



Infrared spectroscopy and multivariate calibration to monitor stability quality parameters of biodiesel

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ABSTRACT

This paper evaluates analytical methods based on near infrared (NIR) and middle infrared (MIR) spectroscopy and multivariate calibration to monitor the stability of biodiesel. There was a focus on three parameters: oxidative stability index, acid number and water content. Ethylic and methylic biodiesel from different feedstocks were used in experiments of accelerated aging, in order to take into account the wide variety of oilseeds and feedstocks available in Brazil. Partial least squares (PLS) and multiple linear regression (MLR) models were developed. Different pre-processing techniques and spectral variable/regions selection algorithms were evaluated. For MLR models, the successive projection algorithm (SPA) was employed. Interval PLS (iPLS) and selection of variables taking into account the significant regression coefficients were used for PLS models. Results showed that both near and middle infrared regions, and all variable selection methods tested were efficient for predicting these three important quality parameters of B100, the root mean squares error of prediction (RMSEP) values being comparable to the reproducibility of the corresponding standard method for each property investigated.

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1. Introduction

Biodiesel is susceptible to degradation reactions caused by exposure to air, light, metals, heat and humidity. Oxidative and hydrolytic reactions lead to biodiesel degradation which has been monitored using the oxidative stability index, water content, acid number, iodine value and kinematic viscosity [1]. Several studies have been reported in the literature employing these parameters to monitor the stability of biodiesel produced by different feedstocks and processes during storage under various conditions [2–5].

Depending on the feedstock composition, biodiesel can contain unsaturated fatty esters which are susceptible to oxidation reactions accelerated by exposure to oxygen and high temperatures [6]. The rate of oxidation increases with the number of unsaturations in the biodiesel ester molecule: linolenic (three unsaturations) > linoleic (two) > oleic (one) > stearic (saturated). The addition of an antioxidant like butylhydroquinones or gallic compounds increases the stability of the biodiesel, but its degradation continues slowly [7].

The reference method used to measure oxidative stability employs a Rancimat apparatus, as described by the EN14112 standard. This is very similar to the determination of the stability rate in oils [1]. The induction period time is measured by the increase of conductivity caused by the formation of oxidized compounds. Alternatively, parameters related to methylic biodiesel stability were monitored by ¹H-NMR [8].

Acidity of biodiesel is an important monitoring parameter during storage because it is directly related to stability. The reference method to determine acidity, recommended by EN14214, is the EN14104, which uses an alcoholic solution of KOH for titration with phenolphthalein as an indicator. ASTM recommends potentiometric titration (ASTM D664).

Water in biodiesel can promote hydrolysis reactions to free fatty acids and cause proliferation of micro-organisms, sediment deposition and corrosion in storage tanks [9]. The reference methods for the determination of water content are the EN 12937 and ASTM 6304 which employ Coulometric Karl Fischer Titration, recommended by EN14214 and Resolution ANP 07/08, respectively. The method ASTM 2709 is recommended by ASTM 6751 [10].

The standard methods for determination of oxidative stability, acidity and water content are generally slow, expensive and require large samples, generating considerable chemical waste. In contrast, new methods like infrared spectroscopy (IR) associated with multivariate

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calibration models have been widely used in industrial process controls to predict sample properties at a low cost, taking less time and in a non-destructive way. Due to the versatility of spectroscopy in the infrared region, works have shown the viability of both near (NIR) and middle (MIR) spectroscopy to monitor the quality of biodiesel blends with conventional diesel fuel [11–16].

Several studies in the literature have also shown the use of infrared spectroscopy (MIR and NIR) and multivariate calibration to monitor the quality of pure biodiesel (B100) and conversion of the transesterification reaction [17–23]. Menezes and co-workers have developed multivariate calibration models employing NIR spectroscopy to predict parameters related to biodiesel stability [18–20]. Water content has been reported by Felizardo et al. [18] using models based on NIR spectroscopy associated with partial least squares (PLS) and principal component regressions (PCR). Baptista et al. [19] have determined iodine value and kinematic viscosity in B100 using NIR and PLS. The acid number and water content were also monitored in vegetable oils for biodiesel production using multivariate near infrared spectroscopy models [20].

Range selection performed by using interval partial least squares (iPLS) can help in searches for the spectral interval that give the most useful information to model the parameter of interest [24]. Near infrared (NIR) spectroscopy combined with spectral range selection by interval partial least squares (iPLS) has been used to determine the quality parameters of edible vegetable oils [25]. MIR infrared spectroscopy and iPLS used for the quantification of contaminants in lubricating oil was reported by Borin and Poppi [26].

