INTERNATIONAL JOURNAL OF HYDROGEN ENERGY 39 (2014) 8754–8758

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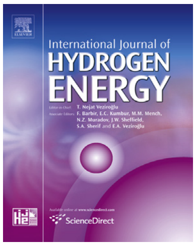

Electrical properties of vegetable oils between 20 Hz and 2 MHz

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ARTICLE INFO

Article history:
Received 2 November 2013
Accepted 4 December 2013
Available online 2 January 2014

Keywords:
Vegetable oils
Conductivity
Permittivity
Electrical properties
FAME
Dielectric spectroscopy

ABSTRACT

Electrical properties (permittivity and conductivity) of vegetable oils were determined in the frequency range from 20 Hz to 2 MHz. Commercial samples of corn, sunflower, soybean, grapeseed, cottonseed, olive, canola and chia oils were measured at temperatures between 300 K and 343 K (stabilized within 0.1 K). The calibration uncertainty in the measuring system was below 1%.

In all the measured samples the real part of the relative permittivity decreases with temperature, with a very good fit to a linear function; and it clearly depends on the oil source. The conductivity increases rapidly with temperature, fitting satisfactorily to an Arrhenius function. The values of the activation energy are between 0.34 eV (chia) and 0.46 eV (olive and soybean), and are consistent with previously reported values. These results are relevant for the application of electrical properties to the characterization of oils during transport and storage, and also to monitor the progress of the transesterification reaction.

1. Introduction

In recent years, vegetable oils (VOs) are becoming increasingly important in industrial (non-food) applications. In particular, they are used as feedstocks for the production of fatty acid methylesters (FAME) through a transesterification reaction, in applications as diverse as biofuels (biodiesel) [1–3], insulating fluids in power systems [4], and the production of inks [5]. The widespread use of VOs makes necessary a better characterization of their properties; it must be remarked that these novel applications require a different approach from the usual in food applications.

The quality of VOs used as feedstocks for FAME production has a strong impact on the quality of the final product [1]. Therefore, it is important to ascertain the quality of VOs before the start of the FAME production process. Moreover, is essential to determine the degree of advance of the reaction during transesterification, and also to detect the presence of VO (due to incomplete conversion) and other contaminants in the final product.

Electrical properties – conductivity and permittivity- provide valuable information on the characteristics and quality of VOs [6]. Although in the literature there are references on the relative permittivity of VOs from different sources [7], there is

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http://dx.doi.org/10.1016/j.ijhydene.2013.12.036

comparatively less information on electrical conductivity. Moreover, in many published works on electrical properties of VOs (and FAME) the omission of adequate calibrations and proper measurement procedures leads to unreliable interpretations of experimental results, due to unaccounted systematic errors.

Dielectric spectroscopy is a fast, economical, nondestructive technique, that adapts well to “on line” automatic control systems and makes possible to determine the electrical properties of samples at different temperatures [8–10]. It has been successfully used to detect the presence of alcohol in the final product of the transesterification process [11] and to characterize methylesters from different sources [12].

The Renewable Energy Group (GER) of the Engineering School of the University of Buenos Aires has several years of experience in the characterization of feedstocks and FAME, and also in the development, at the pilot plant stage, of automated biodiesel production techniques [6,11–22]. It must be remarked that characterization is carried out by means of dielectric spectroscopy, in addition to the techniques indicated in international standards [23,24].

In different countries, feedstocks used for FAME production are obtained from a variety of sources; therefore, it is important to establish typical values for the electrical properties of VOs of the same origin, and to generalize the results previously obtained for other VOs. In this work, dielectric spectra of commercial samples were obtained in the frequency range from 20 Hz to 2 MHz, at temperatures between 300 K and 343 K. These results are relevant to the determination of typical values of electrical properties for the characterization of VOs. Moreover, the differences with the electrical properties of FAME, reported in a previous work [12], are applicable to the monitoring of the progress of the transesterification reaction and the presence of non-converted VO in the final product.

2. Materials and methods

2.1. Samples

Measurements were made on commercial samples of corn, sunflower, soybean, grapeseed, cottonseed, olive, canola and chia oils, acquired in supermarkets. Samples were taken and measured immediately after the containers were opened.

