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Comparing a novel voltammetric method with a standardized method for quality control of biodiesel

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ABSTRACT

Biodiesel is a strong candidate to replace diesel and has its origin in renewable resources. The guarantee of biodiesel quality is a matter of utmost importance in order to take its place in the global energy matrix. One of the parameters that stand out in the monitoring of its quality is the acid number. The evaluation of this parameter is of paramount importance by considering the raw material used in the production of biodiesel up to its storage, since the presence of free fatty acids leads to the formation of deposits in the injector nozzles. The standardized method in Europe, Brazil and the USA is based on potentiometric titration, using KOH as a base. This method has some drawbacks such as long analysis time, parallel reactions with possible contaminants or additives, etc. Recently, our group proposed a method based on the voltammetric reduction of 2-methyl-1,4-naphthoquinone in the presence of acids. The generated pre-peak current is proportional to the concentration of acids in the medium. This paper reports a comparison of the conventional and our method considering analysis conditions, repeatability, limits of detection and quantification, recovery, selectivity, reproducibility and determination of acidity in various biodiesel samples.

Introduction

The advent of the industrial revolution established the use of fuels to operate industrial machinery, cars, trucks and other means of transportation. In this sense, fossil fuels derived from petroleum were the main energy source used and thenceforward still play a major role in the world's energy matrix. Today, we are experiencing the deleterious effects caused by these fuels: emissions of greenhouse gases and gases responsible for acid rain, discharge of carcinogenic compounds in the environment, etc. The non-renewable character of these energy sources is another fact that raises concern [1,2].

This alarming scenario has prompted the research to develop energy sources that are clean and renewable, i.e., sustainable energy sources. For instance, biodiesel is one of the strongest candidates to replace diesel oil, since its production is based on oilseeds or animal fats, which are renewable sources. Several advantages can be identified in biodiesel over diesel fuel, for instance, it emits less CO and CO_2 to the atmosphere due to an almost complete combustion reaction and to the absorption of CO_2 by oilseed plants. The risk of generating acid rain is also diminished by the use of biodiesel, which is almost free of sulphur in its composition [1,3,4]. It has higher lubricating power, 66% better than petrodiesel, and presents a higher value of flash point (423 K) than diesel (337 K), making it more secure for handling and storage [2].

Hence, the quality control of biodiesel is of uppermost importance, and several constraints in certain physico-chemical and chemical parameters must be respected. The Brazilian resolution no. 14 of ANP specifies which tests, methodologies and limiting values must be met for this control [5]. In the U.S., ASTM D6751 performs this role, as well as EN 14214 in Europe.

The acid number is a parameter of great importance for quality control of biodiesel and is expressed as the amount of mg of KOH to neutralize the fatty acids in 1 gram of sample. Free fatty acids, especially polyunsaturated, show a greater tendency to

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self-oxidation, generating oxidation products that decrease the oxidative stability of biodiesel and form polymers (gum generators) that contribute to engine wear and corrosion [1,2,6,7]. One way to monitor the quality of biodiesel during storage is to evaluate its acidity, which increases with storage time [6]. Some degradation products of biodiesel are generated by oxidation of free fatty acids, yielding carboxylic acids. It is also observed that the presence of water favours the hydrolysis reaction of methyl esters, the product of this reaction is nothing more than a free fatty acid. Thus, it is essential to control this parameter in the biodiesel production chain.

The standards adopted for the quantification of the acid number are the American ASTM D664 or the Brazilian NBR 14448 [8,9], which are both based on the determination of the equivalence point by potentiometry, and the European EN 14104 [10], which is different from both by using phenolphthalein as an acid–base indicator to visually indicate the end of the titration. A quantity of approximately 20 g sample is diluted in a solution of toluene and propan-2-ol and titrated with a solution of 0.1 mol L^{-1} KOH dissolved in propan-2-ol. The acids contained in this solution are neutralized, and the value obtained corresponds to the acid number of the sample. However, this method is non-selective because it neutralizes other substances that can react with KOH in addition to the free fatty acids, which will be counted in the acid number final value. The potentiometric method has limitations since the organic medium in which we perform the titration leads to a dry glass membrane of the electrode and, consequently, to slower and less accurate determinations [11]. To keep the pH electrode in good working conditions, one must immerse it in 0.1 mol L^{-1} HCl for at least 5 days for its recovery [11]. Furthermore, overuse and toxicity of toluene and isopropanol render these methods undesirable to the environment [12,13]. Regarding this matter, there is a modified potentiometric method wherein the solution of toluene and propan-2-ol was substituted by the solution of ethanol and water and the titrant solution of 0.1 mol L^{-1} KOH dissolved in propan-2-ol by 0.02 mol L^{-1} NaOH in water. The authors were shown that both methods (standardized and modified) are equivalents [14].