The successive projections algorithm (SPA) [27], proposed as a variable selection strategy for multiple linear regression (MLR), shows the advantage of finding a small representative set of spectral variables with a minimum collinearity. SPA has been successfully applied to select variables in spectroscopy UV–VIS [27–29], NIR [30–32], LIBS [33], ICP-OES [34], among others [35,36].

The present paper evaluates the use of infrared spectroscopy in both MIR and NIR regions with multivariate calibration (PLS and MLR) to monitor three important parameters in the degradation of biodiesel (B100): oxidative stability index, acid number and water content. Strategies for selection of spectral regions and variables were evaluated. The use of IR spectroscopy to determine these parameters, as well as others already reported in the literature (such as viscosity and iodine number), can provide an economic and quick way to monitor the stability of biodiesel during storage.

2. Experimental

2.1. Samples

Considering the wide variety of oilseeds and feedstocks available in Brazil, certified biodiesel from different origins was used for stability experiments. Also with the purpose of including variety in the data set, an antioxidant was added (3000 ppm of butylated hydroxytoluene – BHT) to some samples. The data set consisted of samples of soybean ethylic biodiesel (BES), radish (*Raphanus sativus* L.) ethylic biodiesel (BER) and tallow ethylic biodiesel (BET). Additional samples of soybean methylic biodiesel with additive BHT (BMS) and without additive (BMSpure) were used. Biodiesel samples were submitted to accelerated aging for 6 weeks in a one-liter glass vessel with an open tube at the top for air intake, according to the methodology ASTM D 4625 at 43 °C in atmospheric air. Samples of 60 mL volume were collected at intervals of 3 to 4 days, corresponding to two samples per week. The total set of samples was 72 samples for acid number and oxidation stability analysis and 50 samples for water content analysis.

2.2. Reference methods

The analysis of oxidation stability index was carried out using model 743 Rancimat Mettler equipment, according to EN 14112 standard [37].

3 g of each sample were submitted to a 10 L h⁻¹ air flow at 110 °C. The acid number analysis was measured in a Metrohm Titrimo potentiometric titrator, using 20 g of the sample with 20 mL of solvent IAT (50 vol.% of toluene + 49.5% isopropanol + 0.5% water). Titration with a 0.01 mol L⁻¹ alcoholic solution of potassium hydroxide was accomplished with a silver/silver chloride glass electrode, according to ASTM D 664 standard [38]. The amount of water was measured using a coulometric Karl Fisher titration instrument, according to ASTM D 6304 standard [39], based on the reduction of iodine by sulfur dioxide in the presence of water.

The reproducibility/repeatability values stated by the standard methods are 1.40/0.56 h for oxidation stability index; 0.09/0.008 wt.% for water content and 0.21/0.065 mg KOH g⁻¹ for acid number. The variation ranges observed in the data set under consideration were 1.5 to 8.7 h for oxidation; 0.05 to 0.1 wt.% for water content and 0.14 to 0.82 mg KOH g⁻¹ for acid number.

2.3. NIR and MIR spectra acquisition

The NIR (12,000 to 4000 cm⁻¹) and MIR (4000 to 600 cm⁻¹) spectra, corresponding to the X-matrix in the calibration procedures, were obtained using a Fourier transform infrared (FT-IR) Perkin Elmer Spectrum GX spectrometer. This equipment is equipped with a Michelson interferometer and a DTGS (deuterated triglycine sulfate) 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 ATR (attenuated total reflectance) 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.

2.4. Calibration models

Calibration methods employed in this work were partial least squares regression (PLS) and multiple linear regression (MLR). All models were obtained using full cross-validation (CV) to define the number of factors (PLS) or number of variables (MLR). 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 30% of the total number of samples. Different pre-processing (derivative Savitzky–Golay, varying the number of window points of 7, 11, 15 and 21) and spectral regions were evaluated. The algorithm SPXY (sample set partitioning based on joint xy distances) was used to split the set of samples into calibration set and validation set [40]. For MLR modeling, the variables were selected through the successive projection algorithm (SPA). PLS models were built using only the variables which corresponded to the significant regression coefficients chosen by using the Jack-Knife algorithm [41] from the Unscrambler version 9.7 software. The relevance of information in different spectral subdivisions was evaluated by interval partial least squares regression (iPLS).

3. Results and discussion

3.1. Oxidative stability

The results obtained for the calibration models in MID and NIR regions for the oxidative stability parameter are shown in Table 1. In addition to the PLS models, results of MLR–SPA models as well as iPLS are showed. Only the best results from the pre-processing techniques tested are presented. The RMSEP values for the models developed using NIR spectra show no statistically significant difference (95% confidence level) between them, except for the MLR/SPA (derivative) models. RMSEP values of all models are below the reproducibility value of the ASTM reference method. Correlation coefficients ranged from 0.94 to 0.98 for all models. The number of PLS factors used for the models PLS

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