2.2. Measuring system

The automated measuring system used in this work was described in detail in previous works [8,25]. The temperature of the samples was controlled within ±0.1 K with a thermostat (Lauda). System calibration uncertainty was below 1%; analytical grade cyclohexane (Fluka) was used as reference liquid.

3. Theory

The relative permittivity, as a function of frequency of a substance at the absolute temperature T, $\varepsilon_r(\omega,T)$, may be represented as a complex number. The real part, $\varepsilon_r'(\omega,T)$, describes the dielectric polarization, and the imaginary part, $\varepsilon_r''(\omega,T)$, is related to energy dissipation

$$\varepsilon_r(\omega,T) = \varepsilon_r'(\omega,T) - i\varepsilon_r''(\omega,T) \tag{1}$$

Low-frequency relative permittivity in liquids is measured as the ratio between the complex electrical capacitance of the measuring cell filled with the sample and the capacitance of the empty cell, as described in previous works [6,25].

In the samples studied in this work, ε_r' is practically independent of ω, since there are no dielectric relaxation effects in the measured frequency range. Therefore, the imaginary part ε_r'' describes only the dissipation due to conductive charge transport in the sample. In summary, the complex relative permittivity of the samples studied in this work is modeled as

$$\varepsilon_r(\omega,T) = \varepsilon_r'(T) - i\frac{\sigma(T)}{\varepsilon_0\omega} \tag{2}$$

where $\sigma(T)$ is the conductivity of the sample. The real part of the permittivity, $\varepsilon_r'(T)$, decreases with temperature, since thermal agitation opposes the molecular polarization. In the measured temperature range, a good fit to the experimental data is achieved with a linear function

$$\varepsilon_r'(T) = \varepsilon_r'(T_o) + \frac{d\varepsilon_r'}{dT}(T - T_o) \tag{3}$$

where $\varepsilon_r'(T_o)$ is the relative permittivity at the reference temperature $T_o = 318$ K, and $d\varepsilon_r'/dT$ is the temperature coefficient of the relative permittivity. In this work, all the temperatures are indicated in Kelvin (K).

The conductivity, σ, increases rapidly with temperature, and may be adequately fitted by an Arrhenius function

$$\sigma(T) = \sigma_o \exp\left(\frac{d}{T}\right) \tag{4}$$

where d is proportional to the activation energy ΔE ($d = \Delta E/kT$), σ_o is the pre-exponential factor (in S/m) and k is Boltzmann constant ($1.3806503 \times 10^{-23}$ J K^{-1}).

4. Results and discussion

The dielectric spectra of the samples were fitted by the models described in Section 3, by means of a non-linear minimum-squares procedure. The uncertainties in the model parameters were estimated by the linear regression method.

4.1. Permittivity

Experimental results for the real part of the permittivity, ε_r', as a function of temperature are plotted in Fig. 1. The symbols represent the data and the fitted values are indicated with lines.

In all the samples the relative permittivity decreases with temperature, with a very good fit to the proposed model. In all cases the correlation coefficient (R^2) is greater than 0.996.

The fitting parameters calculated from the experimental data for each sample, $\varepsilon_r'(T_o)$ and $d\varepsilon_r'/dT$, are indicated by symbols in the plot of Fig. 2. The reference temperature is 318 K and the uncertainty intervals (indicated by dotted lines) correspond to two standard deviations.

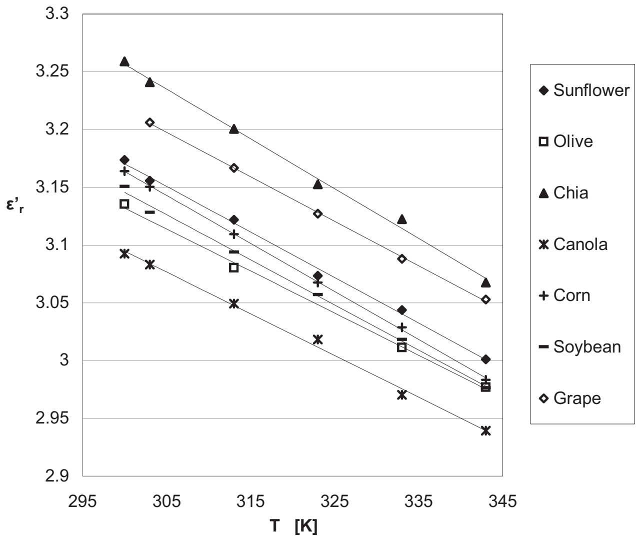

Fig. 1 – Real part of permittivity of the samples, as a function of temperature (ε_r). Symbols: experimental data. Lines: fitted values.

