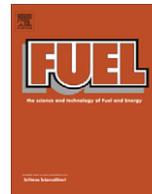




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## A close dielectric spectroscopic analysis of diesel/biodiesel blends and potential dielectric approaches for biodiesel content assessment

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### HIGHLIGHTS

- ▶ A close dielectric spectroscopic analysis of diesel/biodiesel blends is presented.
- ▶ The dielectric responses from these blends diverge from the classical Debye model.
- ▶ The measured conductivity and dielectric constant depend linearly on biodiesel content.
- ▶ Dielectric constant-based sensor function in biodiesel content assessment is verified.
- ▶ Conductivity-based sensor potentiality for biodiesel content appraisal is presented.

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### ABSTRACT

Diesel/biodiesel blends have been more and more used as an alternative fuel due to their economic, social and environmental advantages. This is why, in many cases, legislative policies have been or are being implemented to fix a minimal percentage of biodiesel content to be added in diesel fuels. In order to ensure the mandatory use, of course, it is necessary to develop methods able to quantify the amount of biodiesel in such blends. Despite the fact that the methodology based on the Fourier transform mid-infrared spectroscopy is the standard one used to determine the biodiesel content, several other techniques have been, in the last years, proposed as alternative methods to overcome some limitations presented by infrared spectroscopy. In particular, impedance spectroscopy has been proposed as a cheaper alternative technique in this quantification process. Owing to the very high resistivity response from diesel/biodiesel blends, nevertheless, development of dielectric-based biodiesel content sensors has been mainly focussed on measuring the corresponding dielectric constant. By using a sample holder with adequate dimensions, it was possible to carry here out a much complete dielectric spectroscopic study of diesel/biodiesel blends, discussing the results in terms of Debye versus modified-Debye models. The dielectric constant as well as electrical conductivity responses from these blends particularly revealed, at least over the compositional range studied (up to 10 volume% of biodiesel), linear behaviors upon biodiesel content variation, suggesting as well viability of development of resistivity-based biodiesel sensors, with the advantageous possibility of being projected and used even in the direct current mode.

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### 1. Introduction

In last years, biodiesel has gained attention because is a biofuel which can partly or completely replace petroleum-derived diesel [1]. The advantages of biofuels are based on the fact that they may be obtained from renewable sources, and are environmentally friendly [2]. Aiming to reduce the emission amount of carbon dioxide, several countries have implemented the use of diesel/biodiesel (DB) blends, where the biodiesel percentage usually varies between

2 and 20 volume% [1]. To exemplify, Brazil has mandated the use of 5 volume% of biodiesel in the DB blends [3]. Logically, it is necessary to have analytical methods capable of determining the biodiesel content in these fuels to ensure compliance with legislation. Recently, several methods have been proposed for quantifying biodiesel content in the DB blends [4]. Methods based on ester number [5], liquid and gas chromatography [6–8], near-infrared spectroscopy [4,9,10], saponification number [11], Fourier transform mid-infrared (FT-IR) spectroscopy [12,13], nuclear magnetic resonance spectroscopy [4], ultraviolet absorption spectroscopy [14], radio-carbon analysis [15,16], fluorescence spectroscopy [17], and X-ray spectroscopy [18] have been reported.

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Considering that electrical properties from DB blends should as well reflect their composition, it is intuitive to imagine the use of such properties to also determine the biodiesel content in these fuels. By using Impedance Spectroscopy (IS), for instance, González Prieto et al. reported room-temperature dielectric constant values of 2.2 for diesel and 3.3 for biodiesel [19]. The former value reproduced well a similar one previously reported for diesel by Yule et al. [20]. In fact, according to Koehler et al. [21] and Tomlinson [22], IS technique gives an effective way for predicting the biodiesel percentage in the DB blends. By using the equivalent formalism of electric modulus for data analysis, these authors found a linear correlation between dielectric constant and biodiesel content. A similar sensorial approach on oil quality from measuring the complex dielectric constant may also be found in the work by Pérez and Hadfield [23]. In the same direction, moreover, a commercial dielectric properties-based fuel composition sensor, originally projected to quantify gasoline/alcohol fuel blends (with a practical use for *in situ* determination of fuel composition directly in vehicles), was also successfully tested by Tat and Van Gerpen [24,25] to quantitatively characterize diesel/biodiesel blends of several types. In addition to the investigations involving fuel and biofuel, IS has been also proposed for the characterization and analysis of oils. For instance, Perini et al. recently reported that dielectric properties can be used to identify the presence of water in water-in-oil emulsions [26].

