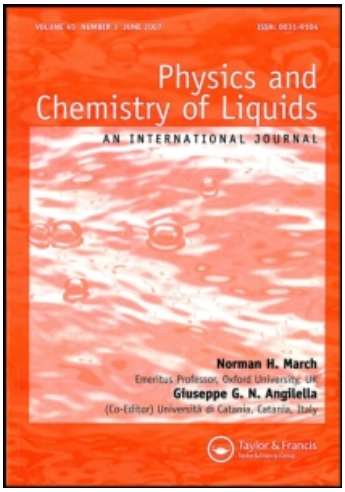

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Physico-chemical and electrical properties for the production and characterization of Biodiesel

P. A. Sorichetti[ab]; S. D. Romano[ab]
[a] Group of Renewable Energy, Faculty of Engineering, University of Buenos Aires (FIUBA) Paseo Colón 850 (1063), Buenos Aires, Argentina [b] Laboratory of Liquid Systems, FIUBA, Paseo Colón 850 (1063), Buenos Aires, Argentina

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Physico-chemical and electrical properties for the production and characterization of Biodiesel

P.A. SORICHETTI and S.D. ROMANO*

Group of Renewable Energy, Faculty of Engineering, University of Buenos Aires (FIUBA) Paseo Colón 850 (1063) Buenos Aires, Argentina and
Laboratory of Liquid Systems, FIUBA, Paseo Colón 850 (1063) Buenos Aires, Argentina

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Biodiesel (BD) is a renewable fuel used in diesel engines as a replacement of Diesel Fuel or in blends. Biodiesel was obtained by a transesterification reaction between used frying oils and methanol, using sodium hydroxide as a catalyst. The oils were treated to eliminate water, thus avoiding the formation of soaps during the chemical reaction.

The physical and the chemical parameters relevant to the production process were optimized. Particular care was taken during the washing process of Biodiesel. Viscosity, density, electrical properties and refractive index of the Biodiesel were measured at the successive stages of the washing process, together with the electrical properties and pH of the effluents. In order to characterize the final product, calorific value and flash point were also measured. The results are in good agreement with the reference values in applicable standards and in the literature.

Keywords: Biodiesel; Electrical properties; Physico-chemical properties; Transesterification process

1. Introduction

Increasing concern about the environmental effects of internal combustion engines [1,2] and the conservation of natural resources has led to a renewed interest in biofuels obtained from the transesterification of vegetable oils, collectively known as Biodiesel [3–5]. Since transesterification of vegetable oils is a key step in the production of Biodiesel and also glycerin, a valuable subproduct, it is of technological interest to determine the physico-chemical and electrical parameters that enable an adequate characterization of the raw material and the product of the process, and ensure that they are also readily measurable in the laboratory and in the production plant [6]. It is also desirable that the parameters be obtainable from "online" measurement systems, in order to automate process control.

*Corresponding author. E-mail: sromano@fi.uba.ar

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In this work, systematic measurements have been carried out on the raw material, the final product and also the effluents of the Biodiesel production process through transesterification of used frying oils. The results presented here make possible the optimization of the transesterification process and the final product in terms of several physico-chemical and electrical variables adequate for laboratory and industrial measurement, and also for automated process control.

2. Experimental

2.1 *Steps of biodiesel production process*

In this work, the treatment of the used frying oils (raw material) is the first stage of the Biodiesel production process. The treatment consists of a filtration step to homogenize the oil, followed by the elimination of the small fraction of water it usually contains. To remove the water, three methods were employed: drying (at 80°C), distillation at atmospheric pressure (at 150°C) and distillation in a partial vacuum at room temperature (final pressure below 1 mm Hg). It is very important to ensure the absence of water in the oil to reduce the formation of soaps during the chemical reaction at a later stage of the process.

After the treatment of the raw material, Biodiesel is obtained in a batch process by a transesterification reaction. This reaction transforms the fatty acids present in the oil in a mixture of their methyl esters. The oil reacts with methanol (20% v/v; Merck, 99.8%) with sodium hydroxide (Anedra, 97%) as a catalyst. The amount of catalyst to be added depends on the acidity of the oil. The latter is measured by titration of 1 mL of oil in 10 mL of isopropyl alcohol and a few drops of phenolphtalein, with an aqueous solution of sodium hydroxide (at a concentration of $1\,g\,L^{-1}$).