In attempt to overcome the disadvantages of the standardized methods, several instrumental methods such as gas chromatography (GC), infrared Fourier transform (FTIR), high performance liquid chromatography (HPLC), ultramicro colorimetric method, and nuclear magnetic resonance (NMR) has been proposed recently. Nearly all of them require a chemical modification of the sample for analysis [15,16].

A simpler alternative method for this measurement relies on the voltammetric reduction of 2-methyl-1,4-naphthoquinone (vitamin K3—electrochemical mediator) in an ethanolic solution in the presence of acids on the surface of a glassy carbon electrode (working electrode) [17].

In aprotic solvents, the voltammogram of quinones presents two cathodic peaks separated by approximately 0.7 V. The appearance of the two peaks is due to the reduction of quinone, Q, to the radical $Q^{-\bullet}$, which undergoes a further reduction to the Q^{2-} species [17]. The potential at which these reductions takes place is related to the solvent polarity [18–20], the nature of the supporting electrolyte [17,21,22] and the presence or absence of acids [23]. Compounds with a pK_a above 10 (for example, alcohols) are able to form hydrogen bonds that occur without proton transfer and thus interact with Q^{2-} species [23]. This interaction will shift the peak of the second reduction to more positive potentials, according to the acid concentration, until it merges with the first reduction peak, which remains unshifted. In the presence of carboxylic acids, the mechanism of this reaction changes, resulting in a new peak that appears before the first reduction peak, called a pre-peak, whose height is proportional to the acid concentration [15,24,25]. These acids are capable of protonating the $Q^{-\bullet}$ species, which explains the appearance of the pre-peak at a more positive potential, showing that it is easier to protonate this reduced species. The reactions involved are [25]:

$$Q + e^- \rightleftharpoons Q^{-\bullet} \quad (1)$$

$$Q^{-\bullet} + H^+ \rightleftharpoons QH^{\bullet} \quad (2)$$

$$QH^{\bullet} + e^- \rightleftharpoons QH^- \quad (3)$$

The height (current) of the pre-peak originated from the presence of fatty acids is proportional to the concentration thereof. By the construction of an analytical curve ($i\,(A) \times C\,(\text{mol L}^{-1})$), it is possible to determine the acid number of biodiesel [17]. The half-peak potential of the pre-peak shifts to a negative value along with an increase in pK_a of the added acid [26], and its height is virtually independent of pK_a but proportional to the acid concentration [27]. This voltammetric method by the quinone reduction was studied for determining the total acidity of beverages [27,28], the free fatty acid content in fats and oils [28] and biodiesel samples [17].

This paper aims to make a comparison between the conventional method and the proposed voltammetric method, evaluating the limit of quantification, repeatability, reproducibility, recovery, accuracy, selectivity, analytical conditions and values of acid number in biodiesel samples by both methods.

Experimental

Materials

All reagents used were of analytical grade and were used without further purification. Palmitic acid (98%), lauric acid (99%), linoleic acid (90–100%), ethanol, acetone, lithium perchlorate and concentrated hydrochloric acid were purchased from VETEC. USP-grade menadione (2-methyl-1,4-naphthoquinone, vitamin K3) was purchased from SIGMA-ALDRICH. Gas for dissolved oxygen removal: Nitrogen 5.0 analytical (WhiteMartins); Antioxidants: BHT (butylated hydroxy toluene), PrG (propyl gallate), BHA (butylated hydroxyanisole), PG (Pyrogallol) and TBHQ (*tert*-butylhydroquinone) were acquired from SIGMA-ALDRICH and had purities greater than 97%.

Preparation of standard solutions

Standard solutions of fatty acids were prepared in acetone to obtain the analytical curve. Fatty acid standards were used to evaluate the recovery of the methods. The selectivity was analyzed by employing biodiesel samples doped with the aforementioned antioxidants. All solutions were sealed and stored under refrigeration.

Apparatus

Voltammetric method

The experiments were conducted using the AUTOLAB model μautolab type III potentiostat with the General Purpose Electrochemical System Version 4.9-Ecochemie software equipped with a 3 mm diameter glassy carbon electrode purchased from Metrohm as the working electrode, a Ag/AgCl/3 mol L^{-1} KCl system as the reference electrode and a platinum wire as the auxiliary electrode.

Potentiometric method

The potentiometric titrators of Metrohm (models 848 Titrino plus and 751GPD Titrino) were employed according to the standardized potentiometric method. They were equipped with a Metrohm stirrer and an electrode system with a combined glass