In dielectric characterization of materials, the simplest measurable (di)electrical properties are capacitance and resistance, thereby convertible (by ruling out the effect from the associated geometrical factor) to dielectric constant and electrical resistivity or conductivity, respectively, which are instead the corresponding true intrinsic properties of the materials. Nevertheless, because of low charge mobility [20,27], it is well known that oily substances are generally very poor conductors of electricity (showing conductivity values as low as  $10^{-12}$  S/cm), justifying their broad use as insulators in many electrical apparatus. This fact may also explain why conductivity of DB blends has not been yet considered for assessment of biodiesel content. A provisional solution approach proposed by Schilowitz et al. [28] was to make measurements in temperatures above about 50 °C, a procedure that may, however, alters the materials' properties due to thermodegradation processes. Theoretically, because of simplicity in data measurement and processing, optimization of measuring cells specifically aimed at developing impedance sensors for highly resistive (non-aqueous) industrial fluids reveals actually quite interesting [29]. An equivalent approach, involving simply optimization of measuring cell geometrical factor, was in the present study considered in order to achieve a close dielectric spectroscopic analysis of DB blends, representatively presented here in terms of impedance complex plane, conductivity and dielectric constant spectra, followed by evaluation of development viability of dielectric constant- as well as electrical resistivity-based biodiesel sensors for the compositional characterization of such blends.

## 2. Material and methods

### 2.1. Biodiesel production and diesel/biodiesel blends preparation

Biodiesel was obtained via methanolic route by transesterification process from refined soybean oil by using a 6:1 M ratio of methanol/oil as described in details in our previous paper [17]. The NaOH catalyst (0.4 wt.% with respect to oil weight) was dissolved in methanol and then poured into a beaker containing soybean oil preheated at 60 °C. The reaction was performed under constant stirring during 60 min at 60 °C and then placed in a separating funnel for 24 h. After that two phases were observed, one

containing mostly biodiesel and 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 excess of methanol. Afterward, the biodiesel was washed four 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. Finally, the diesel/biodiesel blends were prepared from B0 to B10, where BX means that there is X percent of biodiesel (in volume) in the blend, in steps of 1%. The blends were prepared using the certified diesel obtained from Petrobras (Petróleo Brasileiro S.A.).

### 2.2. Impedance Spectroscopy (IS)

The DB blends prepared here were electrically characterized at room temperature by performing alternating current (ac) measurements in the 0.1 Hz–100 kHz frequency ( $f$ ) range, with a 100 mV of (maximum) potential strength, using a Solartron Model SI 1260 impedance/gain-phase analyzer, operating with a 1296A Dielectric Interface System. In particular, a sample holder consisting of two parallel and circular stainless steel plates with an outsized diameter of 110 mm, and spaced by just 1 mm, were used as electrodes. In terms of dielectric spectroscopy study and correlation, the impedance ( $Z^*(\omega) = Z'(\omega) - jZ''(\omega)$ ) data measured in these experiments were also analyzed in terms of admittance ( $Y^*(\omega) = Y'(\omega) + jY''(\omega) = 1/Z^*(\omega)$ ) and complex capacitance ( $C^*(\omega) = C'(\omega) - jC''(\omega) = Y^*(\omega)/j\omega$ ), as presented and properly discussed in the next section. As mentioned above, a special attention was in this study paid to verifying the most reliable dielectric model applicable for an accurate data description, together with authenticity and achievability of biodiesel content quantification through performance of dielectric measurements.

