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A preliminary study on traceability of biodiesel mixtures based on the raw materials profiles from Brazilian regions and fourier transform infrared spectroscopy (FTIR)

Victor Hugo J.M. dos Santos, Víctor Z. Pestana, Jean S. de Freitas, Luiz F. Rodrigues*

Institute of Petroleum and Natural Resources, Pontifical Catholic University of Rio Grande do Sul, Av. Ipiranga, 6681 – Building 96J, 90619-900, Porto Alegre, Brazil

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ABSTRACT

There are still few initiatives studying applications for the classification of biodiesel derived from a mixture of raw materials, whether pure (B100) or mixed with diesel. The present study aims to conduct a preliminary assessment on the classification of pure biodiesel blends, and their mixtures with diesel at a proportion of 10%, based on FTIR spectroscopy and multivariate analysis. The work is contextualized around the monthly raw material consumption of Brazilian regions along a year. From this work, it is possible to verify that FTIR analysis, combined with multivariate methods, can be applied to classify both pure biodiesel blends and those mixed with diesel. The PCA showed great potential for recognizing the data patterns, while the HCA are able to discriminate the B100 blends from different Brazilian regions and cluster the samples according to the region biodiesel profile. For the B10 fuel blends, the OSC-PLS-DA achieved 100% sensitivity and specificity and can be applied for the classification procedure of biodiesel/diesel blends.

1. Introduction

One of the current environmental concerns is the use of fossil resources as the main source of raw materials and energy [1]. Because of this issue, academic research has been dedicated to finding renewable alternatives to reduce dependence on mineral resources. Within this context, biofuels have been presented as viable renewable alternatives to petroleum derivatives [2].

Biodiesel is a biomass-derived fuel, obtained through the transesterification of triglycerides with short-chain alcohols, resulting in a mixture of alkyl esters. Even though biodiesels can completely substitute for diesel oil, they are almost exclusively consumed blended with conventional mineral diesel [3–6].

Brazil has a plentiful supply of renewable raw materials, resulting from extensive agricultural production, abundant natural resources and a favorable climate, which favors investment in biofuel research [7–9]. The National Program of Production and Use of Biodiesel (PNPB), promotes Brazilian biodiesel production due the need to reduce diesel imports, meet increasing energy demand, and reduce the environmental footprint of energy generation [10,11].

The publication of Law No.11,097/2005 officially introduced biodiesel, blended with fossil diesel, into the Brazilian energy matrix, creating a mandatory and growing demand for biofuel production [12]. The initial target of 2% (B2) was reached in the early years of the program, and the current Brazilian regulatory framework (Law No. 13,263/2016) establishes a mandatory target of 10% (B10) to be reached by 2018 [11,12].

In order to meet this impending demand, the application of fast analytical methods, combined with multivariate data analysis, seems to be the best approach to perform high throughput data analysis and ensure fuel quality standards [13]. Several analytical techniques have already been applied to biodiesel assessment such as: UV–vis spectroscopy [14], digital imaging [15,16], mid-infrared spectroscopy (MIR) [17], near-infrared spectroscopy (NIR) [18], X-ray spectrometry [19], spectrofluorimetry [20], liquid scintillation counter radiocarbon analysis [21], gas chromatography–mass spectrometry (GC–MS) [22–24], nuclear magnetic resonance spectroscopy (NMR) [25,26] and isotope ratio analysis (IRMS) [27,28].

Abbreviations: FTIR, Fourier transform infrared spectroscopy; HATR, horizontal attenuated total reflectance; ASTM, American Society for Testing and Materials; PLS-R, partial least squares regression; PLS-DA, partial least squares discriminant analysis; PCA, principal component analysis; SVM, support vector machine; SIMCA, soft independent modeling of class analogy; HCA, hierarchical clustering analysis; C-SVM, C-support vector classification; OSC, orthogonal signal correction; MIR, mid-infrared spectroscopy; NIR, near infrared spectroscopy; NMR, nuclear magnetic resonance; ANP, national petroleum, gas and biofuels agency

* Corresponding author.
E-mail address: frederico.rodrigues@pucrs.br (L.F. Rodrigues).

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Among them, Fourier transform infrared spectroscopy (FTIR) spectroscopy has all of the desired characteristics for an analytical technique, being rapid and economical, generating large amounts of data, and combining perfectly with chemometrics methods [3,29]. Chemometrics methods already have been applied to fuel and oil classification. Samples of gasoline [30], conventional diesel [31–33], motor oil [34] and fuel oil (furnace oil, gas oil and mazut oil) [35] have been studied for purposes such as origin traceability, type identification, and assessment of adulterated and unadulterated samples.

Many studies of chemometrics methods combined with infrared spectroscopy, have been applied to biodiesel derived from a single source or binary biodiesel/diesel fuel blends [36–46]. When applied to the analysis of biodiesel and its fuel blends, infrared spectroscopy can be used for: adulteration control [38,47]; prediction of variables [5,48]; monitoring of the biodiesel content in fuel blends [3]; monitoring of the transesterification efficiency [49]; classification [50]; and discriminant analysis of samples [13,44,51].

For biodiesel and biodiesel/diesel fuel blend classification, several papers have been published in recent years with very diverse focuses and classification strategies [32,34–37,39–42,52]. Applied to feedstock discrimination of B100 samples, the Balabin and co-authors presented a comprehensive research on the application of NIR, combined with multivariate methods, to classify B100 samples derived from several feedstocks [41]. In addition, they also investigated the influence of the spectra pretreatment to the classification models efficiency and described the combination of Second-order Savitzky-Golay derivative, Mean Centering and Orthogonal Signal Correction as the best option [41].

