ARTICLE IN PRESS

INTERNATIONAL JOURNAL OF HYDROGEN ENERGY XXX (2013) 1–5

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Short Communication

Evaluation of the dielectric properties of biodiesel fuels produced from different vegetable oil feedstocks through electrochemical impedance spectroscopy

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ARTICLE INFO

Article history:
Received 10 April 2013
Received in revised form
14 May 2013
Accepted 16 May 2013
Available online xxx

Keywords:
Biodiesel
Vegetable oil
Impedance spectroscopy
Dielectric properties
Viscosity

ABSTRACT

Biodiesel fuels were prepared from different vegetable oil sources (canola, soybean, sunflower, and corn) and studied through electrochemical impedance spectroscopy. The dielectric constant from these biofuels evidenced no important dependence on feedstock, suggesting basically no change in fuels' polarity from varying the raw materials. In a different way, huge variations of the electrical resistivity and relaxation frequency were found when comparing among the studied biodiesels. Our findings demonstrate that these variations are closely associated with changes in the biodiesel viscosity, which is known to modulate charge mobility and was feedstock dependent. Accordingly, the impedance spectroscopy is here revealed to be a sensitive, alternative and reliable analytical approach for distinguishing among different feedstock-related biodiesels and monitoring certain biofuels' properties, like viscosity and interrelated parameters, usually connected with fatty acid structural profiles in biodiesel fuels.

1. Introduction

In order to reduce the environmental pollution related to carbon dioxide emission, a special attention has been given, in recent years, to motivate and introduce the use of biofuels to partially or completely replace petroleum-derived diesel [1,2]. This is the case of biodiesel which is an environmentally friendly, biodegradable, and renewable fuel with excellent engine performance [2]. Biodiesel generally consists of fatty acid methyl or ethyl esters (FAME or FAEE, respectively), and can be easily produced from vegetable oils as well as animal fats, usually by the transesterification reaction with an alcohol (methanol or ethanol) in the presence of a catalyst [3]. The transformation of vegetable oil to its biodiesel results in

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http://dx.doi.org/10.1016/j.ijhydene.2013.05.086

an important reduction in viscosity, which is verified to be dependent on the type of oil used as raw material [4–6]. Fuel viscosity is a very important parameter because high viscosity may induce excessive fuel injection pressures during engine warm-up as well as starve the engine for fuel at low temperatures as the fuel moves slowly through the fuel filter and fuel lines [7]. Aiming to evaluate the biofuel quality and to monitor the production process, there has been a need of developing or improving analytical methods to assess, as closely as possible, the physico-chemical properties of biodiesel. To illustrate, Fourier transform mid-infrared (FT-IR) spectroscopy [8], viscosity measurements [4] and fluorescence spectroscopy [9] have been applied to monitor conversion effectiveness of oil into biodiesel.

Although the current standards for analysis of biodiesel and diesel do not yet include dielectric characterization [10], there has been an increasing number of works exploring and suggesting the use of this method to also evaluate biofuel properties. In this way, electrochemical impedance spectroscopy (EIS) has been proposed as a relatively simple and non-invasive way to characterize biodiesel, diesel and their blends [11–13]. The data obtained from using this technique allows a close determination of physical magnitudes like fuels' dielectric constant, resistivity and relaxation time or frequency. These properties have shown to be fairly sensitive to certain internal characteristics of fuels, strongly encouraging application of EIS in studies involving biodiesel and/or diesel, including monitoring biofuel production processes and evaluation of quality of the final products [11–13].

Of course, as a large compositional variability exists across the range of feedstocks from which biofuels can be produced, it is clear that differences in the physico-chemical and mechanical properties among the synthesized biofuels may have an important impact on the combustion engine operation [2,7,14]. Such properties are mostly modulated by the FAME or FAEE structural features, including, especially, chain length and degree of unsaturation. For this reason, the present work has considered measuring the dielectric and viscosity properties of biodiesels produced from different vegetable oil feedstocks, with the purpose of performing a comparative analysis between electrical, dielectric and mechanical behaviors in such biofuels. Motivation for achieving this comparative study also lies in the fact that, for some reasons including climate and vegetable sources availability, the kind of biodiesel currently produced for use elsewhere differs around the world [15]. Concretely, our findings show the existence of a strong correlation between certain (di)electrical properties and viscosity, revealing that EIS can in fact be applied for sensing different feedstock-related biofuels and has, therefore, a really great potential for also assessing the conversion of any given vegetable oil into its biodiesel.