## 3. Results and discussion

Fig. 1 illustrates, representatively, the measured impedance spectra for the B1, B5 and B9 samples. For the sake of comparison, 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 ( $A$ : electrodes' surface area and  $h$ : electrodes' spacing). Results from the other DB blends studied were qualitatively similar. That is, each impedance spectrum consisted of a single semicircle that can be fitted through the formalism of equivalent circuit by considering a parallel resistance–capacitance ( $R-C$ ) network, as directly indicated in Fig. 1 inset, according to the ideal model originally proposed by Debye [30–32]. As also found in literature for most liquids and single-crystal solids, the present result is in accordance with the high-degree of homogene-

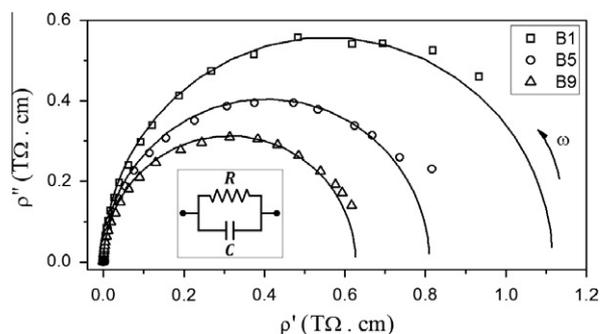


Fig. 1. Impedance spectra, presented in terms of  $\rho''$  versus  $\rho'$  complex plane plots, measured on the B1, B5 and B9 samples. The solid lines arose from fitting the data with a modified-Debye model involving the use of a constant phase element (see text), the Debye R-C circuit model being the one shown in this figure inset.

ity expected in DB blends when compared, for instance, to polycrystalline materials where bulk and internal interfaces normally traduce into occurrence and resolution of two impedance/resistivity semicircles [31,32]. The admittance and impedance corresponding to the above Debye model-related equivalent circuit satisfy, respectively, the following expressions:

$$Y^*(\omega) = Y'(\omega) + jY''(\omega) = G + j\omega C \quad (1)$$

$$Z^*(\omega) = Z'(\omega) - jZ''(\omega) = \frac{R}{1 + j\omega\tau} = \frac{R}{1 + \omega^2\tau^2} - j\frac{\omega R\tau}{1 + \omega^2\tau^2} \quad (2)$$

where  $\omega = 2\pi f$ ,  $G(\equiv 1/R)$  is the conductance, and  $\tau = RC$  refers to the relaxation time, directly linked to the relaxation frequency (frequency at the semicircle maximum) through the simple  $f_o \equiv 1/2\pi\tau$  relationship. From expression (2), it is possible to deduce that the diameter of an impedance (resistivity) semicircle basically reduces to  $R(\rho)$ . Accordingly, Fig. 1 suggests that addition of biodiesel enhances the conduction processes across the DB blends. Just for reference, in the present study the enhancement occurred by a factor of about 3 from diesel (B0) to biodiesel (B100) (data not shown). In any case, from the quantitative viewpoint, notice in Fig. 1 that the measured values of resistivity reveal really quite high, that is, in the magnitude order of  $\sim 10^{12} \Omega \text{ cm}$ . This is perhaps why, instead of resistivity, monitoring the materials' dielectric constant (calculated from capacitance) has been presented elsewhere as the optimal choice when looking for a dielectric-based method directed to assessing biodiesel content in DB blends [21–25]. The observation is that success in achievability of any dielectric experiment aimed at evaluating directly strength of the conduction processes in the DB blends requires, in normal conditions, consideration of a measuring cell with appropriate geometrical factor.