The treated oil is heated to 50°C and sodium methoxide is added. The chemical reaction takes place under constant stirring in a thermostatized bath at a constant temperature of 50°C. After the reaction, glycerin (subproduct) is separated by decantation.

Biodiesel is purified by three washing steps. The first one is carried out with water acidified with acetic acid and the remaining two steps are with deionized water. The washing process deserves particular attention since its objectives are both to separate any remaining traces of methanol and to adjust the pH of the end product.

An inherent difficulty in the washing process is that water must flow through the Biodiesel with minimum agitation. The formation of emulsions must be avoided since they diminish the process yield.

In this work, the Biodiesel as obtained from the transesterification reaction (before any washing steps) is indicated as BD-0 whereas BD-1 and BD-2 indicate Biodiesel after the first and the second washing steps, respectively. The end product (after the third washing step) is referred to as BD.

2.2 *Physico-chemical measurements*

The production steps of Biodiesel and the final product were characterized by several physicochemical and electrical techniques. These techniques were applied to the measurements in the oil, BD-0, BD-1, BD-2, BD, and also to the effluents of the washing steps.

The viscosity and density measurements were carried out according to requirements of ASTM D 445-03 [7] and ASTM D 1298-99 [8]. The measurements of viscosity were made with a Cannon–Fenske Series 50 (a kind of modified Oswald viscosimeter) at a temperature of 40°C, as specified by the standard. The density measurements were carried out at room temperature (25°C), using a precision balance Mettler AE 200 and a Gay Lussac type picnometer.

The flash point of BD was measured by the Pensky–Martens method, according to standard ASTM D93-02a [9].

The pH of the effluents of the washing steps were measured with a pH-meter made by Parsec (Argentina) and an electrode from the same manufacturer.

The calorific value (heat of combustion) is a very important parameter for any fuel. In the present case, although not required by the standards, its measurement is of interest to compare Biodiesel with diesel fuel. In fact, it is particularly important with regard to the specific consumption of engines. The measurements in this work were made by the Junkers continuous-flow method [10].

A refractive index [11] was measured by a refractometer of the Abbe type (based on the limiting angle principle) made by PZO, Polskie Zaklady Optyczne (Poland).

2.3 *Measurement of electrical properties*

Dielectric Relaxation Spectrometry (DRS) [12–14] was employed as an electrical technique making it possible to characterize the mixtures and detect contaminants in real time, regardless of the colour or turbidity of the liquid phases. DRS is based on the interaction of a macroscopic sample with a time-dependent electric field. The substance to be measured is placed in a cell with a system of electrodes connected to the measuring circuit. A generator excites the cell and the response signal is digitized, processed and compared with the excitation signal, to determine the complex permittivity of the sample as a function of frequency.

The capacitance of the empty cell, C_o, is given by

$$C_o = k_o \cdot \varepsilon_o$$

where ε_o is the free space permittivity (8.85 pF/m) and k_o is the "cell constant" which depends on the geometry of the cell. Therefore, the admittance of the empty cell (assumed loseless), under sinusoidal excitation at a frequency f is:

$$Y_o(\omega) = \mathrm{i} \cdot \omega \cdot C_o$$

where ω is the angular frequency given by $\omega = 2\pi f$.

When the measurement cell is filled with the sample, the admittance takes the complex value $Y(\omega)$:

$$Y(\omega) = G(\omega) + \mathrm{i} \cdot B(\omega)$$

where the conductance $G(\omega)$ is associated to energy dissipation and the susceptance $B(\omega)$ represents energy storage in the cell. The equivalent complex capacitance of the cell $C(\omega)$ is therefore defined by:

$$Y(\omega) = \mathrm{i} \cdot \omega \cdot C(\omega)$$

where it must be remarked that $C(\omega)$ is, in general, a complex number that depends on the excitation frequency. Therefore, the apparent relative permittivity of the sample at an angular frequency ω is given by:

$$\varepsilon_r(\omega) = \frac{C(\omega)}{C_o} \quad \text{where } \varepsilon_r(\omega) = \varepsilon_r'(\omega) - \mathrm{i}\varepsilon_r''(\omega)$$

