Fuel 160 (2015) 57–63

Contents lists available at ScienceDirect

Fuel

journal homepage: www.elsevier.com/locate/fuel

Quantification of biodiesel and adulteration with vegetable oils in diesel/biodiesel blends using portable near-infrared spectrometer

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HIGHLIGHTS

- Portable NIR spectrometer was used to quantify biodiesel and vegetable oil in diesel.
- Performance of the portable NIR spectrometer was compared with the benchtop one.
- PLS and MLR regression models with variable selection were developed.
- Portable NIR spectrometer is feasible for monitoring quality of diesel blends.

ARTICLE INFO

Article history:
Received 14 May 2015
Received in revised form 7 July 2015
Accepted 20 July 2015
Available online 29 July 2015

Keywords:
Diesel/biodiesel blends
Diesel/biodiesel adulteration
Portable near-infrared (NIR) spectrophotometer
Multivariate calibration
Variable selection

ABSTRACT

The performance of a portable near infrared spectrophotometer to determine biodiesel content in diesel/biodiesel blends, as well as to quantify adulteration by vegetable oil, was evaluated. The NIR transmittance/absorbance spectra of 118 samples in the range 950–1650 nm were acquired using an ultra-compact spectrophotometer (MicroNIR), and also by using a Fourier transform benchtop instrument (FT-NIR) from 800 to 2500 nm. In a preliminary step, partial least squares (PLS) models aimed at the determination of biodiesel quality parameters were developed by using full spectral information. Thereafter, the variables showing significant regression coefficients were selected and the PLS models were re-processed. Successive Projections Algorithm (SPA) was used to screen for the most orthogonal variables to be used in a model constructed by using Multiple Linear Regression (MLR). For determining the contents of both biodiesel and vegetable oil in diesel/biodiesel blends, using MicroNIR and FT-NIR, the results indicated MLR-SPA as the best modelling strategy. RMSEP values of 0.22% v/v (MicroNIR) and 0.13% v/v (FT-NIR) for biodiesel and 0.34% v/v (MicroNIR) and 0.22% (FT-NIR) for vegetable oil contents were obtained. LOD values of 0.31% (MicroNIR) and 0.22% (FT-NIR) for biodiesel and 0.40% (MicroNIR) and 0.34% (FT-NIR) for vegetable oil determination were achieved. The results revealed comparable performances between the portable and the benchtop instruments, demonstrating the feasibility of monitoring *in situ* the quality characteristics of diesel/biodiesel blends according to biodiesel content and for detection of adulteration with vegetable oils by using the portable spectrophotometer.

1. Introduction

The prevalent fuel commercialized in Brazil is a blend of diesel with (7.0 ± 0.5)% (v/v) of biodiesel. These blends are highly subject to adulteration with vegetable oil, either as an illegal addition of this cheaper raw material, or as a result of incomplete conversion of the oil into ester during processing [1–3]. Therefore, it is important to ensure that diesel blends are in accordance with quality standards and regulations.

Standard methods, such as EN 14078 and ASTM D7371-07, which use middle infrared (MIR) with univariate and multivariate methods, respectively, are described for determination of biodiesel in diesel fuel [4,5]. However, these methods do not consider the presence of vegetable oil as a contaminant.

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http://dx.doi.org/10.1016/j.fuel.2015.07.067
0016-2361/

The use of Near Infrared (NIR) spectroscopy is very attractive for the purpose of quality control of blends since it does not require sample treatment and enables fast analysis [6–9]. The literature reports extensively on methods using Near Infrared (NIR) spectroscopy with multivariate calibration for the determination of biodiesel and vegetable oil contents in diesel, suggesting the applicability of this technique.

Pimentel et al. [10] have described the use of NIR spectroscopy to quantify biodiesel content (0.0–5.0%, v/v) in diesel/biodiesel blends employing Partial Least Square (PLS) regression models. Their results demonstrate the possibility of quantifying biodiesel content using a root mean squared error of external validation (RMSEP) of 0.18% v/v even in the presence of raw vegetable oil. Oliveira et al. [11] developed PLS and Neural Networking (ANN) models using NIR spectra to quantify different methyl esters in biodiesel/diesel blends (0.0–100% w/w). Two groups of samples, Group I (one type of methyl ester + diesel) and Group II (three types of methyl ester + diesel), were employed. The best RMSEP, 0.06% w/w (Group I) and 0.32%, w/w (Group II), were obtained using PLS models.

Fernandes et al. [12] have evaluated the use of NIR spectroscopy, PLS models and Multiple Linear Regression (MLR), with and without variable selection by the Jack-Knife algorithm (PLS-JK), Successive Projection Algorithm (MLR-SPA) and Stepwise (MLR-SW) to determine the biodiesel content in diesel/biodiesel blends. The best RMSEP was 0.64% w/w using MLR-SPA. Overall, the use of variable selection improved the results compared with PLS models constructed by using full spectrum.

