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DETERMINATION OF PALM OIL RESIDUE IN PALM KERNEL AND PALM OIL METHYL ESTERS USING NEAR INFRARED SPECTROSCOPY

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ABSTRACT

An analytical method by near infrared spectroscopy using a partial least square regression was developed for the determination of palm oil residue in palm kernel methyl esters (Model 1) and palm oil methyl esters (Model 2). The wavelength region selected for modeling was between 4500 and 10 000 cm^{-1}*. For Model 1, the calibration plot had a coefficient correlation (*R^2*) of 0.9996 and a standard error of calibration (SEC) of 0.06. Validation of the Model 1 calibration produced a plot with *R^2* of 0.9962 and a standard error of prediction (SEP) of 0.176. The Model 2 calibration plot had *R^2* of 0.9986 and SEC of 0.108. Validation of Model 2 produced a plot with *R^2* of 0.9978 and SEP of 0.128. Both models exhibited good linearity with low standard errors. The differences between the predicted and actual percentages of oil residue were minor. This method was able to predict oil residue contamination ranging from 1% to 10% in the two types of palm-based methyl esters.*

Keywords: palm oil residue, palm kernel oil methyl esters, palm oil methyl esters, near infrared spectroscopy, partial least square regression.

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INTRODUCTION

Palm oil methyl esters derived from palm oil and palm kernel oil are alternatives to fatty acids as intermediate materials for the production of a variety of oleochemicals, *e.g.* palm methyl ester sulphonates (Maurad *et al*., 2006), and in fatty alcohol manufacture. Palm-based methyl esters are also used as biodiesel (Ma *et al*., 1993). Currently in Malaysia, palm biodiesel is being produced commercially and exported overseas. In 2009, 1.03 million tonnes of oleochemicals with a value of RM 3037.2 million were exported. Palm-based methyl esters accounted for 11% of the total exports of oleochemicals.

The most commercially viable process for the manufacture of methyl esters is by the transesterification of vegetable oils with methanol catalysed by sodium hydroxide, a suitable basic catalyst. If the transesterification process is incomplete, there will be residual oil left in the methyl esters produced.

Purity of the methyl ester is a very important criterion because it may affect the conversion of the methyl ester to oleochemical derivatives, or its performance as biofuel. The European Standard, EN 14214, for biodiesel specification requires biodiesel oil to be below 0.2% in mass. The residual oil should be monitored and removed to ensure a high quality grade of methyl esters.

The analysis of methyl esters for trace contaminants, *e.g.* mono-, di- ,triacylglycerols, methanol and glycerol, using gas chromatography has been reported (Mariani *et al*., 1991; Mittelbach, 1993; Mittelbach *et al*., 1996). Currently, the method for detecting oil in methyl esters is based on the international biodiesel testing method (EN 14105) using gas chromatography with internal calibration. However, this technique is tedious and time-consuming. The increasing concern over the use of large volumes of solvents and reagents in quality control laboratories has prompted the industry to explore the application of instrument-based

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methods which are usually rapid, efficient and accurate (Steiner, 1993). A possible solution to what is required by the industry may be in using near infrared (NIR) spectroscopy, because of its many viable features which include accuracy, robustness, fast analyses time, operational ease, non-destructive to the samples, and virtually dispensing with the use of solvents. NIR spectroscopy is also currently adopted to replace chemical methods in sample analysis in the biodiesel field.

The NIR technique using a fibre optic probe has been applied in monitoring transesterification, assessing biodiesel quality, and also in determining the blend level of mixtures of biodiesel with conventional fuel (Knothe, 1999). This study intends to use NIR spectroscopy to monitor trace oil in methyl esters, at concentrations above those specified in biodiesel standards. This method measures any unreacted feedstock oil residue as well as detects the occurrence of intentional adulteration of palm oil methyl esters.

MATERIALS AND METHODS

Materials

Crude palm kernel oil and crude palm oil were obtained from local refineries. Palm kernel and palm oil methyl esters were obtained from a local oleochemical company.