The real part ε_r' represents the polarization of the dielectric, while the imaginary part ε_r'' is originated by the dissipative processes, including the conduction currents associated with the presence of free charge carriers. Therefore, the tangent of the phase angle $\delta(\omega)$ between the excitation voltage and the current through the cell is given by the quotient between the imaginary and real parts of $\varepsilon_r(\omega)$:

$$\mathrm{tg}\,\delta(\omega) = \frac{\varepsilon_r''(\omega)}{\varepsilon_r'(\omega)}$$

It is also customary to indicate $\mathrm{tg}\,\delta(\omega)$ as the dissipation factor of the dielectric, since it gives the ratio between energy dissipation and storage in the dielectric, under sinusoidal steady-state excitation.

The results of DRS measurements are usually given as plots of the real part of permittivity, $\varepsilon_r'(\omega)$ and the dissipation factor, $\mathrm{tg}\,\delta(\omega)$.

The spectral response characterizes the amplitude and the time scale of charge and polarization fluctuations inside the sample. The measurements presented in this work were carried out with a measurement system model 5100 made by Topward (Taiwan) and a measurement cell for liquids with platinum electrodes made by Parsec (Argentina). The measurement range was from 100 Hz to 15.7 KHz.

3. Results

3.1 *Physico-chemical parameters*

In this work, all the measurement uncertainities are smaller than the last indicated digit unless otherwise noted.

Table 1 shows the measured values of the kinematic viscosity (ν) and the density (δ) for the Biodiesel after the successive washing steps. In the last row, the reference values from ASTM-D 6751-03a [15] (table 1) are shown.

In table 2 are shown the results of pH measurements for the effluents of the washing process. In the last row, the pH of deionized water is shown.

The calorific values measured for BD were 38.1 MJ/kg (upper) and 36.0 MJ/kg (lower), whereas for commercial Diesel Fuel they were 44.4 MJ/kg and 41.4 MJ/kg, respectively.

Table 1. Measured values of viscosity (ν) and density (δ) for Biodiesel.

Sample	ν (CStk)	δ (g cm^{-3})
BD-0	4.04	0.877
BD-1	4.06	0.880
BD-2	4.18	0.880
BD	4.39	0.880
ASTM ref. values	3.50–5.00	0.875–0.900

Table 2. pH of washing effluents.

Sample	pH
Effluent of 1st washing step	7.91
Effluent of 2nd washing step	7.84
Effluent of 3rd washing step	7.16
Deionized water	6.13

The refractive index for the used frying oil measured for D line of Sodium was 1.4710 ± 0.0005, whereas for Biodiesel after the successive washing steps (BD-0, BD-1, BD-2 y BD) the measured value was 1.4550 ± 0.0005, constant within the stated uncertainity.

3.2 *Electrical properties*

Electrical properties (conductivity and permittivity) were measured in oil, BD-0, BD-1, BD-2, BD and also in the effluents from the washing steps. The measurements were made at a temperature of $22 \pm 2^{\circ}$C. The uncertainty of results for the real part of permittivity (ε_r') is less than 5% and for dielectric losses (tg δ), less than 10%.

Tables 3 and 4 show the values of the ε_r' and tg δ for the treated oil (filtered oil, dried oil, distilled oil and vacuum distilled oil) as a function of frequency, respectively.

Tables 5 and 6 show the results of the same measurements on Biodiesel (BD-0, BD-1, BD-2, BD) whereas tables 7 and 8 are for the effluents (1st, 2nd, 3rd washing step) and deionized water.

In figure 1 are the plots of ε_r' of the treated oil (filtered oil, dried oil, distilled oil and vacuum distilled oil), whereas the dielectric losses are shown in figure 2. Figures 3 and 4 show the plot for the electrical properties (real part of permittivity and dielectric losses, respectively) of the different steps of BD production (BD-0, BD-1, BD-2, BD), whereas figures 5 and 6 plot the same measurements for the effluents (1st, 2nd, 3rd washing step) and deionized water.

4. Discussion

From table 1 it may be seen that the density of Biodiesel is unchanged by the successive washing steps, although its viscosity increases slightly. This is reasonable since the washing steps remove the remaining methanol in solution in the Biodiesel.