To get further insight into the features of the dielectric responses from such blends, we choose to subsequently show, in Fig. 2, the frequency spectra of the real part of conductivity ( $\sigma^* = Y^*L$ ), as observed, for instance, for these B1, B5 and B9 samples. Notice that conductivity ( $\sigma'$ ) data depart from the frequency independent behavior expected from expression (1). That is, contrary to the Debye model, our results show that  $\sigma'$  is almost constant but only in the low-frequency range, where direct current (dc) conduction processes may be truly appraised, while turning variable toward high frequencies. The data toward the low-frequency window are highlighted in Fig. 2 inset, showing an increase of conductivity with rising biodiesel content. For the high-frequency conductivity contribution, that we found to satisfy a relation of the type:  $\sigma'(\omega) \propto \omega^s$ , and usually referred to as ac conductivity involving limited motion of given charge carriers

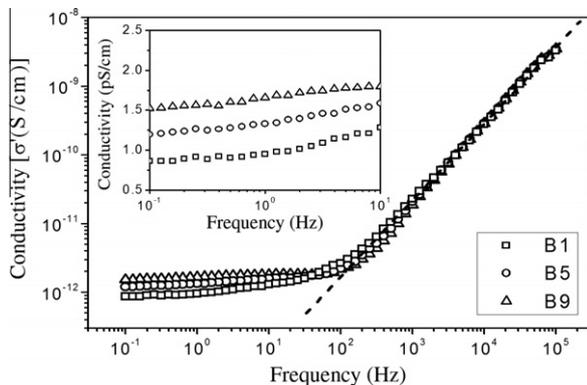


Fig. 2. Frequency spectra of the real part of conductivity ( $\sigma'$ ) corresponding to the B1, B5 and B9 samples. The dashed line refers, representatively, to the linear data fitting achieved for B5, this procedure revealing here applicable for all these blends.

around equilibrium positions [30–32], the frequency exponent directly estimated from the graphs of all the DB blends were roughly comparable, giving an average value of  $\bar{s} \approx 0.993 \pm 0.005$ . In terms of impedance spectra, this fact normally involves observation of a small depression of the semicircle centers below the real axis by a given  $\alpha\pi/2$  angle. This feature was also verified in this study after a close analysis of all Fig. 1-like impedance spectra, realizing that the diameters of all the impedance semicircles revealed slightly higher than twice the expected radii in the vertical ( $\rho''$ ) axis. From applying the corresponding analytical geometry method of impedance semicircles analysis [31], a really small but perceptible average value of  $\bar{\alpha} \approx 0.010 \pm 0.003$  was roughly estimated.

In the following, Fig. 3 illustrates the frequency spectra of the real part of dielectric constant ( $\varepsilon^* = C^*/C_o$ ) for these B1, B5 and B9 samples, where  $C_o(\equiv \varepsilon_o/L; \varepsilon_o = 8.854 \text{ pF/m})$  refers to the capacitance of the vacuum cell. The values of real part of capacitance measured in this work remained all around about  $1.8\text{--}2.0 \times 10^{10} \text{ F}$ . In terms of capacitance magnitude order, considering sample holder dimensions, these values indicate to be here dealing with the inner DB fuels' bulk dielectric response [31,32]. The relatively significant dielectric data dispersion observed in this figure toward the low-frequency region (especially below 10 Hz), as also detectable, indeed, in the resistivity spectra illustrated in Fig. 1, might be ascribed to (i) the effect of approaching the sensitivity threshold of the measuring impedance/gain-phase analyzer equipment (in terms of measurable impedance), besides (ii) the fact that the DB fuels' dielectric response toward this frequency window might, eventually also, include the beginning contribution from the Maxwell–Wagner-like material-electrode (interfacial) polarization effect [21,22,31,32], to which higher capacitance values are associated [31,32]. As shown in Fig. 3 inset, therefore, this region was not considered for subsequent analysis of the dielectric constant magnitude and behavior from these blends. From the quantitative viewpoint, *grosso modo*, the dielectric constant increased with rising biodiesel content in the DB blends, an expected result due to the fact that biodiesel is of relatively higher polarity than diesel [19,33]. In the context of the Debye model-related  $R - C$  circuit, it is imperative to point out that the complex capacitance, obeying the relationship  $C^*(\omega) = Y^*/j\omega$ , satisfies an expression of the type:

$$C^*(\omega) = C'(\omega) - jC''(\omega) = C - j\frac{G}{\omega} \quad (3)$$

Accordingly, one should theoretically expect the real part of capacitance to remain basically independent on frequency, in total contrast with the results shown in Fig. 3 for the dielectric response ( $\varepsilon'$ ) of these DB blends, suggesting accomplishment of a

