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Near Infrared Technology As a Robust and Environmental Friendly Approach To Biofuel Analysis: Rapid Biodiesel Classification and Quality Prediction

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Abstract

The use of ethanol and biodiesel, which are alternative fuels or biofuels, has increased in the last few years. Modern official standards list 25 parameters that must be determined to certify biodiesel quality. In order to determine biofuel quality, several methods were already widely used in which most of them were based on solvent extraction followed by other laboratory procedures. Yet, these methods are expensive, laborious and complicated processing for samples. Near infrared reflectance spectroscopy (NIRS) can be considered as a fast, pollution-free and non-destructive method in determining biofuel quality parameters. The objective of this study is to apply near infrared technology in classifying biodiesel based on KOH (0.3, 0.5 and 0.7) and to predict related biodiesel quality properties (water content, linolenic fatty acid, oleic acid, and stearic acid) based on its infrared reflectance. Biodiesel infrared spectrum was acquired in wavelength range from 1000 to 2500 nm for different mentioned three KOH content. Principal component analysis (PCA) with non-iterative partial least square (NIPALS) was applied to analyze biodiesel spectral data. The result showed that two principal components (PC1=97% ad PC2 = 2%) based on infrared reflectance data were successfully able to recognize and classify biodiesel based on their used KOH. Moreover, the wavelength range of 1000 – 1140 were to be believed related to linolenic fatty acid whilst 1450 nm and 1930 nm were associated with water content. Stearic acid can be predicted in wavelength range of 1330 – 1380 nm and wavelength range of 1725 – 1790 nm were related to oleic acid of biodiesel. This may conclude that infrared technology was feasible to use as a rapid, effective and non-invasive method in biofuel classification and evaluation.

Keywords **:** *Near infrared; biofuel; catalyst; classification; prediction*

Teknologi *Near Infrared* Sebagai Teknologi Yang Kuat dan Ramah Lingkungan Untuk Menganalisis *Biofuel* : Memprediksi Secara Cepat Kualitas dan Klasifikasi Biodiesel

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Abstract

Penggunaan etanol dan biodiesel, sebagai alternatif bahan bakar atau bahan bakar nabati (BBN), mengalami peningkatan beberapa tahun terakhir ini. Kualitas biodiesel secara resmi ditentukan oleh 25 standar. Untuk memnetukan kualitas bahan bakar nabati, beberapa metode yang sudah banyak digunakan dengan melakukan

ekstraksi berdasarkan standar prosedur laboratorium. Pengujian seperti ini sangat mahal dan membutuhkan sampel dan proses laboratori yang cukup menyulitkan. Teknologi *Near infrared reflectance spectroscopy* (NIRS) dapat bekerja secara cepat, bebas polusi, dan dengan metode tanpa merusak bahan (non-destructive method) dalam menentukan parameter kulitas bahan bakar nabati (*biofuel*) tersebut. Tujuan dari penelitian ini adalah untuk menerapkan teknologi *near infrared* dalam mengklasifikasi biodiesel berdasarkan komposisi KOH (0,3, 0,5 and 0,7) dan memprediksi hubungan sifat-sifat kualitas biodiesel (kadar air, *linolenic fatty acid*, *oleic acid*, dan *stearic acid*) berdasarkan panjang gelombang *infrared*. Spektrum *infrared* biodiesel berada pada panjang gelombang 1000 sampai dengan 2500 nm untuk tiga perbedaan kandungan KOH tersebut. *Principal component analysis* (PCA) dengan *non-iterative partial least square* (NIPALS) telah dilakukan untuk menganalisis spektra data biodiesel pada penelitian ini. Hasilnya menunjukkan dua *principal components* (PC1= 97% dan PC2 = 2%) berdasarkan data panjang gelombang *infrared* telah berhasil diperoleh dan diklasifikasikan berdasarkan komposisi KOH. Selain itu, panjang gelombang dari 1000 – 1140 adalah merupakan pertanda berhubungan dengan *linolenic fatty acid* juga untuk panjang gelombang 1450 nm dan 1930 nm adalah berhubungan dengan kandungan air. Nilai *stearic acid* dapat diprediksi pada panjang gelombang 1330 – 1380 nm dan panjang gelombang 1725 – 1790 nm adalah berhubungan dengan nilai *oleic acid* dari biodiesel. Hasilnya dapat disimpulkan bahwa teknologi *infrared* sangat layak digunakan karena hasilnya yang cepat, efektif, dan merupakan metode *non-invasive* (tanpa pembedahan) pada klasifikasi dan evaluasi bahan bakar nabati (BBN)/*biofuel*.