Table 3. Real part of permittivity (ε'_r) as a function of frequency for treated oil.

Sample	Frequency (Hz)						
	100	120	400	1000	5000	10,000	15,700
Filtered oil	3.35	3.38	3.19	3.13	3.07	3.05	3.06
Distilled oil (150°C)	3.39	3.23	3.17	3.09	3.06	3.04	3.09
Dried oil (80°C)	3.68	–	3.12	3.01	3.04	2.98	3.02
Vacuum distilled oil (room temp.)	3.40	–	3.14	3.01	3.02	2.97	3.01

Table 4. Dissipation factor ($\mathrm{tg}\,\delta$) as a function of frequency for treated oils.

Sample	Frequency (Hz)						
	100	120	400	1000	5000	10,000	15,700
Filtered oil	7.0×10^{-2}	5.7×10^{-2}	1.9×10^{-2}	7.7×10^{-3}	2.6×10^{-2}	2.9×10^{-2}	3.5×10^{-2}
Distilled oil (150°C)	6.9×10^{-2}	6.1×10^{-2}	1.9×10^{-2}	7.9×10^{-3}	1.5×10^{-2}	1.7×10^{-2}	2.3×10^{-2}
Dried oil (80°C)	6.1×10^{-2}	7.2×10^{-2}	1.9×10^{-2}	8.2×10^{-3}	1.6×10^{-3}	6.0×10^{-3}	2.6×10^{-3}
Vacuum distilled oil (room temp.)	6.8×10^{-2}	7.1×10^{-2}	1.9×10^{-2}	8.2×10^{-3}	3.2×10^{-3}	1.2×10^{-2}	7.3×10^{-3}

Table 5. Real part of permittivity (ε'_r) as a function of frequency for different steps in Biodiesel production.

Sample	Frequency (Hz)			
	1000	5000	10,000	15,700
BD-0	3.77	3.63	3.59	3.59
BD-1	4.39	3.81	3.66	3.58
BD-2	3.76	3.43	3.37	3.39
BD	3.36	3.35	3.35	3.35

Table 6. Dissipation factor ($\mathrm{tg}\,\delta$) as a function of frequency for different steps in Biodiesel production.

Sample	Frequency (Hz)			
	1000	5000	10,000	15,700
BD-0	7.4×10^{-1}	2.0×10^{-1}	1.0×10^{-1}	7.0×10^{-2}
BD-1	4.9×10^{-1}	1.9×10^{-1}	1.6×10^{-1}	1.3×10^{-1}
BD-2	1.5×10^{-1}	9.5×10^{-2}	5.7×10^{-2}	3.9×10^{-2}
BD	7.1×10^{-3}	1.4×10^{-3}	3.0×10^{-3}	2.9×10^{-3}

Table 7. Real part of permittivity (ε'_r) as a function of frequency for washing steps effluents.

Sample	Frequency (Hz)			
	1000	5000	10,000	15,700
1st washing step	1.15×10^{2}	7.33×10^{1}	7.30×10^{1}	7.28×10^{1}
2nd washing step	1.02×10^{2}	7.55×10^{1}	7.52×10^{1}	7.64×10^{1}
3rd washing step	8.28×10^{1}	7.89×10^{1}	7.85×10^{1}	7.82×10^{1}
Deionized water	8.66×10^{1}	7.32×10^{1}	7.14×10^{1}	7.04×10^{1}

Table 8. Dissipation factor ($\mathrm{tg}\,\delta$) as a function of frequency for washing steps effluents.

Sample	Frequency (Hz)			
	1000	5000	10,000	15,700
1st washing step	434.2	136.6	68.7	43.8
2nd washing step	424	114.9	57.7	36.1
3rd washing step	123	26.5	13.5	8.7
Deionized water	54.4	12.9	6.7	4.3