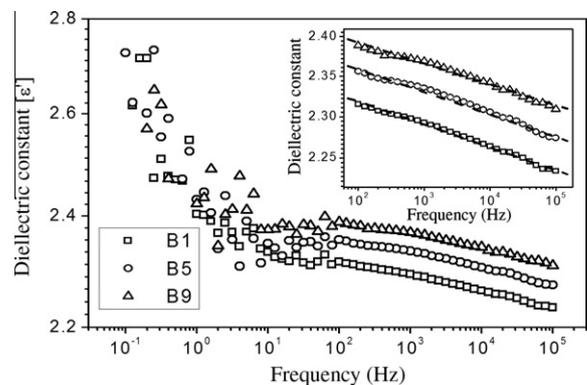


Fig. 3. Frequency spectra of the real part of dielectric constant ( $\varepsilon'$ ) corresponding to the B1, B5 and B9 samples. The dashed lines refer to the corresponding linear data fittings (see text).

dependence of the type:  $\epsilon''(\omega) \propto \omega^{-\gamma}$ . Direct evaluation of the  $\gamma$  exponent from the measured data revealed as well comparable values between the DB blends, averaging  $\bar{\gamma} \cong 0.005 \pm 0.002$ .

At this stage, it is straightforward concluding that, as most often also presented and discussed in the literature on frequency-domain dielectric properties of materials [30–32], the dielectric response of the DB blends investigated in the present study do not really follow the ideal Debye model. In practice, to achieve better agreement with experimental data, an empirical constant phase element (CPE)-type frequency-dependent parameter, in place of the ideal capacitance  $C$ , has been normally used elsewhere for high-quality fittings [31,32]. This formalism of data analysis and fitting was here adopted, and the professional ZView software [34], which comprises consideration of Debye as well as modified-Debye models, including the  $R - Y_{CPE}$  circuit option, was used. One but simple approach consists in considering the CPE element to have an admittance of the type:  $Y_{CPE}(\omega) = Q(j\omega)^n$ , with  $0 \leq n \leq 1$ , different from the ideal capacitance-associated  $Y(\omega) = j\omega C$  admittance. While the original Debye model presupposes to be dealing with relaxation processes from non-interacting dipoles or charges floating in a viscous medium and showing a single relaxation time, the parameter  $n$  in the modified model is usually proposed to reflect either the existence of a distribution of relaxation times or a correlation degree of charges interaction in real dielectric media [30–32]. Data fitting quality arising from considering the  $R - Y_{CPE}$  equivalent circuit was here constantly monitored through the ZView chi-squared error parameter, remaining its values in the order of  $10^{-2}$ .

The following analysis gives a good idea of the frequency behaviors and/or characteristics to be hence expected for the dielectric response of materials, when involving such a CPE parameter. Remembering that  $j = \exp(-j\pi/2) = \cos(-\pi/2) - j \sin(-\pi/2)$ , notice that  $Y_{CPE}$  satisfies the expression:

$$Y_{CPE}(\omega) = Q(j\omega)^n = Q \cos(n\pi/2)\omega^n + jQ \sin(n\pi/2)\omega^n \quad (4)$$

Therefore, the total admittance of a  $R - Y_{CPE}$  circuit obeys an expression of the type:

$$Y^*(\omega) = Y'(\omega) + jY''(\omega) = G + Q(j\omega)^n = (G + A\omega^n) + jB\omega^n \quad (5)$$

where  $A = Q \cos(n\pi/2)$  and  $B = Q \sin(n\pi/2)$ . Expression (5) suggests that the real part of conductivity should consist of two contributions, one of them involving a potential dependence on frequency, as truly found in Fig. 2. Moreover, notice that impedance of the  $R - Y_{CPE}$  network should obey the expression:

$$Z^*(\omega) = Z'(\omega) - jZ''(\omega) = \frac{R}{1 + QR(j\omega)^n} \quad (6)$$

