INTERNATIONAL JOURNAL OF HYDROGEN ENERGY 37 (2012) 14735–14739

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Electrical properties of mixtures of fatty acid methyl esters from different vegetable oils

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ARTICLE INFO

Article history:
Received 6 October 2011
Accepted 12 December 2011
Available online 5 January 2012

Keywords:
Fatty Acid Methyl Ester (FAME)
Conductivity
Permittivity
Characterization

ABSTRACT

The dependence on temperature of the permittivity and conductivity of mixtures of Fatty Acid Methyl Esters (FAME) was determined between 300 K and 343 K, in the frequency range from 20 Hz to 2 MHz. Samples were made from oil of sunflower, corn, grape, chia, canola, jatropha, coconut and cottonseed.

Permittivity fits very well to a linear function of temperature, the fitting parameters falling within a narrow range for all samples. Conductivity follows an Arrhenius dependence with activation energies between 0.202 eV and 0.252 eV.

The results show that measurements of electrical properties, successfully used for the characterization of FAME from soybean oil, as reported in previous works, can also be employed in FAME obtained from different feedstocks. This generalization is relevant for laboratory and industrial characterization and quality control, and also for the application of "on line" measurements in automated production systems.

1. Introduction

Mixtures of Fatty Acid Methyl Esters (FAME) are obtained by the transesterification of vegetable oil or animal fat and an alcohol [1–3]. The most important uses of FAME include biofuels, as a replacement of Diesel Fuel and in blends [1-3], as a liquid insulator in power transformers [4] and in the manufacture of cosmetics.

Dielectric Spectroscopy is a fast, non-destructive, and low-cost technique that makes possible the measurement of electrical properties (permittivity and conductivity) at different temperatures [5,6]. The determination of electrical parameters is relevant for the production of FAME from biomass since it makes possible the characterization of the sample and the detection of moisture and other contaminants that impact on the quality of the feedstocks and the final product [7–9]. It is also important to note that electrical properties are adequate for measurements in both laboratory and industrial environments, including automated process… control from "on line" measurement systems [10].

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0360-3199/$ – see front matter
doi:10.1016/j.ijhydene.2011.12.089

List of symbols

FAME	Fatty acid methyl ester
ε_0	permittivity of vacuum (8.85×10^{-12} F/m)
ε_r	complex relative permittivity
ε'_r	real part of complex relative permittivity
ε''_{rpol}	relative permittivity related to dielectric polarization
f	frequency, Hz
ω	angular frequency, 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 ($1.3806503 \times 10^{-23}$ J K^{-1})
T	absolute temperature, K

Buenos Aires has been producing and characterizing FAME for several years, from vegetable oils sources. The Group also studies automated production techniques, at the pilot plant stage. The characterization of FAME for using in Diesel engines is carried out by measuring the properties required by international standards [11,12] and electrical properties. Studies of FAME from soybeans oil at the several stages of the production process were reported in previous works [10,13], including feedstocks.

At present, a wide variety of edible or non-edible vegetable oils from many species are used for the production of FAME in different countries [14]. Therefore, it is important to extend previous results on the application of electrical techniques to the characterization of FAME obtained from other feedstocks. In this work the parameters that describe the dependence of permittivity and conductivity with temperature were determined for FAME obtained from oils of sunflower, corn, grape, chia, canola, jatropha, coconut and cottonseed.

2. Theory

2.1. Introduction

The relative permittivity of a substance with dielectric losses may be represented as a complex number where the real part, $\varepsilon'_r(\omega)$, is related to the storage of electrostatic energy due to electric polarization and the imaginary part to the dissipation of energy due to different processes [5,7] as follows:

$$\varepsilon_r(\omega, T) = \varepsilon'_r(\omega, T) - i\varepsilon''_{rpol}(\omega, T) - i\frac{\sigma(T)}{\varepsilon_0 \omega} \tag{1}$$

The term $\varepsilon''_{rpol}(\omega)$ describes the dissipation of energy associated to the relaxation processes of dielectric polarization and it is related to the real part $\varepsilon'_r(\omega)$ through the Kramers–Kronig relations. In consequence, $\varepsilon''_{rpol}(\omega)$ has a value appreciably different from zero only in the range of frequencies around the inverse of the characteristic time of the relaxation process. On the other hand, the conductivity term σ/ω describes the dissipation associated to charge transport phenomena, and at low frequencies ($\omega \to 0$) dominates the imaginary part of the complex permittivity.

