of FFA in palm oil. This result means that the model is 64.04% reliable for predicting the FFA value for an unknown spectrum, which is moderate performance. Prediction performance may require improvement by using a more robust model, for example, a back-propagation artificial neural network. In future work, a wider range of NIR spectral data may also be used to obtain more information on the FFA content in palm oil.

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REFERENCES

[1] K. Brodersen, "Exploration of the Use of NIR Reflectance Spectroscopy to Distinguish and Measure Attributes of Conditioned and Cooked Shrimp (Pandalus borealis)," *Technol*, vol. 34, pp. 533-541. 2001.

[2] K.S. Chia andH. Abdul Rahim, "Neural Network and principal component regression in non-destructive soluble solids content assessment : a comparison," *Biomed & Biotechnol*, vol. 13, pp. 145-151. 2012.

[3] Y.B. Che Man and M.H. Moh , " Determination of Free Fatty Acids in Palm Oil by Near-Infrared Reflectance Spectroscopy," *Journal of the America Oil Chemists' Society (JAOCS*), vol. 75. pp. 557 – 562. 1998.

[4] O.M.B. Saeed, S. Sankaran, A.R. Mohamed Shariff, H.Z. Mohd Shafri, R. Ehsani, M. Salem Alfatni and M.H. Mohd Hazir, "Classification of oil palm fresh fruit bunches based on their maturity using portable four-band sensor system," *Computers and Electronics in Agriculture*, vol. 82, pp. 55-60.2012.

[5] Q. Yuan, W. Hanselmann and R.C. Anantheswaran, "Moisture and sucrose transfer in fractionated palm kernel (PKO) based films immersed in liquid solutions" *Journal of Food and Engineering*, vol. 108, pp. 13-21, 2012.

[6] T. Atinmo, "Palm Fruit in Traditional African Food Culture," *Asia Pasific J Clin Nutr*, vol. 12, pp. 350-354. 2003.

[7] K. Sundram, R. Sambanthamurthi and Y.-A. Tan, "Palm fruit chemistry and nutrition," *Asia Pacific J Clin Nutr*, vol. 12 , pp. 355-356. 2003.

[8] S. Kanagaratnam, M. Enamul Hoque, M. Mat Sahri and A. Spowage, "Investigating the effect of deforming temperature on the oil-binding capacity of palm oil based shortening," *Journal of Food Engineering*, vol. 118, pp. 90-99. 2013.

[9] M. Makky andP. Soni, "In situ quality assessment of intact oil palm fresh fruit bunches using rapid portable non-contact and non-destructive approach,"*Journal of Food Engineering*, vol. 120, pp. 248-259. 2014.

[10] F. Westad, A. Schmidt, and M. Kermit, "Incorporating chemical band-assignment in near infrared spectroscopy regression models,"*Journal of Near Infrared Spectroscopy,* vol. 16, pp. 265-273. 2008.

[11] J. GordonBell*et. al* "Substituting fish oil with crude palm oil in the diet of Atlantic salmon (Salmo salar) affects muscle fatty acid composition and hepatic fatty acid metabolism,"*The Journal of nutrition,* vol. 132, pp. 222-230. 2002.

[12] A. Garrido-Varo*et. al*, "Near infrared spectroscopy for enforcement of European legislation concerning the use of animal by-products in animal feeds," *Biotechnol. Agron. Soc. Environ*., vol. 9, pp. 3-9.2005.

[13] B. Stuart, "Infrared Spectroscopy: Fundamentals and Applications," *John Wiley & Sons*., 2004

[14] J. Stuth, A. Jama, D. Tolleson,"Direct and indirect means of predicting forage quality through near infrared reflectance spectroscopy," *Field Crops Research,*vol. 84, pp. 45-56. 2003.

[15] M. Oubaha, P. Etienne and S. Calas, "Derived Organic and Inorganic Hybrid Materials for Photonic Applications: Contribution to the Correlation Between the Material Structure and the Transmission in the Near Infrared Region," *Journal of Sol-Gel Science and Technology*, vol. 33, pp. 241-248. 2005.

[16] A.A. El-Rahman and H.A.A. Badawy, "Ultraviolet, Visible and Infrared Wavelengths for Determination of Palm Oil Quality,"*New Trends in Agricultural Engineering*, pp. 777-793. 2006.