This expression is essentially equivalent to that from the Cole-Cole model, earlier proposed in literature to apply in real dielectric materials in place of the ideal Debye model [30–32]. Such impedance dispersion is expected to give rise to impedance semicircles having their centers depressed below the real axis by an angle of  $(1 - n)\pi/2$ . Finally, it is also possible to deduce from expression (5) that the complex capacitance of the  $R - Y_{CPE}$  circuit obeys:

$$C^*(\omega) = C'(\omega) - jC''(\omega) = B\omega^{n-1} - j\left(\frac{G}{\omega} + A\omega^{n-1}\right) \quad (7)$$

noting that the real part of capacitance is as well a function of frequency, as also found in Fig. 3. In passing, it is worth to point out, in terms of frequency behavior of dielectric properties, that  $Y'(\omega) \propto A\omega^n$  while  $C'(\omega) = B\omega^{n-1}$ . From the quantitative viewpoint, the ZView data fit performed in this study allowed estimating as well essentially comparable  $n$  values for all the DB blends, averaging  $\bar{n} \cong 0.994 \pm 0.002$ . Notice total agreement of this  $\bar{n}$  value with that of  $\bar{s} (\cong 0.993)$  presented above. This fact validates the use of the

$R - Y_{CPE}$  model for analyzing and fitting the dielectric responses measured in these DB blends. This concluding remark is further supported by verification that, when comparing between the values of  $\bar{s}$ ,  $\bar{\alpha} (\cong 0.010)$  and  $\bar{\gamma} (\cong 0.005)$  roughly estimated and presented above, the  $\bar{s} \cong 1 - \bar{\gamma} \cong 1 - \bar{\alpha}$  correspondence also applies, as rightly expected from this modified-Debye ( $R - Y_{CPE}$ ) model.

At this point, it is important to formulate the following comments. Firstly, it is clear, from the mathematical formulation, that the  $R - Y_{CPE}$  model reduces to the ideal Debye one when  $n = 1$ . Secondly, in consequence, application of modified-Debye models (including the  $R - Y_{CPE}$  one) in the study of dielectric responses from materials is often presented as a procedure of data analysis to be straightforwardly considered [31,32]. This is fundamentally obvious in many cases where the measured factor of impedance semicircle depression departs more or less significantly from unity (1). We however note that the experimental values of  $n$  estimated in the present work, which remained in the 0.992–0.996 range, really approach unity, meaning that depressions of the semicircles, appraisable through  $(1 - n)\pi/2$ , are really irrelevant. Irrespective of this fact, nevertheless, inconsistency of considering the ideal Debye model is evident when looking, for instance, at Fig. 2 showing clearly the materials' conductivity to be not constant, but rather a function of frequency toward high frequencies ( $\sigma'(\omega) \propto \omega^n$ ). In other words, the remark is that any minimum deviation from the ideal Debye model appears to be sufficient to manifestly oblige consideration of modified-Debye models for achieving accurate data analysis and fitting during the dielectric characterization of materials. To the best of our knowledge, in fact, frequency-independent conductivity ( $\sigma'$ ) data have been to date not yet measured elsewhere, that is, over common frequency windows extending up to the MHz range. This simple but recurrent experimental fact, as easily verifiable in the open literature, strongly suggests the Debye model to be just an instructive but actually not realistic approach for interpreting dielectric responses from real materials, in line with the early proposition by Jonscher that the expression  $\sigma'(\omega) = \sigma_{dc} + A\omega^n$  is to be considered as the universal dynamic (dielectric) behavior [30].