2. Materials and methods

Canola, sunflower, corn and soybean biodiesel fuels were obtained here via methanolic route by transesterification process from their respective refined oils by using a 6:1 M ratio of methanol/oil as described in details in our previous papers [9,16]. The NaOH catalyst (0.4 wt. % with respect to oil weight) was dissolved in methanol and then poured into a beaker containing the oil preheated at 60 °C. The reaction was performed under constant stirring during 60 min at 60 °C, and then placed in separating funnels for 24 h. After that, two phases were observed: one containing mostly biodiesel and the other consisting of glycerol. Both phases were separated, and the biodiesel was rotary-evaporated under reduced pressure during 1 h at 70 °C to eliminate methanol excess. Then, the biodiesel was washed three times using tap water (3:1, v/v) at room temperature and intervals of 30 min. At the end, the biodiesel samples were filtered through sodium sulfate to eliminate traces of water. One of the methods used here to monitor the effective conversion of oil to biodiesel consisted in performing viscosity measurements, for which final values lower than 7 cP are expected [4]. The viscosity data were collected at room temperature (~26 °C) using a DV-III Ultra Rheometer (Brookfield). Fluorescence (not treated here) was the other analytical method we used for assessing the conversion of oil into biodiesel, as previously reported [9]. In addition, in the present work, the biodiesels were electrically characterized, also at room temperature, by measuring their impedance, $Z^*(\omega) = Z'(\omega) - jZ''(\omega)$, using a Solartron Model SI 1260 impedance/gain-phase analyzer, operating with a 1296A Dielectric Interface System, and stainless steel electrodes. These measurements were performed in the 0.1 Hz to 100 kHz frequency ($f = \omega/2\pi$) range, with a potential strength of 100 mV.

3. Results and discussion

The impedance spectra measured on the four biodiesels produced and studied in this work are illustrated in Fig. 1. In terms of intrinsic property, the data have been converted into complex resistivity, $\rho^*(\omega) = \rho'(\omega) - j\rho''(\omega) = Z^*/L$, where $L(\equiv h/A)$ represents the measuring cell's geometrical factor ($A \equiv 94.81$ cm^2: electrodes' surface area and $h \equiv 0.105$ cm: electrodes' spacing, in this study). In this figure, *grosso modo*, the spectra consist of well-defined single semicircles, each of which could be ideally fitted using an equivalent circuit built

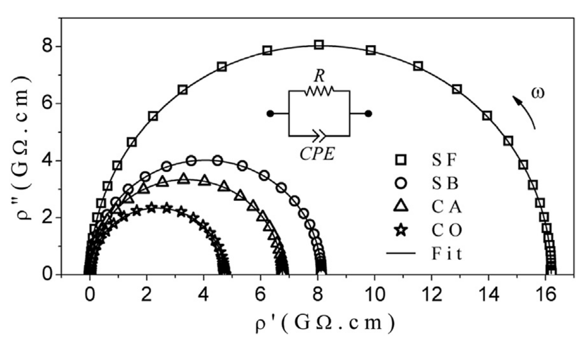

Fig. 1 – Impedance spectra, presented in terms of ρ'' versus ρ'complex plane plots, measured on the biodiesel fuels from different feedstocks: sunflower (SF), soybean (SB), canola (CA) and corn (CO). The solid lines arose from the data fittings performed using the near-Debye model circuit indicated in the figure (see comments in the text for further details).

Please cite this article in press as: M'Peko J-C, et al., Evaluation of the dielectric properties of biodiesel fuels produced from different vegetable oil feedstocks through electrochemical impedance spectroscopy, International Journal of Hydrogen Energy (2013), http://dx.doi.org/10.1016/j.ijhydene.2013.05.086