Preparation of Calibration Standards

The samples of palm oil, palm kernel oil, palm kernel oil methyl esters (PKOME) and palm oil methyl esters (POME) were homogenised by heating in an oven at 60°C. Calibration standard samples in four replications were derived by spiking the methyl esters with ratios of neat oil (w/w), varying from 1% to 10%. The number of calibration standards for the calibration models, namely, % oil in PKOME (Model 1) and % oil in POME (Model 2), were 20 and 16, respectively. The samples were shaken vigorously on an Autovortex mixer to ensure complete homogenisation.

Instrumentation

Near infrared spectroscopy, sample handling and spectra collection. Fourier Transform-NIR spectroscopy was performed on the samples using a Bomem MB160 spectrometer with a deuterated triglycine sulphate (DTGS) detector, covering a range of wavelengths from 2000 to 15 000 cm^{-1}. The spectrometer was controlled by a Dell PC equipped with a Windows-based Bomem-Grams/32 software. Galactic Industries Corporation software packages were used, such as AIRS for quality control assurance and discriminate analysis, and PLS plus/IQ for statistical analysis of data and to build calibration models.

The samples were transferred into disposable glass vials (1-ml volume) with a 7 mm outer diameter (o.d.). The vials were placed into the NIR spectrometer's temperature-controlled multi-sampling compartment, and temperature was controlled at 70°C ± 0.2 to ensure that the samples were in liquid form. The spectra of the background and of the samples were acquired over the 4500-10 000 cm^{-1} wavelength range, co-adding the spectra at 128 scans, at a resolution of 16 cm^{-1} to increase the signal-to-noise ratio of the spectra. The co-added spectra were then ratioed and changed into absorbance spectra. The partial least square (PLS) models were validated by the leave-one-out cross-validation procedure or by using external validation. The external validation data sets further evaluated the performance of the models, which was reflected by the standard error of prediction.

RESULTS AND DISCUSSION

Figure 1 shows the overlay spectra of palm kernel methyl esters (PKOME) spiked with different percentages of oil as compared to neat PKOME. However, in this study, from the comparison of the spectra with regard to quantifying oil content, there was no difference between the spectrum of

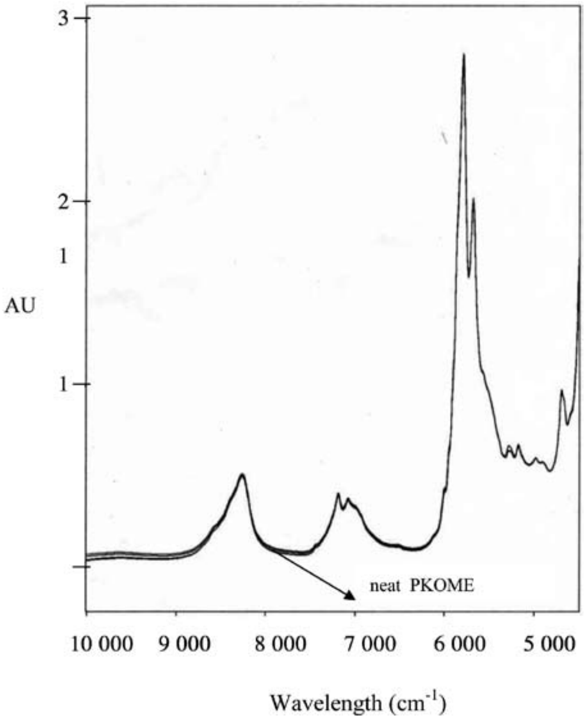

Figure 1. Near infrared (NIR) spectra overlay of palm kernel methyl esters with 1%, 4% and 9.8% oil residues and neat palm kernel oil methyl esters (PKOME).

neat PKOME and the spectra of PKOME spiked with different percentages of palm oil. Although not shown, there was also no discernible difference in the spectra for palm oil methyl esters (POME) spiked with different percentages of oil (0%, 1% and 9.8%).