In the following, finally, Figs. 4 and 5 show (in mono-log scales for convenience) the variations of, respectively, conductivity ( $\sigma'$ ) and dielectric constant ( $\epsilon'$ ) with DB composition, as estimated from the ZView software. In particular, for the  $R - Y_{CPE}$  circuit model here considered, the dielectric constant should be understood as calculated from the equivalent frequency-independent coefficient of capacitance involved in the CPE element, i.e.,  $C_{CPE} = B = Q \sin(n\pi/2)$ , as can be deduced from expression (7). The estimated frequency-independent values of dielectric constant remained in the 2.27–2.38 range, revealing comparable to those values previously reported in literature [19]. In fact, notice from both Figs. 4 and 5 that

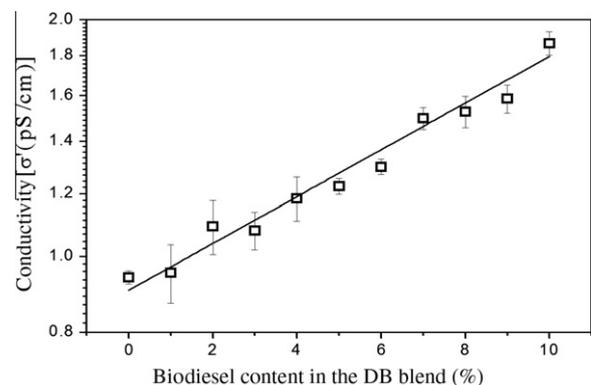
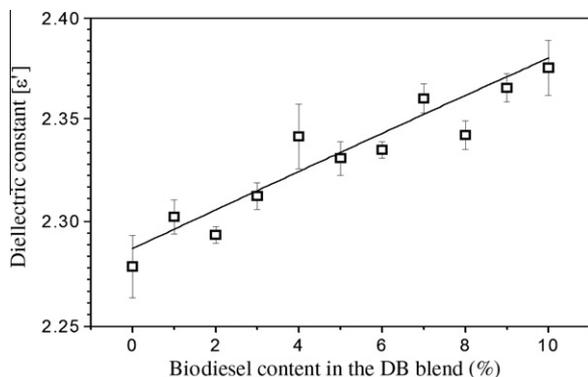


Fig. 4. Biodiesel content dependence of the frequency-independent (dc) conductivity from the studied DB samples.



**Fig. 5.** Biodiesel content dependence of the dielectric constant ( $\epsilon'$ ) from the studied DB samples.

the variations of conductivity and dielectric constant between the B0 and B10 blends reveal really small. That is why, depending on measuring set-ups, equipment sensitivity and conditions, the fact of using a  $R - Y_{CPE}$ , instead of the simple Debye-like  $R - C$ , circuit for data fittings could, maybe or eventually, traduces into an improvement of degree of accuracy when evaluating the strength of dielectric data dispersion between the DB blends. In both figures, a nearly linear dependence of the properties on biodiesel content is observed over the studied range of DB blend compositions, i.e., at least up to 10% of biodiesel volume content. This result is interesting when looking for potential dielectric methods aimed at assessing biodiesel content in DB-like blends. In fact, as was mentioned earlier, sensorial potentiality of considering this procedure has been proposed elsewhere in the case of the dielectric constant behavior from such blends [19,21–25]. Just for reference, let us point out that, in particular, except for the fact of using here the  $R - Y_{CPE}$ , instead of the applicable but less accurate simple Debye-like  $R - C$ , equivalent circuit for better describing and fitting the frequency-dependent DB blends' dielectric data behavior, the electric modulus ( $M^*$ ) approach proposed in Koehler et. al. [21] and Tomlinson [22] patents for appraising biodiesel content in DB fuels is basically equivalent to that of the dielectric constant ( $\epsilon^*$ ) presented here in Fig. 5. This statement is based on the fact that  $M^* = 1/\epsilon^* (\equiv j\omega C_0 Z^*)$ , being correspondently realizable, therefore, that the real part of electric modulus decreases with rising the biodiesel content [21,22]. In addition to the dielectric constant property, the present work shows that monitoring variation of resistivity upon biodiesel content modification might also be a further alternative way that could be considered for development of biodiesel sensor devices for DB blends, with the advantage that measurements could be performed even in the dc electrical mode and, therefore, at a probably lower cost than development of dielectric constant-based sensors, provided that these latter actually require a high-frequency electric field input.

