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A new spectrophotometric method for determination of biodiesel content in biodiesel/diesel blends

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HIGHLIGHTS

- The new method allows the determination of biodiesel content in diesel blends.
- It is applied in a large range of biodiesel content in biodiesel/diesel blends.
- It is applicable to colorimetric device operating at 420–440 nm wavelength range.

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ABSTRACT

In this paper a new quantitative analytical method is described for determining the biodiesel content in biodiesel/diesel mixture through of the fatty acid methyl ester reaction with hydroxylamine hydrochloride and iron(III) nitrate. The ferric hydroxamate complex diluted in n-heptane was analyzed by UV–visible spectroscopy in a range of 420–440 nm wavelength to determine the biodiesel content in biodiesel/diesel blends. The method has shown excellent repeatability and linearity for determining biodiesel content in biodiesel/diesel blends in the 0.5–5.0% quantification range and in small intervals of biodiesel content in diesel oil (0.1%). For levels over 5% of biodiesel in biodiesel/diesel blends, the linearity and repeatability is also excellent but it is necessary to increase the dilution of n-heptane of the ferric hydroxamate complex to still obtain a linear relationship between concentration and absorbance. The results obtained for biodiesel produced from different feedstocks are very similar, except for biodiesel produced from castor oil, what means that the method purposed has low influence of the feedstock used in biodiesel production. The parameters evaluated indicate that the method proposed is analytically reliable for determining biodiesel content in biodiesel/diesel blends.

1. Introduction

Fatty acid alkyl esters, known as biodiesel, may be obtained from vegetable or animal fat and oils. The acyl group chain of the esters produced normally ranges from 12 to 24 carbon atoms and the number of unsaturated bonds normally ranges from 0 to 3, both chain length and unsaturation varies significantly depending on the feedstock used. Biodiesel can be blended with petroleum-derived diesel fuel. For instance, currently Brazil determines a 5% biodiesel rate by volume in the biodiesel/diesel blend (BDB) but, in the initial stage of the Brazilian Program of Production and Usage of Biodiesel (PNPB) 2%, 3% and 4% BDB were also used, such as in many countries which are starting the utilization of BDB as a fuel [1].

In view of the wide range of feedstock available for production biodiesel [2], in which the biodiesel have been produced with varying characteristics, the quality assessment of biodiesel and BDB is a crucial stage to ensure production reliability as well as the fuel's use in diesel engines. To achieve for the required quality parameters, considerable technical–scientific researches have been carried out in the new methods development to ensure the reliability of results [3,4]. Several studies have reported the determination of biodiesel content in diesel, including the use of techniques such as infrared (IR) spectroscopy, ^{1}H NMR and chromatography [5–10]. However, many of them do not show selectivity [5], whereas others may be applicable only in restricted BDB concentration intervals or employ costly [7], slow techniques that require high reagent consumption [8–10].

Determining biodiesel content in diesel may be performed by IR spectroscopy, as states Brazilian technical standard NBR 15568 [10], but in association with multivariate analysis. Data generated

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by Fourier Transform Infrared Spectroscopy (FTIR) is analyzed using chemometric methods, and specialized human resources are required in view of the considerable amount of data produced by these methods [11]. In addition, IR spectroscopy is usually more costly than techniques such as ultraviolet–visible (UV–Vis) spectroscopy [12].

Nuclear Magnetic Resonance (NMR) is an excellent technique for determining biodiesel content with high correlation coefficients in a broad quantification range. However, this is technique that requires employ costly [6].

UV–Vis spectroscopy has been used to determine the content of large, heptane-diluted BDB concentration intervals. For biodiesel, UV spectra show two intense absorption bands along the 230–260 nm wavelength. Variation in the composition of diesel aromatics may falsify results, given the fact that they show intense absorbances in these spectral regions. This method proved to be non-applicable to short BDB concentration intervals [7]. Nevertheless, UV–Vis spectroscopy provides easier and faster results in routine analyses, due to reduced analysis time and lower reagent consumption. Despite all these methods, research studies continually attempt to develop alternative methods, combining low cost and fast and accurate results. Amid efforts to develop a methodology that is capable of meeting all necessary requirements, UV–Vis spectroscopy may be a potential tool to quantify biodiesel content in BDB.

In this sense, an experimental procedure known as hydroxamic acid test is traditionally used to confirm the ester functional group [13]. Hydroxamic acids form basic compounds for the qualitative determination in colorimetric analyses of metal ions [14]. They are produced by a nucleophilic reaction between a carboxylic acid derivative and hydroxylamine in an alkaline medium [15]. Among the features of hydroxamic acids is their ability to form stable complexes with transition metals, particularly iron(III) ions [16]. All hydroxamic acids from *N*-hydroxylamine react with iron(III), resulting in mononuclear complexes with *O,O*-hydroxamate bidentate ligands in octahedral geometry (Fig. 1) [17,18].