2.2. Complex permittivity in FAME

The parameters in Eq. (1) were measured in FAME from dielectric spectra in the frequency range from 20 Hz to 2 MHz. Relaxation effects are not to be expected until much higher frequencies [15] given the molecular structure del FAME, as described in previous works [7,13]. In consequence, in this work the real part of permittivity ε'_r may be considered as independent of frequency, and the related term of the imaginary part $\varepsilon''_{rpol}(\omega)$ may be neglected. However, dissipation effects related to charge transport may occur in FAME, due to the presence of contaminants and also by thermal effects. Therefore, the conductivity σ/ω must be included in the imaginary part of the complex permittivity.

In summary, in the frequency range studied in this work the complex dielectric permittivity as a function of temperature and frequency in FAME is modeled as:

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

Since thermal agitation tends to oppose to the polarization associated to molecular orientation, in liquids like FAME the real part of the complex permittivity, $\varepsilon'_r(\omega)$, usually decreases when the temperature increases.

Therefore, in this work $\varepsilon'_r(T)$ is fitted as a linear function of the absolute temperature T is given by:

$$\varepsilon'_r(T) = \varepsilon'_r(T_0) + \frac{d\varepsilon'_r}{dT}(T - T_0) \tag{3}$$

where $\varepsilon'_r(T_0)$ is the fitted value of the real part of the permittivity at the reference temperature T_0 (in this work, $T_0 = 318$ K) and $d\varepsilon'_r/dT$ is the rate of change of ε'_r with temperature, which may be assumed constant in the range of temperatures studied in this work.

On the other hand, the conductivity $\sigma(T)$ increases rapidly with temperature, and in consequence it is fitted to an Arrhenius law (Eq. (4)), as indicated in previous works [7,13]:

$$\sigma(T) = \sigma_0 \exp\left(\frac{d}{T}\right) \tag{4}$$

where the fitting parameter d may be considered as proportional to an activation energy ΔE:

$$d = \frac{\Delta E}{kT} \tag{5}$$

where k is Boltzmann constant ($1.3806503 \times 10^{-23}$ J K^{-1}).

3. Experimental

3.1. Sample preparation

Fatty acid methyl esters (FAME) samples studied in this work were prepared by transesterification of different vegetable – edible and non-edible – oils with methanol. The alcohol to oil ratio was 25% (v/v). The transesterification reaction was carried out at 60 °C, using sodium hydroxide as a catalyst and under constant agitation [3].

Edible oils (sunflower, corn, grape, chia and canola) were bought at the supermarket. Coconut, cottonseed and jatropha oils had been stocked for a long time. In consequence, the acid index of last ones was too high for the usual process of basic transesterification. For this reason it was necessary to add a previous step of esterification to coconut and cottonseed oils and a step of neutralization to cottonseed oil, in order to diminish the acid index to a values lower than 1.

Once the separation of the glycerin obtained as a co-product was completed, FAME was purified by washing and drying steps in order to eliminate the impurities remaining after chemical the reaction.

3.2. *Measuring system*

Measurements presented in this paper were made with an automated measuring system described in previous works [16,17]. Samples were placed in cell with temperature controlled to within ±0.1 K by a thermostat (Lauda). System calibration was carried out using analytic-grade cyclohexane (Merck) as reference liquid. The real part of permittivity (ε'_r) at each temperature is determined with an accuracy better than ±1%.

4. Results and discussion

Dielectric spectra from the studied FAME samples were fitted to the model presented in Section 2.2. Using a non-linear least squares method (Leventhal–Marquardt). A linear regression analysis was performed to estimate the uncertainty in the fitted parameters. Measurements were made at 300 K, and from 303 K to 343 K in 10 K steps.

4.1. *Real part of permittivity* (ε'_r)

Fig. 1 presents experimental results for ε'_r as a function of temperature for the studied FAME samples. Symbols indicate the measured values at each temperature, and the lines correspond to the linear least-squares fit of Eq. (3).

