Liquid–liquid microextraction in a multicommuted flow system for direct spectrophotometric determination of iodine value in biodiesel

Andréia C. Pereira, Fábio R.P. Rocha *

Centro de Energia Nuclear na Agricultura, Universidade de São Paulo, P.O. Box 96, Piracicaba, SP 13400-970, Brazil

HIGHLIGHTS

- First flow-based procedure for iodine value determination in biodiesel.
- Simple, fast and reliable procedure.
- Detection without sample pretreatment or phase separation.
- Liquid–liquid microextraction with low sample and reagent volumes.
- Avoid toxic reagents and organic solvent used in the reference procedure.

GRAPHICAL ABSTRACT
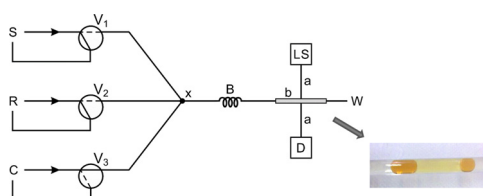
ABSTRACT

A flow-based procedure was developed for the direct spectrophotometric determination of the iodine value (IV) in biodiesel. The procedure was based on the microextraction/reaction of unsaturated compounds with triiodide ions in an aqueous medium by inserting the reagent solution between the aliquots of biodiesel without any pretreatment. The interaction occurred through the biodiesel film formed on the inner walls of the hydrophobic tube used as the reactor and at the aqueous/biodiesel interfaces. The spectrophotometric detection was based on the discoloration of the I_3^- reagent in the aqueous phase by using a glass tube coupled to a fiber-optic spectrophotometer as the detection cell. Reference solutions were prepared by dilution of biodiesel samples with previously determined IV in hexane. The analytical response was linear for IV from 13 to 135 g I_2/100 g with a detection limit of 5 g I_2/100 g. A coefficient of variation of 1.7% ($n = 10$) and a sampling rate of 108 determinations per hour were achieved by consuming 224 μL of the sample and 200 μg of I_2 per determination. The slopes of analytical curves obtained with three different biodiesel samples were in agreement (variations in slopes lower than 3.1%), thus indicating an absence of any matrix effects. Results for biodiesel samples from different sources agreed with the volumetric official procedure at the 95% confidence level. The proposed procedure is therefore a simple, fast, and reliable alternative for estimating the iodine value of biodiesel.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

The successful introduction of biodiesel as a fuel has been accompanied by the establishment of standards to ensure product quality [1]. Biodiesel must be within a rigid series of physico-chemical parameters recommended by the regulatory agencies in order to improve performance and avoid environmental pollution. These standards tend to become increasingly restrictive, requiring the improvement of both production processes and the analytical procedures for quality control [2].

The oxidative stability of biodiesel is directly related to the degree of unsaturation of its alkyl esters. The oxidation of

* Corresponding author. Tel.: +55 19 3429 4778; fax: +55 19 3429 4610.
E-mail address: frprocha@cena.usp.br (F.R.P. Rocha).

unsaturated fatty compounds is fostered by the number and position of the double bonds. Iodine value (IV) is used to measure the total degree of unsaturation in biodiesel [3], and is therefore an important parameter for quality control. The greater the number of unsaturation, the higher the molecule susceptibility is to degradation in thermal and oxidative ways. These reactions form insoluble products that cause fouling and clogging of the fuel injection system of the engine. It also affects the density and viscosity of the biodiesel and thus its performance as a fuel [3,4].

IV is a chemical parameter based on the reactivity of unsaturated fatty acids. The recommended procedure for its determination in biodiesel is based on the Wijs' method [5], in which an excess of iodine monochloride is added to the sample for the halogenation of double bonds, and then the excess of reagent is titrated with $Na_2S_2O_3$. The results are expressed as the equivalent mass of iodine (I_2) consumed per 100 g of sample. This procedure requires sample solubilization in a suitable organic solvent (e.g., carbon tetrachloride) and a minimum reaction time of 1 h in the dark. It is then time-consuming, expensive and yields large amounts of toxic wastes. Another drawback is the exposure of the analyst to the toxic vapors of organic solvents, and this becomes even more critical in large-scale analysis.

Alternative procedures for IV determination in biodiesel have been reported in the literature [6–9]. Friedmann's method for oils and fats was adapted for determination of IV in biodiesel employing ethanol as solvent and iodine solution as reagent with visual [6] or potentiometric [7] detection. Despite their good analytical performance, these procedures are susceptible to errors due to the various steps involved and the risks of iodine losses by volatilization. Procedures using gas chromatography [8] or ^{1}H RMN [9] are also described; however, these techniques involve high implementation and operational costs.

The need for reliable and greener analytical procedures has encouraged the development of alternatives to replace the conventional methods that show environmental restrictions. In this sense, flow analysis allows the development of rapid and reproducible analytical procedures with minimum reagent consumption and effluent generation [10]. Moreover, sample processing occurs in closed systems, which avoid the loss of volatile species and minimize exposure of the analyst to hazardous substances [11]. Despite these advantages, a few automated procedures have been proposed for fuel analysis [12], and none for IV determination in biodiesel.