The spectral profiles of methyl esters and spiked methyl esters in the NIR region were nebulous and not as detailed as that from mid infrared (IR) spectroscopy, mostly comprising overlapping and poorly defined overtones and combination bands resulting from the basic absorptions in the mid IR region. The strong absorption bands in the NIR region were carbon-hydrogen bond (C-H) overtones and combination bands. The region covering wavelengths of 6200-5500 cm^{-1} was the first C-H overtone with second C-H overtone at 8500-8200 cm^{-1}, while the first methylene (C-H_2) combination bands were at 4500-4000 cm^{-1} and the second combination bands at 7500-6500 cm^{-1}. The extensive band overlap of the NIR spectrum made it harder to extract information for quantitative purposes. A chemometric technique with PLS regression therefore was used, as it can mathematically correlate spectral changes to changes in the measure of interest, *e.g.* percentage oil in the methyl esters.

An analytical technique using NIR spectroscopy with PLS has been developed for the prediction of soyabean oil (feedstock) in methyl soyate (biodiesel) using spectra regions of 4600-4350 cm^{-1} and 6005 cm^{-1} to build a PLS calibration model (Knothe, 1999). These regions were so identified to be able to distinguish between NIR spectra of triacylglyceries (soyabean oil) and the corresponding methyl esters (methyl soyate). However, in this study, the whole NIR spectrum range of the 4500-10 000 cm^{-1} region was chosen, because there was a lack of specific regions that showed discernible changes in the absorbance corresponding with the increase in percentage of palm oil used for spiking both PKOME and POME.

Calibration Models for Varying Percentages of Oil Residue in Palm Kernel Methyl Esters and Palm Methyl Esters

The information from the collected NIR spectra of the samples from the calibration set, together with the weighted values of the percentages of palm oil residue, were incorporated into the chemometric program to generate the PLS calibration plots.

Figures 2 and 3 and *Figures* 4 and 5 show the calibration-validation plots for Model 1 and Model 2, respectively. *Tables 1* and 2 show the partial listing of the NIR predicted versus actual values for Model 1 and Model 2, respectively. The residual values were low at <0.12, showing good agreement between the percentage of oil measured gravimetrically and by the NIR predicted values.

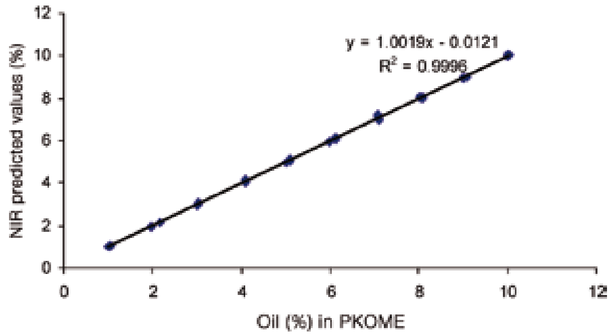

Figure 2. Calibration plot for percentages of oil in palm kernel oil methyl ester (PKOME) (Model 1).

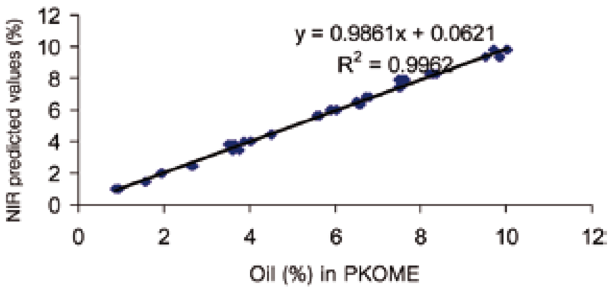

Figure 3. Validation plot for percentages of oil in palm kernel oil methyl esters (PKOME).

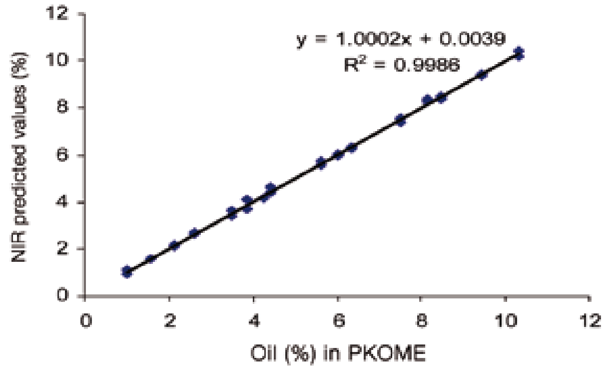

Figure 4. Calibration plot for percentages of oil in palm oil methyl esters (POME) (Model 2).

