# Analysis of water content in biodiesel palm oil using near infrared spectroscopy

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# Introduction

Biodiesel is widely used as an alternative energy source. There are several advantages to its use, such as the advantage that it can be produced from several vegetable oils, or refined from waste frying oil.<sup>1,2</sup> However, the quality control of this product is complicated by the requirement of controlling 25 parameters, following the European Standard EN 14214, because biodiesel oils are produced from a wide range of materials, and by different techniques.<sup>3,4</sup> The presence of water in biodiesel oils can lead to various problems during the utilization in diesel engines, including smoking, corrosion, and pitting. For this reason it is desirable to develop a convenient method for detecting the water content of biodiesel oils. It is noted that near infrared (NIR) spectroscopy is very sensitive to the content and structure of water, even with trace amounts in the material. In the present study, we have investigated the feasibility of using NIRS to determine the water content in biodiesel oils.

# **Experimental section**

## Materials

Samples obtained from a factory plantation, were supplied by Patum Vegetable Oil Co., Ltd. (Pathumthani, Thailand) at the rate of 10 samples per week. A total of 100 samples were randomly divided into two sets, a calibration set with 70 samples, and a validation set with 30 samples.

## Spectra acquisition

NIR measurements were performed on an InfraAlyzer 500 (Bran & Lubbe), equipped with an InGaAS detector. The spectra were recorded in reflectance mode over the region of 1100–2500 nm,

Set	Range	Average	Standard deviation
Calibration set	0.018-0.078	0.051	0.014
Validation set	0.021-0.065	0.051	0.0099

Table 1. Composition (water content) of the calibration and validation sample sets.

at 2 nm resolution. Before the measurement, samples were immersed in a water bath at 28°C for 15 minutes to control temperature.

#### Water analysis

Samples of about 0.5 g were weighed and analyzed using the Karl Fisher titration method by a coulometric titrator (Mettler Toledo DL32, Switzerland), following ASTM standard method D4928–00

#### Data analysis

Recorded spectra were collected by Sesame software built into the NIR instrument. The Unscrambler software (Camo, Oslo, Norway) was used for further calculation, including spectral management, second derivative pretreatment (Savitsky-Golay algorithm, polynomial order=2,



Figure 1. The second derivative spectra of biodiesel oils.

left and right averaging = 20 nm each), and regression analysis. Partial least squares (PLS) regression was used to perform and validate calibration models, with the test set validation method. Moving window partial least squares regression (MWPLSR) written by this laboratory for wavelength selection was calculated using Matlab  $7.0.^{5}$ 

### **Results and discussions**

Composition results of the water content in biodiesel analyzed by the Karl Fisher method are shown in Table 1.

The second derivative spectra of biodiesel oils are shown in Figure 1. Although, strong absorption bands in the regions of 1600-1800 nm and 2200-2500 nm originate mainly from C-H stretching vibrations, a notable contribution from water can still be observed in the range of 1800-1960 nm. To observe these informative bands, the spectral region from 1800 nm to 1960 nm has been enlarged and inserted in Figure 1. Three peaks at 1820 nm, 1900 nm and 1934 nm, assigned to the combination of O-H and C-H stretching, the second overtone of C=O stretching, and the combination of asymmetric stretching and bending of water molecule,<sup>6</sup> respectively, can easily be seen in the inset. These bands show a marked decrease in intensity with the decrease in water content in the biodiesel oil. The whole region of PLS and MWPLS was used to develop calibration models as a comparative study. Spectra were pretreated by second order derivative of Savitsky-Golay method for reduction of the scattering effect and spectral enhancement, before calibration model development. Figure 2 reveals an important informative region from 1820 nm to 2000 nm, which corresponds to stretching vibrations of the OH group of water and C=O of carboxylic acid groups.



Figure 2. Plot of log sum square of residual calculated from second derivative spectra.

Wavelength (nm)	F	Calibration		Prediction	
		r	RMSEC	RMSEV	Bias
1100–2500	4	0.7885	0.0082	0.0069	0.0001
1810–2000	3	0.8781	0.0064	0.0059	-0.0007
1630–1740,1810–2000	3	0.8552	0.0069	0.0062	0.0004
1340–1510,1820–2000	1	0.8537	0.0070	0.0055	-0.0002
1340-1510,1630-1740,1820-2000	5	0.8927	0.0061	0.0059	-0.0007
1340–1510,1630–1740, 1820–2000, 2200–2280	6	0.8959	0.0060	0.0062	-0.0007

Table 2. Summary of statistical results for prediction of water in biodiesel fuels using NIR spectra that were pretreated with second derivative.

*F*: the number of factors used; *r*: the correlation; *RMSEC*: root mean square error of calibration; *RMSEP*: root mean square error of validation, Unit: %w/w.

This implies that the O–H bonding of water molecule has interaction with the C=O group of carboxylic acid groups. It may be concluded that the calibration model for prediction of water content in biodiesel is strongly affected by this association between the C=O and O-H groups. Other regions from the error plot (Figure 2) were selected for combination to enhance the prediction and comparison of the calibrations. All statistical results for prediction of water content are presented in Table 2.

The best calibration was developed using the regions of 1340–1510 and 1820–2000 nm with the *R*, *RMSEC* and *RMSEP* of 0.8537%, 0.0070% and 0.0055%, respectively.

# Conclusion

The comparison of PLS regression calibration models built by using the whole wavelength region and selected sub-regions determined by MWPLS shows that MWPLS, in combination with NIRS is a useful method for the determination of water content in biodiesel samples. The results indicated that the C=O groups in the carboxylic acid grouping, in combination with O-H stretching yielded the most useful information for the calibration models.

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