Preference for exploration of a conductivity-based biodiesel sensor option in DB blends could also be justified by considering the following interesting argument. This arises from comparing between the sensitivities of the resistivity versus dielectric constant magnitudes shown by these fuels upon biodiesel content variation. We just remember that, in terms of Debye model (taken at this instant just as a reference), accomplishment of the relationship  $\tau = RC$  for the relaxation time implies that  $\tau = \rho\epsilon_0\epsilon'$ . This means that  $\tau$  and, hence, the relaxation frequency  $f_0 (\equiv 1/2\pi\tau)$  are as well intrinsic properties of the dielectric response of any material, and can be therefore also used for biodiesel sensorial function in the DB blends. From B0 to B10,  $f_0$  was in this study found to vary from about 0.2 to 0.7 Hz, as directly estimated from the measured Fig. 1-like impedance spectra. In other words,  $\tau$  decreases with rising biodiesel content and, therefore, variations of conductivity ( $\sigma'$ ) are

actually much more important than those of dielectric constant ( $\epsilon'$ ). This result remains in accordance with observation that the angular coefficient ( $\phi$ ) values directly calculated from Figs. 4 and 5 are, respectively, about 0.028 versus 0.002, i.e.,  $\phi_{\sigma'} \cong 14\phi_{\epsilon'}$ .

Finally, if intending and setting up real biodiesel sensorial devices based on dielectric measurements, a last quite important remark should be here pointed out. That is, firstly, it is clear from this work and open literature [21,22] that proposing or using impedance/dielectric spectroscopy for biodiesel sensing is actually achievable. Secondly, the results presented in the present work particularly refer to basically water contamination-free blends, resulting in occurrence of well-defined single impedance semicircles (Fig. 1), different from the results that may be found, for instance, in water-in-oil emulsions where the presence of water may induce (i) the incidence of an additional semicircle [26] or simply, if dealing with supposedly highly-homogeneous water-oil blends, (ii) a huge increase of the blends' conductivity and dielectric constant. Therefore, in real scenarios, the magnitude of the measured fuels' dielectric properties may be affected by different factors such as presence of different contaminants (e.g., residual alcohol after the transesterification reaction and water after the washing process), fuels' viscosity, and measuring temperature [19,26]. Presently, in terms of work extension, further dielectric studies on these DB blends are in progress in order to closely assess these effects, together with verification of whether the nearly well-behave linear function of the dielectric properties ( $\sigma'$  and  $\epsilon'$ ) with biodiesel content applies from not only B0 to B10 but also B0 to B100. In any case, the above remark means that, if proposing a real dielectric-based biodiesel sensorial device, calibration curves involving consideration of different potential effects should be provided by the manufacturer. In practice, in the case of an important number of potential effects, this could be achieved from the computational viewpoint by training, for instance, a neural-like net.

#### 4. Conclusion

Diesel/biodiesel blends were prepared and studied in this work in terms of dielectric spectroscopy. It was verified that, although showing dielectric spectra consisting of single impedance semicircles depressed really only faintly from the real axis, the dielectric responses from these blends significantly diverge from the classical Debye model that involves consideration of a simple  $R - C$  equivalent circuit for data fittings. Instead, the dielectric dispersions measured for resistivity, conductivity as well as dielectric constant were all better fitted by applying a modified-Debye model that consisted of a  $R - Y_{CPE}$  circuit, this approach being equivalent to considering, for instance, the original Cole–Cole model. From the quantitative viewpoint, it was observed that the real parts of conductivity, toward low frequencies (reflecting basically the dc conductivity), and dielectric constant, toward high frequencies, from these blends depend linearly on biodiesel content, that is, at least over the range of blend compositions studied (up to 10 volume% of biodiesel). This unique feature may be hence used for developing resistivity- as well as dielectric constant-based sensorial devices aimed at appraising biodiesel content in such blends. When compared to the dielectric constant option, there is some advantage of considering the resistivity one because of achievability of the electrical measurements even in the dc mode, meaning a comparatively lower production cost in terms of sensorial device development.

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