Keywords **:** *Near infrared;* Bahan bakar nabati (BBN)*;* katalis*;* klasifikasi*;* prediksi

INTRODUCTION

Increased industrialization and motorization are the major cause of environmental pollution and diminishing petroleum reserves. These concerns are leading energy policies to promote research in the field of new alternative fuels. Environmental problems associated to fossil fuels have increased general awareness about renewable energies, with less environmental impact. The alternatives should be economically competitive, technically possible, environmentally acceptable and with high availability. Therefore, to decrease the dependence on fossil fuels, the use of renewable energies will have to be widespread and biodiesel is one of these alternatives (Dorado et.al, 2004; Baptista et.al, 2008).

Biodiesel is a fuel produced mainly through trans-esterification of fatty acids from vegetable oils or animal fats with an alcohol (mainly methanol) to produce an ester and a byproduct, glycerol (Baptista et.al, 2008, Siregar et.al, 2013; Siregar et.al, 2015). This reaction occurs stepwise, with mono and diglycerides as intermediate products. Potassium hydroxide (KOH) can be considered to be used as a homogeneous catalyst. At the end of the reaction period, the glycerol-rich phase is separated from the ester layer by decantation or centrifugation (Baptista et.al, 2008). The refined biodiesel has similar properties to conventional fossil diesel, which allows its use as an alternative fuel. Moreover, biodiesel allows the reduction of greenhouse gases, particle matter and sulphur emissions (Pinzi et.al, 2009; Lima et.al, 2003).

Biodiesel can be produced using several different feed-stocks and technologies, including different catalyst concentration, and that may lead to different properties of the final

product. Therefore, the quality control of biodiesel is very important issue. Modern official standards list 25 parameters that must be determined to certify biodiesel quality (Knothe et.al,2001).

In order to determine biofuel quality, in general, several methods were already widely used in which most of them were based on solvent extraction followed by other laboratory procedures. Yet, these methods are expensive, laborious and complicated processing for samples (Torres-Jimenez et.al,2010). Near infrared reflectance spectroscopy (NIRS) can be considered as a fast, pollution-free and non-destructive method in determining biofuel quality parameters (Munawar et.al, 2016).

The NIRS is a technique or method which uses near infrared radiation (780 – 2500 nm) of the electromagnetic spectrum to analyze the chemical composition of organic matter. It provides information through spectra signatures and patterns, regarding with the intrinsic organic bonds of the molecules and thus the primary chemical constituents of the object can be determined (Cen et.al, 2007; Nicolai et.al, 2007).

Since NIRS itself cannot reveal chemical information in the spectra, chemometrics analysis like principal component analysis (PCA) and partial least square (PLS) to extract the information about quality attributes buried on NIR spectra through a process called multivariate calibration for biodiesel classification and quantification of desired quality attributes.

Therefore, the main objective of this present study is to apply NIRS technique combined with PCA for rapid biodiesel classification based on KOH concentration. The study also attempted to predict corresponded wavelengths in the region of NIR which are related to biodiesel quality attributes.

MATERIALS AND METHODS

NIR spectra acquisition

Diffuse reflectance spectra data in wavelength region from 1000 to 2500 nm were acquired using the Fourier transform NIR instrument for a total of 33 biodiesel samples with three different KOH concentration (0.3, 0.5 and 0.7). Sample measurement with integrating sphere was chosen as a basic measurement in this study. Background spectra correction was performed every hour to minimize noise and light scattering effect.