The values of $\varepsilon'_r(T_o)$ are between 3.03 (canola) and 3.18 (chía); the relative uncertainty is less than 0.2% for all the samples. The temperature coefficient, $\frac{d\varepsilon'_r}{dT}$, is in the range from -4.3×10^{-3} (chía) to -3.6×10^{-3} (olive), with a relative uncertainty below 8% for all the samples.

From these results, it is evident that the fitting parameters of the real part of the permittivity fall within a narrow range, and that the origin of VOs clearly influences their electrical properties. Moreover, the permittivity of FAME, reported in previous works [12] is clearly different from that of VOs. In summary, electrical properties may be a useful tool to distinguish between VO samples from different origins, to monitor the progress of the transesterification reaction and to detect the presence of VO in the final product.

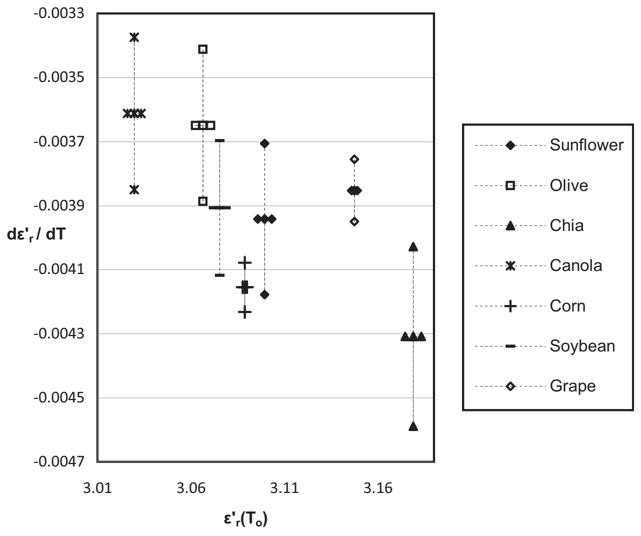

Fig. 2 – Fitting parameters of the real part of the permittivity of the samples as a function of temperature $\varepsilon_r(T_o)$ and $d\varepsilon'_r/dT$. The reference temperature is 318 K.

The values of the relative permittivity reported in this work differ slightly from those reported in previous works [6]; the relative differences are in the range from 0.6% (canola) to 4% (soybeans). This may be originated by the variability of the oil-bearing plants, and also by differences in extraction and processing techniques used in the production process of the samples reported in previous works. For instance, the composition of sunflower oil depends on the climate of the production zone, the time of the year of the harvest, etc. [26]. Therefore, it is reasonable to expect differences in the electrical properties even in samples obtained from identical production processes. This suggests that further study (to be reported in future works) is necessary to determine the variability of the permittivity of VOs from the same origin but obtained from different producers.

4.2. *Conductivity*

The experimental values of the conductivity, as a function of the inverse temperature (1/*T*) are plotted with symbols in Fig. 3. The lines represent the fitted Arrhenius dependence, obtained by logarithmic regression. It may be seen that the fitting is satisfactory.