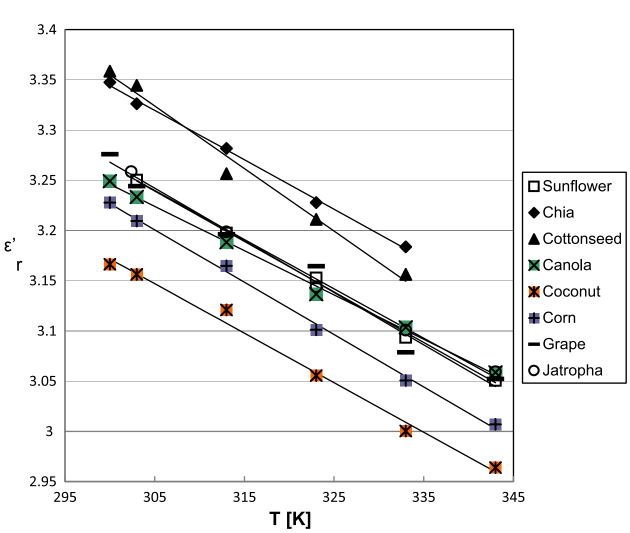

Fig. 1 – Real part of permittivity (ε'_r) as a function of temperature for FAME produced from different vegetable oils.

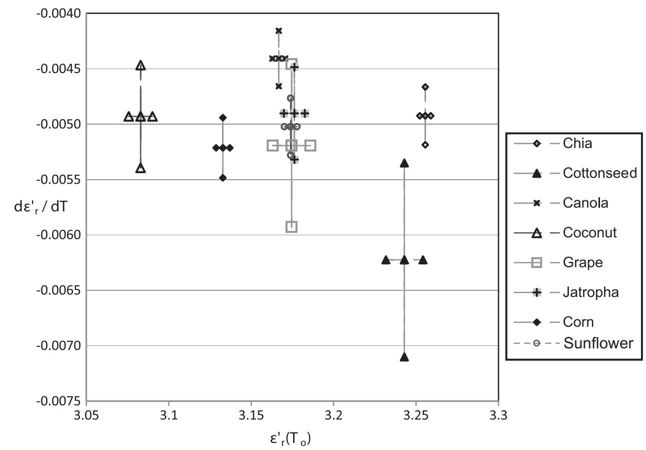

Fig. 2 – Fitting parameters for the dependence of the real part of relative permittivity on temperature for FAME produced from different vegetable oils. The reference temperature is $T_0 = 318$ K.

In all the samples ε'_r decreases with temperature, with a good fit to the proposed linear model. The correlation coefficients (R^2) were between 0.985 and 0.998. From the measured values, the fitting parameters in Eq. (3) were obtained, together with their uncertainties from the linear regression analysis. The fitted values of $d\varepsilon'_r/dt$ and $\varepsilon'_r(T_0)$ for $T_0 = 318$ K for each FAME sample are plotted in Fig. 2.The uncertainty bands for each parameter correspond to two standard deviations.

The values of $\varepsilon'_r(318\ \text{K})$ for FAME from the different oils range from 3.08 (coconut) to 3.26 (chia). In all cases the estimated relative uncertainties are less than 0.35%. Furthermore, $d\varepsilon_r/dT$ is within -4.4×10^{-3} (FAME from canola oil) and -6.2×10^{-3} (FAME from cottonseed oil). The estimated uncertainties for this parameter fall within 5% and 14%.

From the presented results it seems that the permittivity of the studied FAME samples depend little on the vegetable oils used in their production, whether edible or not. This is easy to understand, given the characteristic molecular structure of FAME, as explained in previous works [7,13]. Furthermore, this

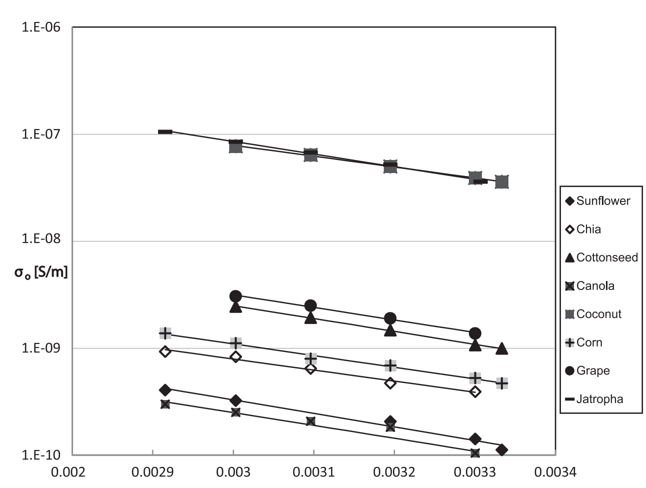

Fig. 3 – Conductivity (σ) as a function of temperature for FAME produced from different vegetable oils.

