



Simultaneous determination of quality parameters in biodiesel/diesel blends using synchronous fluorescence and multivariate analysis

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ABSTRACT

An analytical method was developed to determine four quality parameters (Biodiesel percentage, Cetane Number, Heat of Combustion Gross and Color) in biodiesel/diesel blends through a simple synchronous fluorescence spectrum of the samples.

For this purpose, chemometrics models based on fluorescence spectra and PetroSpect data obtained from mixtures of biodiesel/diesel were built. A variable selection by the successive projections algorithm (SPA) was used in order to obtain simple multiple linear regression (MLR) models based on a small subset of wavelengths. The SPA-MLR results were compared with a partial least squares (PLS) full spectrum regression.

The best values found for the root mean square error of prediction using external validation were 0.37% (w/w) for the biodiesel in diesel, 0.5 for cetane number, 0.013 MJ/kg for heat of combustion and 0.1 for color.

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1. Introduction

Over the past decade, the world trends are the use of renewable sources of energy to replace fossil fuels partially or totally. Among biofuels, biodiesel is one the best alternatives for fuel. It is obtained from vegetable oils, animal fats and recycled greases (also called cooking oil or yellow grease).

Argentina is now the first biodiesel exporting country. Most of Argentina's pure biodiesel (known as B100) is already exported to foreign markets, and production capacity is expected to increase 300% in the next 3 years. The biodiesel Argentine industry is mainly based on the use of soybean as feedstock. In the first 3 months of this year, the production of Argentinean biodiesel increased in 44%, to reach up 693.124 tons of this product [1].

The world production and consumption of pure biodiesel and its binary mixtures with diesel have increased substantially. In early 2010, the Argentine government allowed the commercial use of biodiesel blends. Today, the domestic market for transport fuels requires the addition of 7% (B7) of biodiesel, and in the next months is expected to increase to 10% (B10) [2].

Biodiesel/Diesel blend is a very complex mixture of thousands of individual compounds with carbon numbers between 9 and 23 (number

of carbon atoms per hydrocarbon molecule). Most biodiesel compounds are esters, glycerides, pigments and antioxidants. The diesel compounds are paraffinic, naphthenic and aromatic in different proportions.

The determinations of biodiesel quality parameters are important for end-users, engine manufacturers and petroleum refining to ensure that the biodiesel can be used directly or blended with petroleum diesel. The addition of biodiesel to diesel produces several changes in parameters such as: cetane number, color, combustion heat and sulfur content, volatility, oxidation stability, lubricity, foaming, particles (total contamination), and turbidity [3,4].

There are several papers in the literature related to the use of infrared spectroscopy and multivariate calibration for monitoring the quality of pure biodiesel (B100) obtained [5–9]. Both, near and mid infrared spectroscopy (NIR, MIR) are used to determine quality parameters in mixtures of biodiesel/diesel [10–13]. In fuel laboratories and refineries there are currently compact equipments used to determine chemical and physical properties using this technique [14,15]. Flôres Ferrão worked with HATR-FTIR (Horizontal Attenuated Total Reflectance Infrared) to determine parameters in Biodiesel/diesel blend [16]. ¹HNMR (Hydrogen Nuclear Magnetic Resonance) is frequently used to follow the biodiesel synthesis [17–19], and its correlation with NIR was also described for the determination of soybean biodiesel in diesel [5,17].

Recent works predicts the content of biodiesel in biodiesel/diesel blends using fluorescence spectroscopy [20,21]. Owing to a higher selectivity and simplicity of synchronous fluorescence spectroscopy

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(SFS), this technique has been successfully applied in our previous work to discriminate biodiesel samples with respect to the base oil employed in their production [22].

The SFS was also used to determine residual oil in diesel/kerosene mixtures [23] and to determine PACs (Poly Aromatic Compounds) in crude petroleum products such as petrol and kerosene [24].

In our previous work, the application of chemometric techniques such as SPA-MLR (Successive Projection Algorithm–Multiple Linear Regression) was used utilizing the fluorescence spectral data [25,26].

The SPA-MLR algorithm works in three stages [27–30]. First, it builds ordered chains of variables by selecting variables with the least colinearity with previous ones. It is similar in nature to the approach pioneered by Jurs et al. [31] although the mechanics of the implementation may be different. Then, MLR models for each chain of variables are built and the best model that yields the lower root mean square error (RMSE) values is selected. Finally the algorithm removes the variables that do not contribute significantly to the model. A full cross-validation leave-one-out procedure has been currently used in the SPA algorithm [27].

PLS performs data decomposition into spectral score and loading matrices prior to model building with the aid of these new variables, using spectral and concentration data. MLR yields models are simpler and easier to interpret than PLS, since this calibration technique performs regression on latent variables, which do not have physical meaning. On the other hand, MLR calibration is more dependent on the spectral variables selection.