Towards developing a technique that is low-cost, easy to perform, and which requires only standard instruments and reagents, this article proposes a modified version of the hydroxamic acid test to determine biodiesel content in BDB via the reaction of esters with hydroxylamine chloride in an alkaline medium. According to this version of the method, esters are subsequently complexed with iron(III) ions and heptane-extracted, prior to UV–Vis spectrophotometric analysis [19].

2. Material and methods

2.1. Reagents

All analytical reagents used were manufactured by Tedia Brazil®. Deionized ultra-pure water was used to prepare NaOH, HCl, NaCl, and $Fe(NO_3)_3$ reagent solutions. Ethanol was used to prepare an $NH_2OH{\cdot}HCl$ solution. Diesel oil A S500, according to Resolution n° 50 of the ANP is a distillate fuel for use in diesel engine applications requiring a fuel with 500 mg kg^{-1} sulfur (maximum) and without previous addition of biodiesel was provided by ALESAT, Goiânia, Goiás State, Brazil. Biodiesel was produced from commercial vegetable oils made of canola, sunflower, corn and soy. Biodiesel made of peanut, castor oil, and jatropha were produced with vegetable oils extracted from the seeds.

The biodiesel samples were prepared by transesterification reaction, and the percentage of each individual fatty acid present in each feedstock (Table 1) was determined by Hartman and Lago method [20] followed by gas chromatographic analysis determined by Menezes et al. [21]. The quality control of each biodiesel produced from such feedstocks was determined according described by Prados et al. [22].

2.2. Calibration curve

Volumetric blends of methyl biodiesel and diesel were prepared in 100 mL calibrated volumetric flasks. Different BDB of soybean biodiesel in diesel were prepared and assessed in 0.0%, 0.5%, 1.0%, 1.5%, 2.0%, 2.5%, 3.0%, 3.5%, 4.0%, 4.5% and 5.0% (v v^{-1}) concentrations of biodiesel to determine the calibration curve. Assays involved the preparation of volumetric blends in BDB contents over of 5.0% (v v^{-1}), to verify whether the proposed method shows linearity at levels over 5.0%, in which, the first calibration curve ranged in 5.0%, 6.0%, 7.0%, 8.0%, 9.0% and 10.0% (v v^{-1}), the second in 10.0%, 11.0%, 12.0%, 13.0%, 14.0%, 15.0% and 16.0% (v v^{-1}), and the third in 16.0%, 17.0%, 18.0%, 19.0% and 20.0% (v v^{-1}), following criteria related to the amount of BDB used and to the dilution in heptane. Volumetric blends were also prepared in short

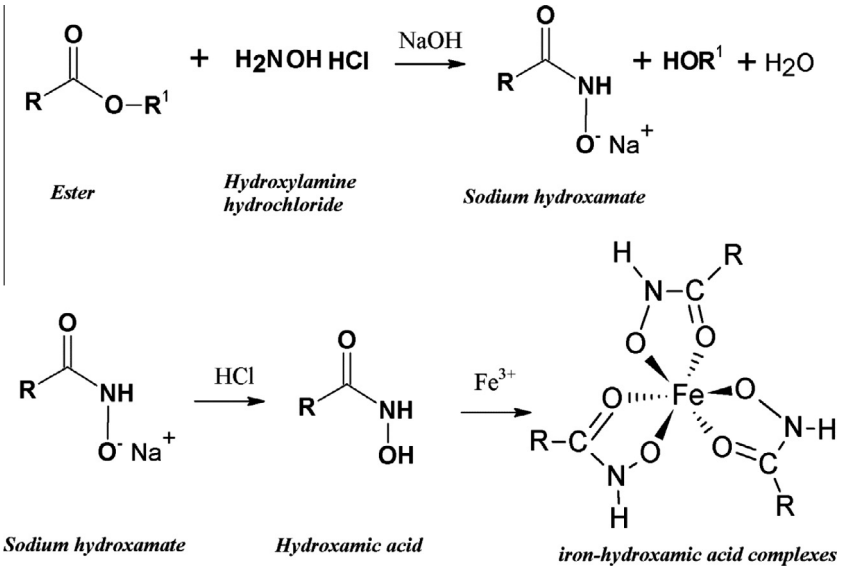

Fig. 1. Chemical reactions involved in the hydroxamic acid test.