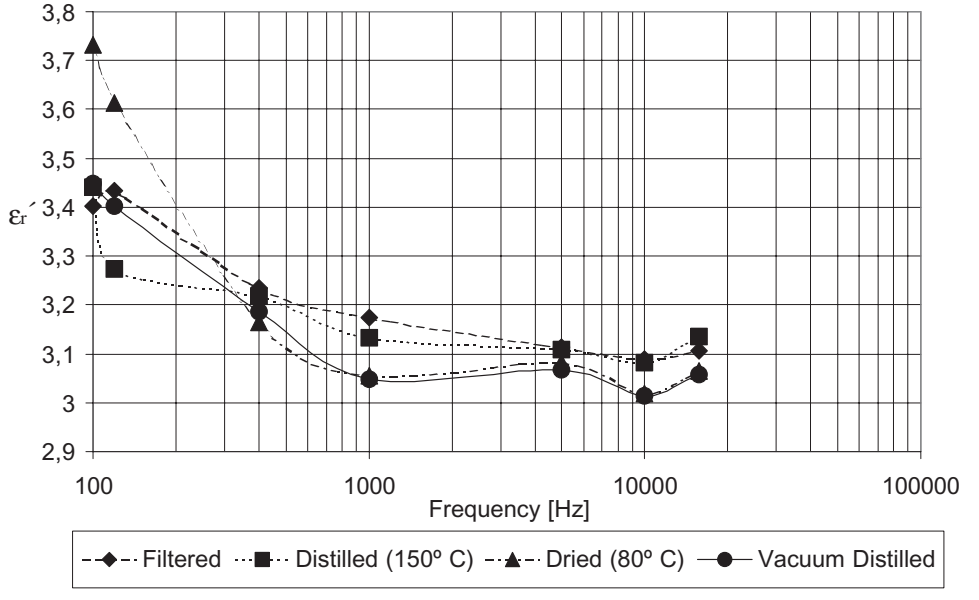

Figure 1. Real part of permittivity (ε_r') as a function of frequency for treated oil.

The calorific value measured both for the Biodiesel and the Diesel Fuel agree with the values usually reported in the literature [16,17]. The results for the BD are lower than those obtained for Diesel Fuel. In this work, the difference is around 14%, in a good agreement with the literature [18].

The information provided by the measurements of electrical properties makes it possible to characterize the different steps of the processing of the raw material and the production of Biodiesel. It is important to note that, in samples with high dielectric losses, the polarization effects in the electrodes result in an increase of apparent dielectric permittivity, making the interpretation of low frequency results difficult [19,20]. This is the case for the effluents of the washing process and the Biodiesel at the first washing step, for frequencies less than 1 KHz.

In figure 2, the reduction of the dielectric losses of treated oil may be attributed to the elimination of water and other contaminants. The final value of permittivity is 3.0 ± 0.15, for frequencies from 1 KHz upwards, for all the treatments. This is indicated in table 3 and figure 1. On the other hand, the final value of $\mathrm{tg}\,\delta$ is less than 4×10^{-2} (see table 4) for frequencies of 1 KHz or higher.

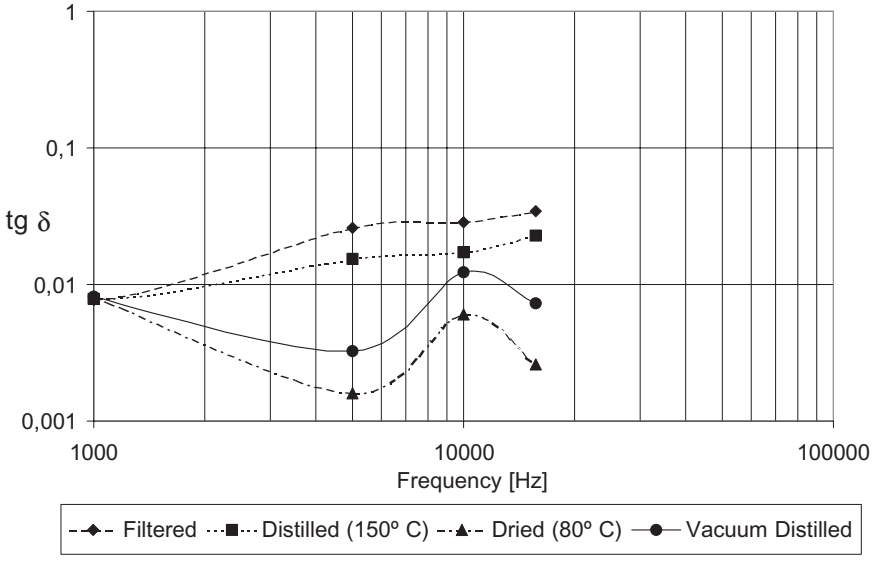

Figure 2. Dissipation factor ($\mathrm{tg}\,\delta$) as a function of frequency for treated oils.