Calibration models based in PLS and support vector machine regression (SVMR) methods without and with variable selection by synergy interval (siPLS and siSVR) were developed by Filgueiras et al. [13], to determine animal fat biodiesel content in soybean biodiesel blends (RMSEP = 0.18% w/w) and 20% w/w biodiesel (animal fat plus soybean)/diesel blends (RMSEP = 0.10% w/w) employing NIR spectroscopy. Vasconcelos et al. [1] have developed several calibration models (PLS, PLS-JK and MLR-SPA) using the NIR overtone region (833–1666 nm) to quantify biodiesel and vegetable oil contents in diesel/biodiesel blends (0.0–10.0% v/v). The use of sample cells with optical path lengths of 10 mm, 20 mm and 50 mm indicated that the best RMSEP were 0.08%, 0.09% and 0.12% v/v for biodiesel content, and 0.37%, 0.45% and 0.57% v/v for vegetable oil content, respectively.

Oliveira et al. [2], demonstrated that the ASTM 4052, ASTM D 445, ASTM D 4737, ASTM D 93, and ASTM D 86 methods are not suitable for identifying diesel samples adulterated with vegetable oil. The authors demonstrated the use of NIR and Raman spectroscopy and Principal Components Regression (PCR), PLS, and ANN based calibration models to determine vegetable oil (0–5% w/w) in diesel/biodiesel blends. For PLS model employing NIR spectra the RMSEP obtained was 0.045% w/w.

The determination of the vegetable oil content in diesel/biodiesel blends (0.0–30% w/w of vegetable oil) was also described by Gaydou et al. [3]. The authors investigated the use of NIR and MIR spectroscopies separately and combined. For the separate regions, the best RMSEP (0.36% w/w) was obtained using the NIR region. For the combined regions, the lowest RMSEP (0.27% w/w) was achieved using Hierarchical-PLS (H-PLS). Recently, Alves and Poppi [14] developed a NIR spectroscopy quantitative models, based on Support Vector Machine (SVM) and PLS, for determination of biodiesel content (0.0–21% v/v) in diesel/biodiesel/hydrocarbon renewable diesel blends. The PLS model shows a RMSEP value of 0.19% v/v for determination of biodiesel content.

Common to all these works is the fact that they employed benchtop spectrophotometers often based on Fourier transform (FT), which undoubtedly offer high spectral resolution, signal-to-noise ratio and better wavelength reproducibility [15–17]. However, FT-NIR spectrophotometers are expensive and less suitable for field analysis, which is important for fuel quality control. In contrast, portable NIR instruments are very attractive for field analysis, despite their reduced spectrophotometric characteristics. Recently, an extremely miniaturized NIR spectrometer, called the MicroNIR (JDSU Corporation, Milpitas, USA), employing a thin film linear-variable filter (LVF) as the radiation analyzing element, became commercially available [18,19]. This instrument uses two small internal tungsten light bulbs as the radiation source, and a 128-element detector (InGaAs) and it is powered and controlled through an USB port of a computer running proprietary software. The instrument is able to obtain spectra in the range 950–1650 nm and has been primarily designed to be used for spectral reflectance measurements.

Several recently published works can be found in the literature employing the MicroNIR spectrophotometer. Alcalà et al. [20] used the MicroNIR in qualitative discrimination between authentic and illegal pharmaceuticals and quantitative determination of acetylsalicylic acid, ascorbic acid and caffeine. O'Brien et al. [21] used reflectance spectra measured with MicroNIR to differentiate very similar fish species with quite different prices, according to their quality. Singh et al. [22,23] employed the MicroNIR and PAT (Process Analytical Technology) tools to monitor a tablet manufacturing process. Rohwedder et al. [24] have developed a miniaturized gas analyzer based on the use of a substrate-integrated hollow waveguide (iHWG) coupled to a MicroNIR. Lutz et al. [25] developed a transflectance measurement cell to be used with MicroNIR to quantify the ethanol content in gasoline.

Up to now, no work has reported on using MicroNIR to access quality parameters of diesel blends, although it is possible to find some commercially available portable FT-MIR spectrophotometers (middle infrared) designed for quantifying biodiesel in diesel/biodiesel blends. The present work describes simple instrumental modifications required to employ the MicroNIR for in-field transmittance/absorbance measurements, and the development of analytical methods based on multivariate regression and variable selection to determine biodiesel and vegetable oil content in diesel.

2. Materials and methods

2.1. Samples

A mixture design with a central point and including internal points was employed to prepare blends using different diesel fuels, oilseeds and soybean ester. Maximum and minimum levels of both biodiesel and oil were 0.0% and 15.0% (v/v). The ratio of ester/oil concentration was varied from 0.25 to 4.0. A set of 118 samples was obtained. The biodiesel, oil, and diesel samples used to prepare the blends in the laboratory were all within the quality specifications and were acquired in the market, from different manufactures, to match real samples.

2.2. Near infrared spectra acquisition

A portable NIR spectrometer, MicroNIR (JDSU Corporation, Milpitas, USA), which operates in the spectral region 900–1650 nm, was used to acquire the NIR spectra. This instrument, powered (5 V) and controlled via USB port of a computer, originally employs two tungsten light bulbs as radiation source, a Linear Variable Filter (LVF) as dispersing element and an uncooled 128-element detector (InGaAs). The MicroNIR resolution is 12.5 nm at 1000 nm. Spectra of the samples were obtained by averaging 50 scans with an integration time of 50 ms resulting in a total measurement time of 2.5 s per sample.