The aim of this work is to propose a fast method to determine four main parameters (fatty acid methyl ester (FAME), Cetane number (CN), Heat of combustion (HOC), and color); that establish the quality of a commercial biodiesel/diesel blend. For that purpose chemometrics models were built by using multivariate calibration and molecular fluorescence spectroscopy.

1.1. Quality parameters of biodiesel/diesel blends

1.1.1. Quantification of biodiesel

Infrared (IR) analysis is the most widely used measurement technology for measuring biodiesel in diesel. Both EN 14078 [32] and ASTM D7371 [33] methods use infrared as the analytical method and more specifically FTIR (Fourier Transform Infrared) spectroscopy. EN 14078 involves dilution in hexane followed by a transmission measurement and comparison of the carbonyl peak height measurement against a calibration curve. The ASTM D7371 specifies an attenuated total reflectance (ATR) measurement on the neat fuel blend and a chemometric partial-least-squares (PLS) model. In the biodiesel measurement, the fatty acid methyl ester (FAME) has a characteristic absorption at 1745 cm^{-1} ($5.4\text{ }\mu\text{m}$) due to the carbonyl group. Both EN and ASTM methods specify this wavelength for the biodiesel measurement.

1.1.2. Cetane number

It is one of the most studied parameters in literature. It is defined as the measure of a diesel fuel ignition quality in a compression-ignition engine. The CN is determined by a standard engine test (ASTM D613) [34], requiring a relatively large volume of fuel sample. Also, because of the time required to conduct the test, this method cannot be used on-line to control diesel blending. Fast and reliable methods were developed to monitor CN in the refinery [35,36].

Lower CN is obtained as higher percentage of biodiesel in the sample [37]. This parameter is influenced by structural features of fatty acid alkyl esters, such as chain length, degree of unsaturation and branching of the chain [38]. Usually, the CN increases with increasing chain length, and decreases with increase in unsaturation in global biodiesel/diesel composition [3].

1.1.3. Heat of combustion gross

The so-called gross heat of combustion or “higher heating value”, also called gross calorific value, is the enthalpy of total combustion of a fuel, that means that, all carbon converted to carbon dioxide, and all hydrogen converted to water.

The precise determination of the HOC is of great interest for trading automotive diesel due to the fact that the HOC is the most important parameter for determining the price of the automotive diesel to be paid. Numerous empirical equations have been published to relate the fuel HOC to the hydrogen elemental composition of fuel as obtained by elemental analysis (ASTM D240) [39]. Another relationship could be made with chain length, instauration and molar weight [40].

1.1.4. Color

Determining the color of petroleum products is an important quality characteristic, since color serves as an indication of the degree of refinement of the material, contamination, degradation, or oxidation of diesel. This occurs when diesel is stored for long periods of time, when it is exposed to temperatures above room temperature or in the presence of moisture. Most diesel compounds, partially hydrogenated aromatic hydrocarbons, hydroxyaromatics, pyrroles, indoles, polycyclic aromatics, as well as olefins are susceptible to oxidation.

The diesel compounds associated to color measurement like indoles, cycloalkylindoles, and benzindoles (predominantly carbazoles), are polycyclic aromatics.

The methodology recommended for determining the color of automotive diesel oil samples is the colorimetry analysis according to ASTM D1500, by which a sample is introduced into a glass cell and the color of the sample is compared with an optical filter color scale [41].

2. Experimental

2.1. Apparatus

FIA Laboratory (INQUISUR, UNS-CONICET):

Spectrofluorimeter Shimadzu RF-5301, with a xenon discharge light source (150 W), was used to obtain all the spectra. Synchronous fluorescence spectra were performed using a quartz cell, $0.2\text{ cm}\times 1\text{ cm}\times 3\text{ cm}=0.6\text{ mL}$. The wavelength interval ($\Delta\lambda$) utilized was 50 nm.

PETROBRAS Laboratory (Refinery Ricardo D. Elicabe, Bahía Blanca):

PetroSpec fuel equipment (PAC) (TD PPA) is a near and mid infrared spectroscopic analyzer. PetroSpec TD PPA was used for determining FAME, CN, HOC and color.

This instrument lets the determination of above mentioned parameters with repeatability and reproducibility agree with those required by the standard ASTM Methods [14]. It has an internal library with a diverse matrix of over 600 fuels, developed globally by major fuel producers (Shell and Ethyl Corp). Table 1 shows the operational range parameters of the PetroSpec analyzer.

Table 1
PetroSpec: parameters range and performance.

	Range	Repeatability	Reproducibility
Biodiesel [% w/w]	0–15	0.1	0.3
Cetane number	30–70	0.3	0.8
Gross heat of combustion [MJ/kg]	44.100– 48.800	–	–
Color	1–5 ^a	–	–

^a ASTM color.

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