Spectra enhancement

The spectra data acquired from NIR instrument may contain unwanted information and noises which are interfered desired relevant quality attributes information. Thus, spectra

enhancement is very necessary to be performed prior to modeling. A multiplicative scatter correction method (SCM)was applied as spectra enhancement algorithm (Munawar et.al, 2016).

Spectra data analysis

NIR spectra acquired from the NIR instrument were analyzed through principal component analysis (PCA). It employs a mathematical procedure that transforms a set of possibly correlated response variables into a new set of non-correlated variables, called principal components. PCA is used as a tool for screening, discriminating and classifying samples based on their similarities or dissimilarities of multivariate data. Principal component analysis with non-iterative partial least square (NIPALS) was applied to analyze biodiesel spectral data and perform classification based on KOH concentration.

RESULTS AND DISCUSSION

Near infrared spectra features of biodiesel

Typical reflectance and absorbance spectrum of biodiesel samples are presented in Fig.1. The NIR spectrum indicates the presence of organic materials as derived from the bands that result from the interaction of molecular bonds of O-H, C-H, C-O and N-H with the incident radiation. These bonds are subject to vibrational energy changes in which two vibration patterns exist in these bonds including stretch vibration and bend vibration.

Based on our prediction analysis, the wavelength range of 1000-1140 were to be predicted related to linolenic fatty acid whilst 1450 nm and 1930 nm were associated with water content, because of O-H tone combination and its first overtone. Stearic acid can be predicted in wavelength range of 1330 - 1380 nm and wavelength range of 1725 - 1790 nm were related to oleic acid of biodiesel. These also in agreement with some literatures noted that absorption bands at around 1400 nm and 1900 nm were previously assigned to water absorption.

Moreover, the absorption bands in the range of 2200 - 2300 nm are suggested to be related to C-H-O structures whilst absorption bands at around 1400, 1800 and 2100 nm are associated with organic acids.

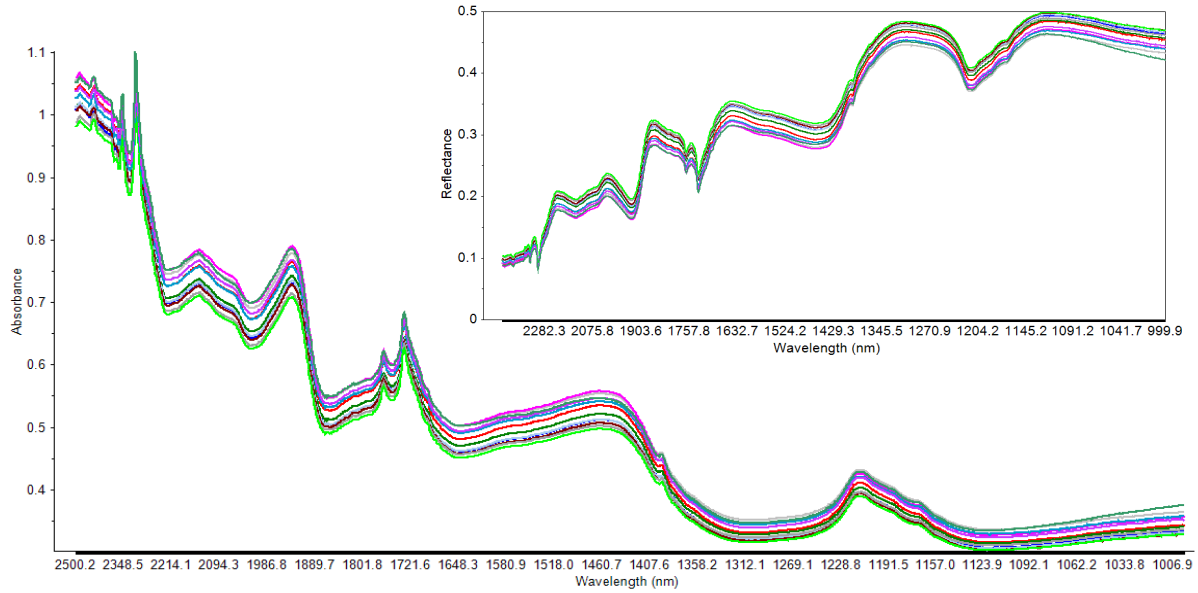

Fig. 1. Typical NIR spectral signatures of biodiesel.