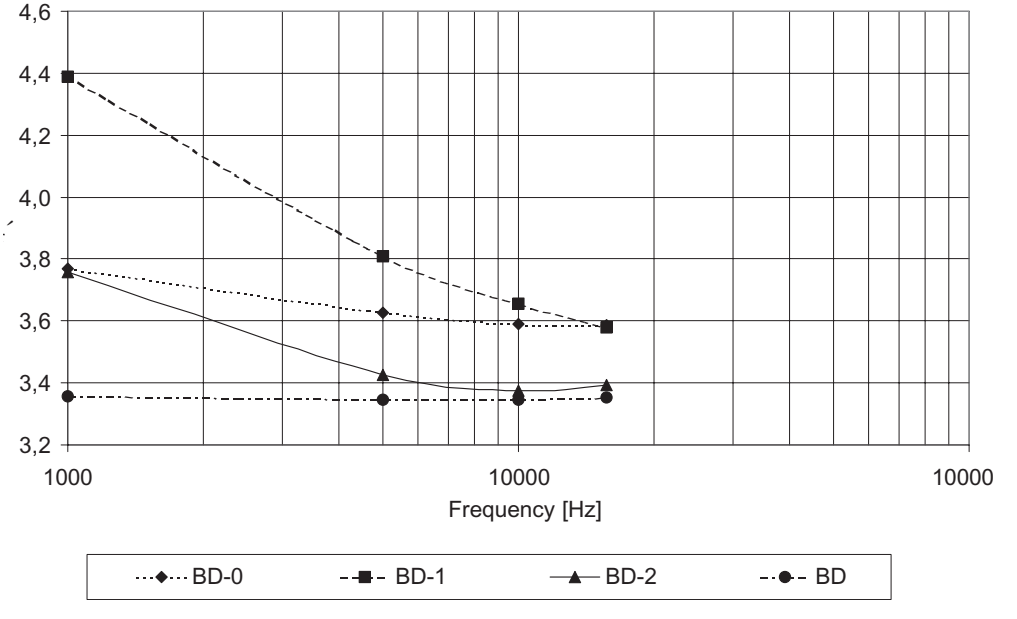

Figure 3. Real part of permittivity (ε_r') as a function of frequency for different steps in Biodiesel production.

Moreover, the successive washing steps on the Biodiesel result in the elimination of the remnants of sodium hydroxide and methanol. This agrees with the behavior of the pH of the effluents, as indicated in table 2. It is worth noting that in the first washing step, the conductivity of the sample increases due to the addition of acetic