Table 3 shows the statistical data for the NIR PLS regression for the calibration and validation plots of the two models. The high R^2 values and low standard error of calibration (SEC), standard error of cross validation (SECV) and standard error of prediction (SEP) show that the region selected was optimal for the prediction of oil residue in palm oil-based methyl esters.

The use of the calibration model was strictly confined to predictions of oil residue in methyl esters which were of the same variety as those used in the calibration set. For industrial quality control (QC), the QC personnel can establish a calibration

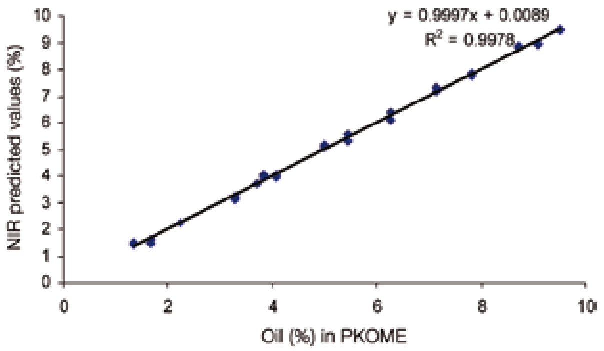

Figure 5. Validation plot for percentages of oil in palm oil methyl esters (POME).

TABLE 1. PARTIAL LISTING OF DATA FROM THE VALIDATION SET

% oil in PKOME	NIR-predicted oil (%)	Residual
1.00	0.98	0.02
2.50	2.66	-0.16
3.50	3.64	-0.14
4.03	4.01	0.02
5.61	5.65	-0.04
6.49	6.54	-0.05
7.39	7.46	-0.07
9.89	10.0	-0.11

Note: NIR – near infrared.
PKOME – palm kernel oil methyl esters.

TABLE 2. PARTIAL LISTING OF DATA FROM THE VALIDATION SET

% oil in POME	NIR-predicted oil (%)	Residual
1.35	1.43	-0.13
2.23	2.23	0
3.29	3.22	0.07
3.71	3.71	0
3.82	3.95	-0.13
4.08	4.07	0.01
5.46	5.30	0.16
7.82	7.76	0.06
9.09	8.96	0.13
9.50	9.51	-0.01

Note: POME – palm oil methyl esters.
NIR – near infrared.

TABLE 3. STATISTICAL PARAMETERS FOR NIR PARTIAL LEAST SQUARES REGRESSION CALIBRATION MODELS FOR QUANTIFICATION OF PERCENTAGES OF PALM OIL RESIDUE IN PALM KERNEL AND PALM OIL METHYL ESTERS

Type of calibration	% oil in PKOME (Model 1)	% oil in POME (Model 2)
SEC	0.060	0.108
SECV	0.061	0.112
SEP	0.176	0.128
R^2 for calibration plot	0.9996	0.9986
No. of factors	9	8

Note: NIR – near infrared.
POME – palm oil methyl esters.
PKOME – palm kernel methyl esters.

model by creating the calibration set using the available methyl esters. The methyl esters should be sourced from those batches that are targeted for monitoring. However, before a particular batch of methyl esters is used in the calibration set, it should be analysed using conventional methods such as gas chromatography to ensure that they are free of any oil residue prior to spiking. There will be no need to purchase commercial standards for use in the analyses, thus making the method less costly.

CONCLUSION

Based on the studies carried out, although no discernible wavelength region was found to change with the measure of interest, *e.g.* increasing percentages of spiked palm oil residue, it was still possible to predict the percentage of oil residue in methyl esters using a PLS regression with a full NIR spectrum-based calibration. Prediction of the amount of oil residue in the two types of methyl esters was successfully demonstrated for percentage contamination ranging from 1% to 10%. The limitation of this method is that it cannot be used for analysis of trace oil in amounts <0.2% in methyl esters as specified by the biodiesel standards. This method is recommended for a fast approximation of the percentage of oil contamination, but if higher accuracy is needed, the gas chromatography method should be used.

This method has the advantage of being simple because calibration standards are easily prepared gravimetrically, and collection of each spectrum can be done in a matter of 2 min, which is much faster as compared to the conventional gas chromatography method.

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