Table 1 – Fitting parameter (σ_0), activation energy ΔE and the correlation coefficient R^2 for FAME from different feedstocks.

Feedstocks	σ_0 [S/m]	ΔE [eV]	R^2
Sunflower	2.06E−06	0.252 ± 0.021	0.980
Chia	1.04E−06	0.207 ± 0.015	0.984
Cottonseed	1.02E−05	0.240 ± 0.004	0.999
Canola	1.00E−06	0.239 ± 0.022	0.983
Coconut	8.73E−05	0.202 ± 0.004	0.999
Corn	2.06E−06	0.217 ± 0.011	0.991
Grape	1.04E−05	0.234 ± 0.013	0.994
Jatropha	2.92E−04	0.235 ± 0.009	0.996

behaviour is shared with the physical and chemical properties specified in the international standards, that also fall within narrow ranges. The correlation relation between these properties and electrical parameters for FAME from soybean oil has already been reported in previous works [7,18]. Therefore, permittivity measurements can be used to detect the presence of contaminants, such as remnants of methanol or non-transesterified vegetable oil.

4.2. *Conductivity as a function of temperature*

The measured values of conductivity (σ) as a function of temperature for the FAME samples studied in this work are plotted in Fig. 3. Symbols indicate experimental results at the different measuring temperatures and the lines correspond to the fit to an Arrhenius dependence, Eq. (4), obtained by logarithmic regression.

It may be seen from Fig. 3 that experiemental results for all the samples are satisfactorily described by the Arrhenius dependence, with similar activation energies. From the parameters given in Table 1, the activation energies, ΔE, are between 0.202 eV (FAME from coconut oil) and 0.252 eV (FAME from sunflower oil), with relative uncertainties lower than 12%. In all cases the correlation coefficient of the logarithmic regression (R^2) is higher than 0.980.

These results from edible and non-edible oils are comparable to the previously reported values for FAME from soybean oil [13].

It must be remarked that the scaling factor, σ_0, in Eq. (4)is not considered an intrinsic property of the sample, since it depends strongly on the presence of moisture and other contaminants. This has been described for FAME from soybean oil in previous works [7,8]. Moreover, the Arrhenius dependence makes possible to relate the values of conductivity measured at different temperatures, in order to compare quantitatively the degree contamination of FAME (for instance, at different stages of the production storage and transport process).

5. Conclusions

Dielectric spectra between 20 Hz and 2 MHz for FAME from vegetable oils were obtained, in the temperature range from 300 K to 343 K. Samples were produced from oils of sunflower, corn, grape, chia, canola, jatropha, coconut and cottonseed.

In all cases, the real part of permittivity of FAME decreases with temperature, and the experimental data are very well fitted by a linear function. The fitting parameters for all the samples fall within narrow intervals, as could be expected from the characteristic molecular structure of FAME. The independence of the permittivity of FAME on the origin of the feedstock is a common feature with the physical and chemical properties required by international standards. Therefore, permittivity measurements can be used to detect the presence of contaminants, such as methanol remnants, or non-transesterified vegetable oil.

The increase of conductivity of FAME with temperature is satisfactorily modeled by an Arrhenius function for all the samples. The values of activation energies for FAME from oil of different species are between 0.202 eV and 0.252 eV. Since the conductivity of FAME depends on the presence of contaminants, these results make possible to use conductivity measurements to compare quantitatively the level of contamination of FAME at different temperatures, for instance, at several stages of the production process and in the storage and transport of the final product.

In summary, the results presented in this work show that measurements of electrical properties, successfully applied to the characterization of FAME from soybean oil at the different stages of the production process as reported in previous works, can be also used in FAME from other vegetable oils. The generalization of these results is relevant for laboratory and industrial characterization and quality control, and also for the application of electrical parameters from “on line” measurements in automated production systems.

Acknowledgments

This work was supported by Project UBACyT “Research and developmente in liquid biofuels” of Universidad de Buenos Aires (University of Buenos Aires, UBA).

The authors wish to thank to Dr. C.A. Querini from INCAPE, Universidad Nacional del Litoral (National University of Litoral, UNL) and Eng. E.P. Dagnino and Dr. R.E. Chamorro from QUIMOBI, Universidad Tecnológica Nacional (National Technological University, UTN) for the cottonseed, jatropha and coconut oil samples.

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