More recently, Mueller and colleagues showed that mid-infrared spectroscopy was able to classify raw materials both in the base oil and in the derived biodiesel [51], while Mazivila and colleagues have broadened the discussion to the potential of Mid Infrared Spectroscopy and chemometrics model to simultaneously discriminate the samples according to their base oil and synthetic route (methylic or ethylic) [53].

Other works focused the research in the ability of the infrared spectra to discriminate the biodiesel/diesel blends sample in respect to its feedstock. Máquina and co-authors conducted a classification study of B7 blends based on the PLS-DA model and obtained 100% accuracy [54], while Mazivila and co-workers identified the raw materials of biodiesel samples, blended at the ratio of 5% (v/v) with conventional diesel. Through the use of mid-infrared spectroscopy and a partial least squares discriminant analysis (PLS-DA) model, they were able to discriminate samples by raw material and synthetic route (methyl or ethyl ester) [44].

In a different approach, Santos and colleagues investigated the ability of the FTIR, regardless of the concentration of biodiesel in the blend, to identify the samples base oil [13]. This approach was applied to three ranges based on the biodiesel content: SET A (B0-B10), SET B (B10-B30) and SET C (B30-B100). As results, the fuel blends ranging from 0.5% to 20% biodiesel are discriminated, according to the sample raw material (soybean or corn), by the chemometrics tools: soft independent modeling of class analogies (SIMCA), PLS-DA and support vector machines (SVM).

In Brazil, a great diversity of raw materials are used to compose its biodiesel production matrix and, very often, the biofuel mixed with conventional diesel is derived from more than one source [55]. The complementary blending of biodiesel derived from different sources is a common practice and are conducted to balance the fuel properties and to meet the technical requirements for application in internal combustion engines [56,57]. Some recent studies investigated the influence of complementary blending on properties such as oxidative stability [57,58], cold flow behavior [57] and engines emission profile [56]. However, only a few works reports the application of chemometrics methods in the analysis of raw material mixtures, such as vegetable oil blends [59], biodiesel mixtures [60,61], and biodiesel blends with diesel [61].

Flores and co-workers used the proton nuclear magnetic resonance spectroscopy (^{1}H NMR) and PCA to discriminate pure samples and binary mixtures of soybean, cotton, peanut, castor, tallow and pinion biodiesel and they were able to identify many of the mixtures through the diallylic hydrogen chemical shifts [60]. In a different approach, Filgueiras, Alves and Poppi [61] applied NIR spectroscopy and SVM regression for evaluation of the animal fat content in a pure binary blend with soybean biodiesel (B100) and in the same blend diluted with diesel (B20). NIR spectroscopy and the support vector machine regression tool successfully quantified the animal fat both in the pure blend (B100) and in the diesel mixture (B20).

Considering that taxes on products and services differ between states, especially for the north and northeast regions, the identification and traceability of the fuel flow are fundamental to financial issues [31,55,62]. In addition, the Brazilian law (Decree Nº 7,768, 27 June 2012) introduce a differentiated tax system by reducing the PIS/PASEP and COFINS federal taxed to encourage: i) the use of palm or castor oil in the North, Northeast and Semi-arid regions and ii) the use of raw materials purchased from family farmers in PRONAF (National Program for Strengthening of Family Farming), updating the aliquots initially regulated by the Decree Nº 5,297, 6 December 2004, and the benefits established by the Social Fuel Seal (SFS). However, there are some misapplication of these tax benefits, since it is common not to find information about the fuel origin in the gas stations [31] and the dysfunctions identified in the SFS operation [55,63].

Since Brazilian biodiesel production is concentrated in the south and center-west regions, and due the range of different raw materials and biodiesel production processes, there are concerns related to quality control and fuel traceability [31]. Until now, there are still few initiatives studying applications for the classification of biodiesel derived from the complementary blending of different raw materials, whether pure (B100) or mixed with diesel. In this way, the development of fast and low-cost methods can be important tools to combat tax evasion, avoid the granting of undue tax benefits, and in controlling the interregional flow of biodiesel and diesel fuel.

Considering the vast Brazilian territory, the use of raw materials for biodiesel production, the tax benefits provided by Brazilian law, and the complementary blending practice, the aim of this work was to conduct a preliminary study on the traceability of biodiesel derived from multiple sources and classify the blends according to the Brazilian regions fuel profiles. The procedure will be carry out through the application of mid-infrared spectroscopy in combination with multivariate methods, while the biodiesel samples were prepared according to the local consumption of raw materials as reported by the National Petroleum, Gas and Biofuels Agency (ANP).

2. Materials and methods

Brazil is divided into five macro-regions: Center-West, Northeast, North, Southeast and South. According to the ANP of Brazil, current production has reached a volume of 20,930.81 m^3 per day, produced by 51 plants unevenly distributed among the Brazilian regions [64]. Fig. 1 shows the Brazilian regions, their productive potential, the number of plants and their respective locations, while a detailed analysis of the structural evolution and characteristics of biodiesel production in Brazil is provided by the Moreno-Pérez, Marcossi and Ortiz-Miranda [55].

An important aspect of the Brazilian biodiesel law is that there is no limitation on the source of the raw material or the industrial biodiesel production process, which allows a diversity of raw material supplies [12]. Therefore, the demand for raw materials depends the available sources in each Brazilian region. Nonetheless, the current main Brazilian biodiesel feedstocks are soybean (65%) and tallow (15%) oils, which are complimented by canola, castor seed, cottonseed, palm and waste cooking oils [9].

The work will be contextualized based on the monthly raw material consumption profiles of the Brazilian regions, observed over a year. The