



Prediction of properties of diesel/biodiesel blends by infrared spectroscopy and multivariate calibration

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ARTICLE INFO

Article history:

Received 12 December 2008

Received in revised form 19 May 2009

Accepted 29 May 2009

Available online 16 June 2009

Keywords:

Biodiesel

Infrared spectroscopy

Multivariate calibration

Partial least square regression

Calibration transfer

ABSTRACT

Partial least squares models (PLS) using near and middle infrared spectrometry were developed to predict quality parameters of diesel/biodiesel blends (density, sulphur content and distillation temperatures). Practical aspects are discussed, such as calibration set composition; model efficiency using different infrared regions and spectrometers; and the calibration transfer problem. The root mean square errors of prediction, employing both regions and equipment, were comparable with the reproducibility of the corresponding standard method for the properties investigated. Calibration transfer between the two instruments, using direct standardization (DS), yielded prediction errors comparable to those obtained with complete recalibration of the secondary instrument.

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1. Introduction

Biodiesel is a potentially renewable substitute for diesel oil. It is a mixture of alkyl esters of fatty acids, generally made by the alcoholysis of vegetable oils or animal fats with short chain alcohols such as methanol and ethanol. There are several possible sources of vegetable oils and animal fats available worldwide that can be used to produce biodiesel [1]. A common use of biodiesel is in blends with petroleum-based diesel fuel. The use of biodiesel as a fuel in Brazil has been legally authorized since 2005, allowing up to a volume fraction of 3% in conventional diesel. This blend is commonly referred to as B3. In 2013, the biodiesel content in diesel will be increased to a volume fraction of 5%. The Standard ASTM E 975-09 describes the specification for biodiesel blends up to 5% biodiesel [2].

Standard methods for assessing the quality of biodiesel blends are time-consuming and require high cost specific equipment [3]. Additionally, they also generate pollutant emissions and residues. Infrared spectroscopy (IR) is an alternative non-destructive analytical technique which allows reliable, direct and fast determination of several properties, without sample pre-treatment. Infrared spectroscopy, when employed as an analytical quantitative tool, could be called a secondary technique, that is, it is necessary to build a

multivariate model to correlate the infrared spectra with the corresponding values of the property of interest (previously determined by a reference method). The ASTM E 1655-05 [4] is a guide for the multivariate calibration of infrared spectrometers used in determining the physical or chemical characteristics of materials. Methods employing IR and multivariate calibration have been widely used to predict physical and chemical properties and certify the authenticity of fuels [5–7]. Recent works have shown the viability of both near (NIR) and middle (MIR) spectroscopy associated with multivariate calibration to monitor the quality of biodiesel. A NIR spectroscopy method for determining the content of soybean biodiesel in conventional diesel fuel was reported by Knothe [8]. Multivariate calibration models based on MIR and NIR spectroscopy have also been developed to determine the biodiesel content in blends with diesel and to evaluate contamination by raw vegetable oil [8–13]. Additionally, NIR [14,15] and MIR [16] spectroscopy have been employed to monitor transesterification reaction. NIR spectroscopy associated with partial least squares (PLS) and principal component regressions (PCR) has been used to predict methanol and water content [17] and iodine value, kinematic viscosity, density and cold filter plugging point [18] in biodiesel (B100). Multivariate near-infrared spectroscopy models have also been employed for monitoring the quality of oils for biodiesel production [19]. In 2008, the Brazilian National Standards Association (ABNT) published a standard test to determine ester content in biodiesel blends using middle infrared spectroscopy and PLS regression

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(NBR 15568:2008). From this point on, infrared spectroscopy will be frequently used in laboratories which monitor biodiesel quality. Given this, it is important to expand the use of this technique in predicting other properties of biodiesel blends and to evaluate practical aspects of its applicability. In the present work, multivariate calibration models were developed employing NIR and MIR spectra to predict important quality parameters of biodiesel blends (density, sulphur content and distillation temperatures). Practical aspects are also discussed, such as composition of the calibration set, efficiency of the models using different infrared regions (NIR and MIR), equipment and also the calibration transfer problem. Models (in NIR and MIR ranges) constructed using two different calibration sets (containing biodiesel blends alone and containing biodiesel blends plus diesel samples) were compared. In the MIR region, the spectra were acquired using two instruments with different characteristics: a Fourier transform infrared (FTIR) Perkin–Elmer spectrometer with an Attenuated Total Reflectance – ATR probe and also with a portable FTIR spectrometer from Grabner Instruments (Analyzer Irox Diesel) using a 0.1-mm cell.