Automation of liquid–liquid extraction allows the replacement of several manual operations susceptible to systematic errors and risks of analyte losses, as well as reduces costs, analysis time, and consumption of organic solvents [13,14]. In this sense, flow-based liquid–liquid microextraction has successfully overcome the drawbacks presented by the conventional processes [15,16]. In this work, a flow-based analytical procedure for the determination of iodine value was developed. The proposed procedure exploited liquid–liquid microextraction and reaction of the unsaturated compounds with triiodide followed by spectrophotometric detection in the aqueous phase. Multicommutation [11] was exploited for automation of the procedure with the aim to improve sampling rate and reproducibility and to minimize reagent consumption and waste generation.

2. Experimental

2.1. Apparatus

The multicommuted flow system was designed with a peristaltic pump (Ismatec, Glattbrugg, Switzerland; model CP 78017-10) equipped with Tygon^{TM} and Viton^{TM} tubes for fluids propelling, three-way solenoid valves (NResearch, West Caldwell,

NJ, USA; model 161T031), and Teflon^{TM} confluence/tubes (0.8 mm i. d.). The manifold was controlled by a microcomputer through a parallel interface coupled to a current drive based on an ULN2803 integrated circuit. Control software was developed in Visual Basic 6.0 (Microsoft, Redmond, WA, USA). Spectrophotometric measurements were carried out with a multi-channel CCD spectrophotometer (Ocean Optics, Dunedin, FL, USA; model USB2000) with a tungsten-halogen light source (Ocean Optics, LS-1) and optical fibers to transport the radiation. Data acquisition was carried out with the software supplied by the manufacturer of the equipment. The detection cell consisted of a glass tube (5 cm length and 4 mm i. d.) fixed to a cuvette holder for common 1-cm flow cells, also supplied by Ocean Optics (CUV-UV holder). The optical fibers were connected to the cuvette holder and the measurement cell was manually aligned to maximize the incidence of radiation.

2.2. Reagents and solutions

All solutions were prepared with deionized water and analytical grade chemicals. The reagent was a 5 mmol L^{-1} I$_2$ solution daily prepared by dissolving the reagent in 0.1 mol L^{-1} KI. Biodiesel samples with their iodine value determined by the reference method [6] containing 135 and 115 g I$_2$/100 g were used for the optimization of the procedure and to prepare reference solutions by dilution with hexane (10–100%). Water was used as carrier and ethanol was used to wash the system. Biodiesel samples from different fat sources (bovine fat, soybean and cotton oils) were directly analyzed without any pretreatment.

2.3. Proposed procedure

The flow system for iodine value determination (Fig. 1) was operated according to the routine described in Table 1. The analytical cycle started with the insertion of the first aliquot of biodiesel or reference solution into the analytical path (step 1) followed by the aqueous I$_3^-$ reagent (step 2) and by the second biodiesel aliquot (step 3) in tandem. The I$_3^-$ solution was then sandwiched between the aliquots of biodiesel without any pretreatment. The sample zone was transported towards detection by the water carrier (C). The reference absorbance signal was obtained in the absence of unsaturated compounds by replacing the sample with hexane. The analytical signal was obtained by the difference between the absorbance values for the reference and sample, both measured at 450 nm. All measurements were carried out in triplicate. The calibration curve was obtained with the reference solutions prepared from the
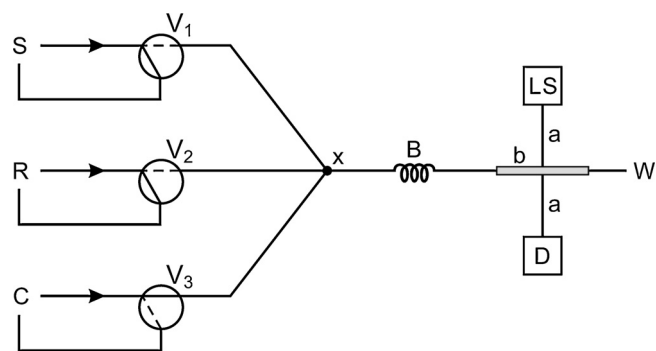
Fig. 1. Multicommuted flow manifold for iodine value determination in biodiesel. S: biodiesel or reference solution; R: 5.0×10^{-3} mol L^{-1} I$_3^-$ in 0.1 mol L^{-1} KI; C: carrier stream (water); V$_1$–V$_3$: three-way solenoid valves; x: confluence point; B: reaction coil (150 cm long and 0.8 mm i.d.); a = optical fibers; b = flow cell (5 cm long and 4.0 mm i.d. glass tube); LS = tungsten-halogen light source; D = multi-channel spectrophotometer; W = waste vessels. Flow rates: 1.0 mL min^{-1} (sample and reagent) and 0.6 mL min^{-1} (carrier).