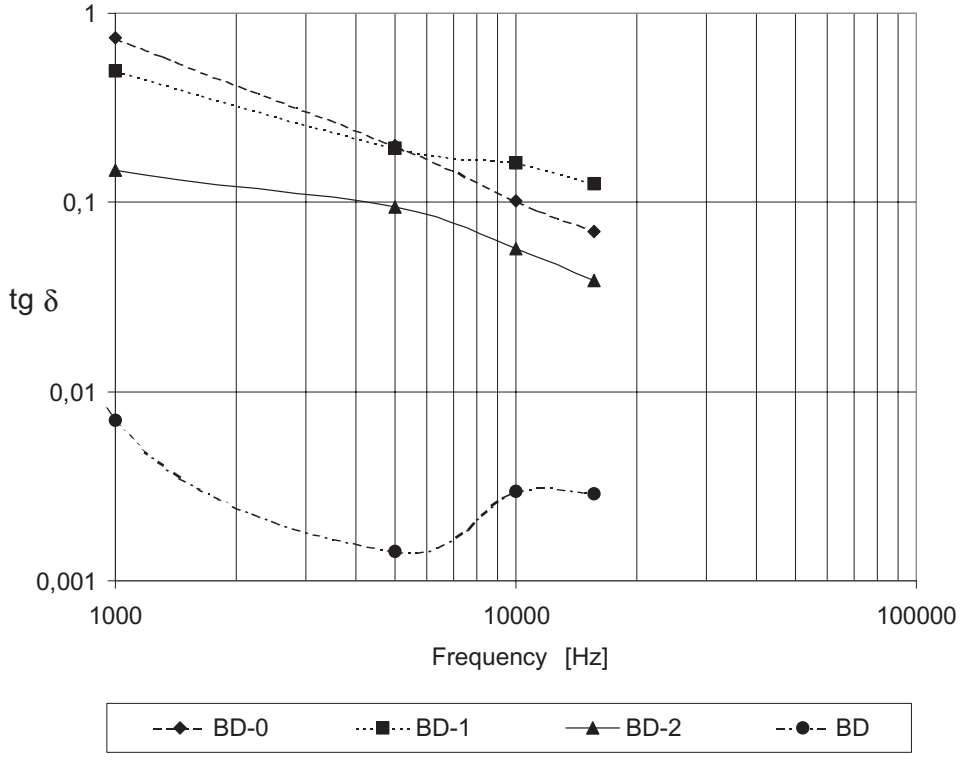

Figure 4. Dissipation factor (tg δ) as a function of frequency for different steps in Biodiesel production.

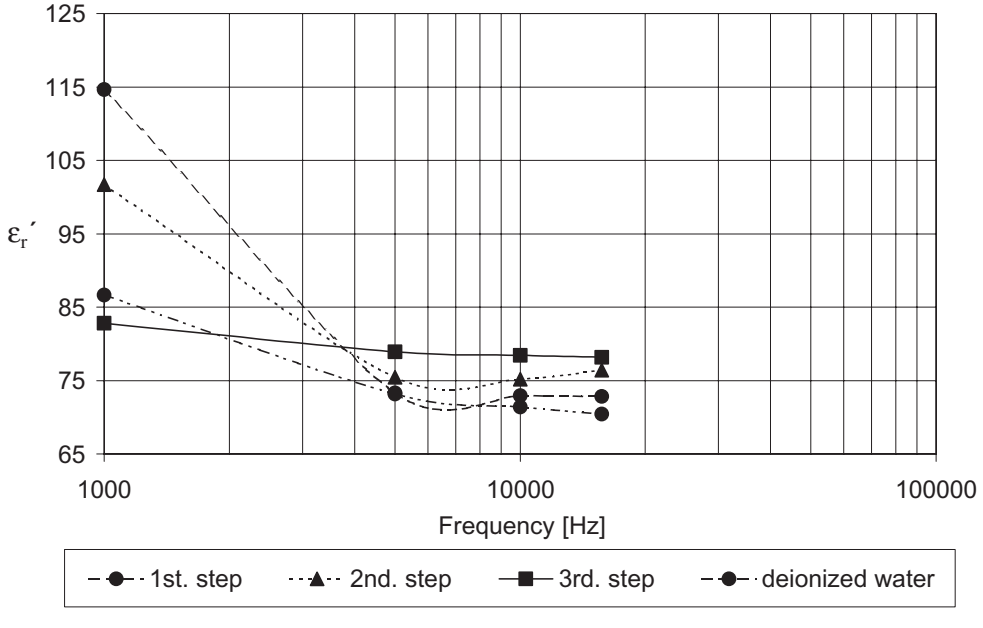

Figure 5. Real part of permittivity (ε_r') as a function of frequency for washing steps effluents.