Biodiesel classification

Near infrared spectra data of all biodiesel samples were then subjected onto the PCA map to extract spectral data based on similarity in which different Potassium hydroxide (KOH) concentration. Prior to PCA classification, multiplicative scatter correction (MSC) was applied to all spectra data in order to enhance and correct NIR spectra data. MSC is used to compensate for additive (baseline shift) and multiplicative effects in the spectral data, which are induced by physical effects, such as the non-uniform scattering throughout the spectrum. The degree of scattering is dependent on the wavelength of the radiation, the particle size and the refractive index. This method attempts to remove the effects of scattering by linearizing each spectrum to an 'ideal' spectrum of the sample, which is normally corresponds to the average spectrum.

PCA classification result is shown in Fig. 2. The first principal component accounts for as much of the variability in the data as possible, and each succeeding component accounts for as much of the remaining variability as possible.

Our obtained results are as follows: PC1=97%, PC 2=2% and PC3=1% from which we may argue that most of spectra data of biodiesel samples can be discriminated using the first component (PC1) while remaining components, PC 2 and PC3, contributes 2% and 1% respectively. Furthermore, judging from the classification result, all three different KOH concentration can be classify precisely and accurately 100% using the NIR spectra data with the support of PCA-NIPALS algorithm.

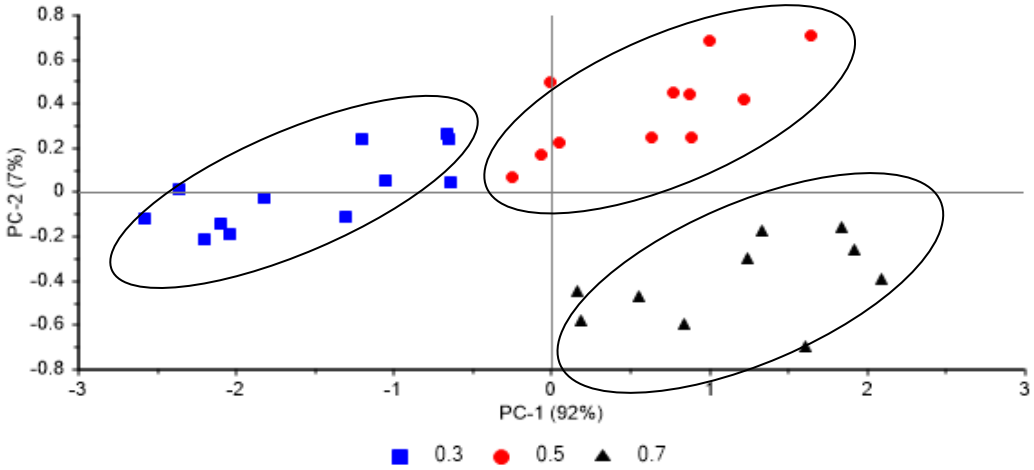

Fig. 2. PCA classification result of biodiesel KOH concentration using NIR spectral data.

CONCLUSIONS

The present study attempted to apply near infrared technology as a fast and non-destructive method for biodiesel classification based on different catalyst concentration (KOH) and quality properties prediction. Obtained results described that NIR technology with the support of principal component analysis was able to 100% classify biodiesel based on different KOH concentration. Further, this technology was to be believed able to predict some important quality parameters such as linolenic fatty acid, water content, stearic acid, oleic acid and other organic properties of biodiesel.

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