A considerable effort, however, may be involved in the multivariate calibration of an IR instrument for predicting biodiesel blends quality parameters. Such an effort involves not only the acquisition of spectra, but also the collection of representative calibration samples (containing different biodiesel sources and diesel samples) and the determination of reference values by standard methods, which can be costly and time-consuming. Therefore, the use of calibration transfer techniques is important for the widespread use of IR spectrometers among a network of biodiesel quality control laboratories. When the differences between instruments are small, reliable results may be obtained by simple preprocessing signal techniques, such as first and second derivatives, multiplicative signal correction (MSC) and standardized normal variates (SNV) [20]. In other cases, multivariate methods such as direct standardization (DS) and piecewise direct standardization (PDS) may have to be employed [21]. These standardization methods transform the spectra from the new (secondary) instrument to resemble those from the original (primary) instrument. Such a transformation is obtained by using spectra of samples recorded in both spectrometers (transfer set). In the DS procedure, the entire spectrum of the secondary instrument is related to each spectral variable (wavelength) recorded in the primary instrument. In PDS, a small window from the secondary spectrum is used instead of the entire spectral range. A drawback of PDS methods with respect to DS is the need to select an appropriate window size. In the present work, the calibration transfer problem is addressed using the DS procedure applied to the two FTIR instruments.

2. Experimental

2.1. Samples

The data set consisted of blends prepared using soybean, castor, sunflower, cottonseed and canola methyl esters, as well as diesel samples. With the purpose of including variety in the diesel composition, blends were made from different samples of diesel fuel obtained from service stations in three States of Brazil (Pernambuco, Alagoas e Sergipe). Ester content in these blends ranged from 1 to 5%w/w, (increments of 0.5%w/w were employed). A total of 161 samples were available for this study.

2.2. Reference methods

The properties considered in the present work were density (ρ), sulphur content (S) and distillation points (T50%, T85%). These parameters were determined by ASTM reference methods D 4052

[22], D 4294 [23] and D 86 [24], respectively (as recommended by ASTM 975-09). The reproducibility values stated by ASTM standards are 0.5 kg/m³ (density), 0.08%w/w (sulphur content), 7.4 °C (distillation point T50%) and 9.7 °C (distillation point T85%). The ranges of variation observed in the data set under consideration were 836–860 kg/m³ (density); 0.03–0.21%w/w (sulphur content); 270–300 °C (distillation point T50%) and 300–360 °C (distillation point T85%).

2.3. NIR and MIR spectra acquisition

The NIR (12,000–4000 cm⁻¹) and MIR (4000–600 cm⁻¹) spectra (the **X**-matrix in the calibration procedures) were obtained with a Fourier transform infrared (FTIR) Perkin–Elmer Spectrum GX spectrometer (named here as the conventional instrument). This instrument is equipped with a Michelson interferometer and a deuterated triglycine sulfate (DTGS) detector. Spectra were acquired, in the NIR region, using a quartz flow cell with a 1.0 mm path length positioned directly in front of the near-infrared radiation beam. In the MIR region, the spectra were acquired using an Attenuated Total Reflectance (ATR) probe. In all cases, the spectra were recorded at room temperature (22 ± 2 °C) with a spectral resolution of 8 cm⁻¹ and 16 co-averaged scans. MIR spectra (1789.4–650 cm⁻¹) were also obtained with a portable FTIR instrument from Grabner Instruments (Analyzer Irox Diesel) using a 0.1 mm cell, with Michelson interferometer and resolution of 4 cm⁻¹. It is important to note that the internal library and the calibration software of this equipment (based on multiple linear regression – MLR) were not used in this work.

2.4. Calibration models

Two types of calibration (and validation) sets were employed: (1) containing only biodiesel blends (2) containing biodiesel blends plus diesel samples. The models constructed using the second calibration set were denominated global models. These global models could be used to predict the properties of both diesel and biodiesel blends. All models were obtained using partial least squares regression (PLS) using full cross-validation (CV) to define the number of factors. The predictive ability of the models was evaluated by the root mean square error of prediction (RMSEP) obtained for the external validation set, composed of approximately 20% of the total number of samples. Various preprocessing procedures were evaluated. In general, the best results were obtained with first derivative using Savitzky–Golay smoothing (a second-order polynomial and an 11-point window) and this preprocessing procedure was employed in this work. The number of latent variables for the PLS models and also the variables which corresponds to the significant regression coefficients of each calibration model were automatically chosen, according to the default settings of the Unscrambler software. These selected variables correspond to IR spectral features most closely correlated to the properties investigated. An *F*-test at a confidence level of 95% was used to assess the statistical significance of differences between RMSEP values.

For the calibration transfer studies a Perkin–Elmer spectrometer was chosen as the primary instrument (PI) and a portable Irox Diesel analyzer, from Grabner, was the secondary instrument (SI). This latter instrument, due to its portability and ease of operation, is frequently found in Brazilian laboratories which monitor the quality of diesel fuel. The spectral range employed was limited by the range available in the Analyzer Irox Diesel (1789.4–650 cm⁻¹). In this equipment, spectrum is acquired at intervals of 0.7 cm⁻¹ in the range 1789.4–1351.5 cm⁻¹ and each 0.8 cm⁻¹ in the range between 1351.5 and 650 cm⁻¹. The calibration and external validation set were composed of 86 and 30 samples,

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