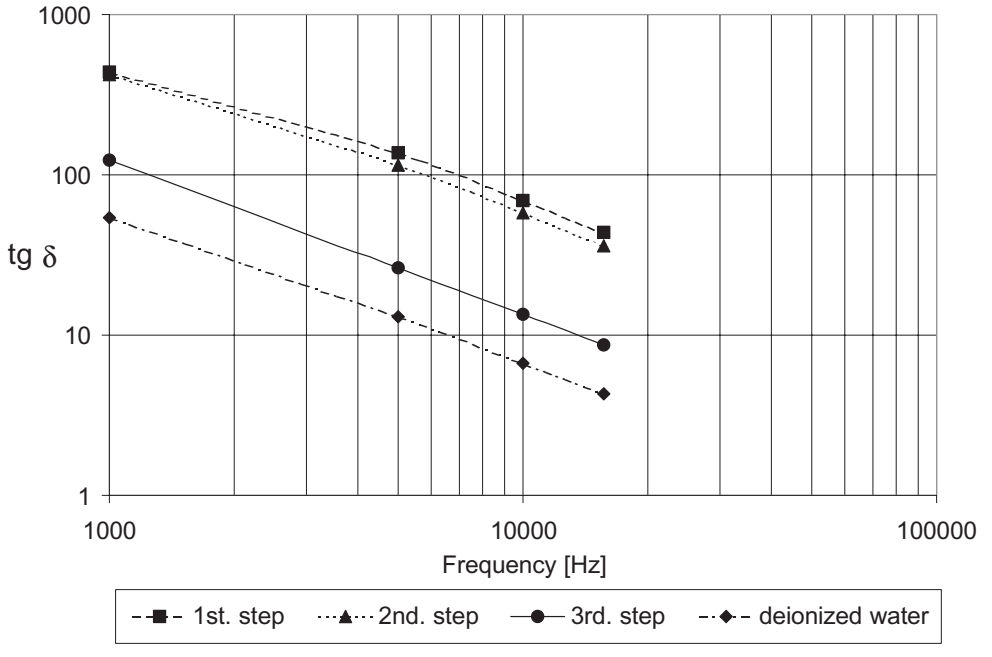

Figure 6. Dissipation factor (tg δ) as a function of frequency for washing steps effluents.

acid to the water used for washing. In consequence, there is an increase in the apparent permittivity and the dielectric losses of BD-1 (due to electrode polarization effects) in comparison with BD-0 (see tables 5 and 6). In the next washing step, with deionized water, the remnants of sodium hydroxide and methanol are eliminated, resulting in a noticeable reduction of dielectric losses and polarization effects on the electrodes (see figures 3 and 4). After the last washing step, the permittivity remains constant at $3.35 +/- 0.05$ for frequencies above 1 KHz (see table 5). Moreover, tg δ of the BD reaches values under 8×10^{-3} (at frequencies over 1 KHz; see table 6). This behavior was to be expected, given the kind of molecules which are found in the Biodiesel. In contrast, no significant polarization effects are observed in the low-frequency permittivity measurements. This is attributable to the lower conductivity of the contaminants in the oil, as compared with BD-0, BD-1 and BD-2.

The effluents show a progressive reduction of dielectric losses and polarization effects at the successive washing steps, as the remnants of methanol and sodium hydroxide are eliminated (see figures 5 and 6). The values for the last washing step are close to those of deionized water, corresponding to an efficient washing process (see tables 7 and 8). This result is consistent with the electrical properties of the Biodiesel obtained as a final product.

The refractive index of Biodiesel remains unchanged after the successive washing steps. This result was to be expected since refractometry techniques essentially measure the electronic polarization of the molecules of fatty acids esters that make up Biodiesel. On the contrary, low-frequency dielectric measurements are also sensitive to polarization effects due to the presence of contaminants.

5. Conclusions

Biodiesel was obtained, at laboratory scale from the transesterification of used frying oil with methanol, using sodium hydroxide as a catalyst, in a batch process.

The permittivity values obtained were 3.0 ± 0.15 for treated oil and 3.35 ± 0.05 for BD, constant in both the cases for frequencies from 1000 Hz to 15.7 kHz. Furthermore, the measured values of $\mathrm{tg}\,\delta$ for the treated oil are less than 4×10^{-2} and for BD are less than 8×10^{-3}, for the same range of frequencies. The elimination of contaminants in the oil after vacuum distillation may be seen from the reduction of dielectric losses. Moreover, permittivity and dielectric losses in the successive washing steps clearly show the elimination of the remaining sodium hydroxide and methanol in BD. In contrast, the refractive index measurements do not show any measurable differences.

Finally, the electrical properties of the effluents at the successive washing steps make it possible to ascertain the efficiency of the washing process, by comparison with the known values of deionized water.

In summary, physico-chemical and electrical properties were measured at different stages of Biodiesel production process. The measurement of electrical properties is an efficient technique for controlling the different stages, from the conditioning of the raw material to the quality control of the finished product.

The values of the physical and chemical properties measured are within the ranges indicated in the ASTM standards, both for the untreated Biodiesel and for the Biodiesel, after the successive washing steps.

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