The pre-exponential coefficient, σ_o, the activation energy ΔE together with its relative uncertainty $\Delta E/E$, and the correlation coefficient R^2 of the fitting for each sample are given in Table 1. It is worth mentioning that R^2 is greater than 0.980 in all cases, with the exception of the corn and olive samples, where the conductivity values are near the operating threshold of the measuring system. The conductivity of the sample from canola is not included either in Fig. 3 or in Table 1, since it is below the measuring threshold. The activation energies are between 0.34 eV (chia) and 0.46 eV (soybeans and olive) and are consistent with the values reported in previous works [6]. As indicated in the previous paragraph, it is known

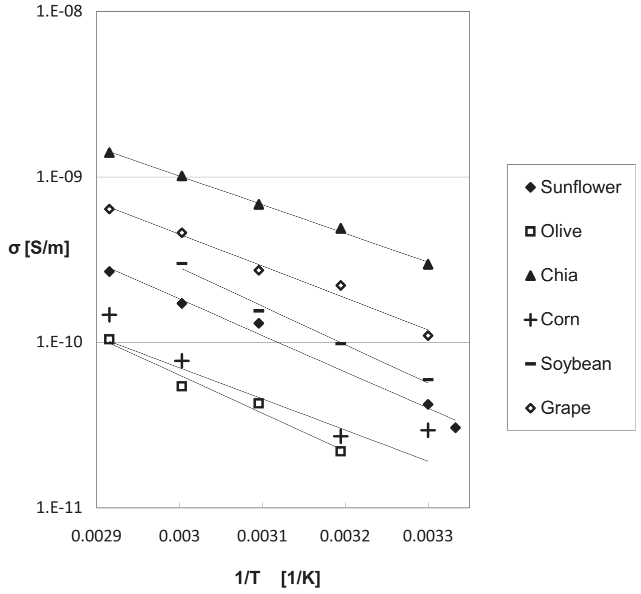

Fig. 3 – Conductivity (σ) of vegetable oil samples as a function of the inverse temperature. Symbols: experimental data. Lines: fitted values.

Table 1 – Fitting parameters and correlation coefficient of VOs from different origins.

Origin	σ_o [S/m]	Activation energy [eV]	ΔE/E [%]	R^2
Sunflower	7,24E-04	0.44	6	0.989
Olive	4,70E-04	0.46	12	0.971
Chia	1,58E-04	0.34	3	0.997
Corn	4,58E-05	0.38	23	0.907
Soybeans	2,53E-03	0.46	7	0.989
Grapeseed	2,68E-04	0.38	8	0.980

that the properties of sunflower oil depend on several factors, as reported in the literature [26]. From the data it is also clear that the activation energy of VOs depends on their origins.

5. Conclusions

In this work, dielectric spectra of vegetable oil samples were obtained in the frequency range from 20 Hz to 2 MHz, at temperatures between 300 K and 343 K. Measurements were made on commercial samples of corn, sunflower, soybean, grapeseed, cottonseed, olive, canola and chia oils, acquired in supermarkets. Samples were taken and measured immediately after the containers were opened. The results presented in this work are relevant to the characterization of feedstocks for the production of fatty-acid methylesters.

In all the measured samples the real part of the permittivity decreases with temperature. The fitting to a linear function is very good, with parameters that depend on the origin of the oil.

The conductivity of the samples increases rapidly with temperature, and may be satisfactorily fitted by an Arrhenius function. The values of the activation energy depend and the origin of the oil, in the range between 0.34 eV (chia) and 0.46 eV (soybeans and olive) and are consistent with the results reported in previous works.

Measurements of electrical properties, successfully applied in previous works to fatty-acid methyl esters, may be also used in the characterization of vegetable oils from different origins. This makes possible to apply dielectric spectroscopy techniques in the storage and transport of feedstocks, and also during the transesterification process.

Acknowledgments

This work was supported by Project UBACyT “Research and development in liquid biofuels”, of the University of Buenos Aires (UBA). One of the auhors, Julian Corach, was supported by CONICET amd PERUILH scholarships.

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Glossary

ε_o: permittivity of vacuum (8.85×10^{-12}F/m)
ε_r: complex relative permittivity
ε_r': real part of complex relative permittivity
ε_r'': relative permittivity related to dielectric polarization
f: frecuency, Hz
ω: angular frecuency, rad s^{-1}
σ: conductivity, $1/\Omega$
d: fitting parameter of Arrhenius law of conductivity, $\Delta E/k$
ΔE: activation energy, J
k: Boltzmann constant (1.3806503 10^{-23} J K^{-1})
T: absolute temperature, K