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Investigation of dielectric properties of the reaction mixture during the acid-catalyzed transesterification of Brazil nut oil for biodiesel production

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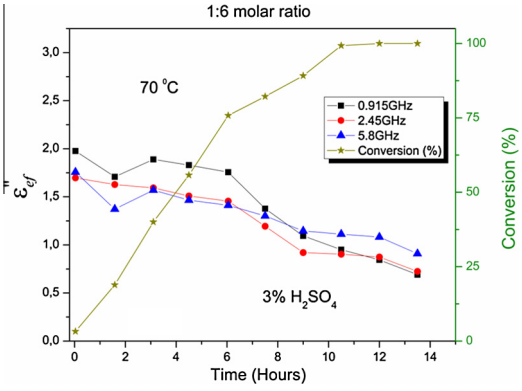
HIGHLIGHTS

- Dielectric properties of the pure samples and reaction mixtures were measured.
- Measurement was made during acid-catalyzed transesterification reaction.
- The dielectric properties were frequency and temperature-dependent.
- At high alcohol concentrations the mobility of counterions and the loss factor are high.
- Catalyst influence on dielectric properties is reduced at low alcohol concentrations.

GRAPHICAL ABSTRACT



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ABSTRACT

The design of processes involving microwave technology is dependent on the dielectric properties of the materials being processed. The dielectric constant and loss factor of the pure liquids methanol, ethanol, glycerin and sulfuric acid, as well as vegetable oils (Brazil nut and soybean), were measured using a vector network analyzer in an open-ended coaxial probe method (frequency range 300 MHz to 13 GHz) at various temperatures. For measurement during acid-catalyzed transesterification two oil:ethanol molar ratios at three different acid concentrations were employed. Dielectric properties of the pure samples and reaction mixtures during the transesterification reaction were frequency and temperature-dependent. The catalyst significantly affects the dielectric properties mainly at high alcohol concentrations where the mobility of counterions and the loss factor are high. The results indicate that the influence of the catalyst is reduced at low alcohol concentrations as the mobility of the counterions becomes more restricted decreasing the ionic conductivity.

1. Introduction

Biodiesel consists of monoalkyl (methyl or ethyl) esters of long chain fatty acids derived from animal fats and vegetable oils and represents a very promising alternative to conventional petroleum diesel, with a view to lowering global warming from gaseous emissions as well as reducing carcinogenic particulate matter emissions. Coupled with environmental issues the increase in energy demand has led to a renewed focus on vegetable oils and animal fats to produce biodiesel, as shown by the vast number of publications in this field of research [1–3]. The transesterification

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reaction (alcoholysis of carboxylic esters) is the main process used to obtain this important source of energy, under basic or acid conditions, and it is performed using primary and secondary monohydric aliphatic alcohols. Due to the reversibility of this reaction excess alcohol is used to shift the equilibrium to the product side. Of the aliphatic alcohols possessing 1–8 carbon atoms, methanol is most-commonly used at the industrial scale since it is associated with low costs and has chemical advantages. Ethanol is less frequently used although it is preferable to methanol since it solubilizes oil more easily, resulting in ethyl esters with increased heat content and a lower cloud point. Also, ethanol is an entirely renewable, agricultural-based feedstock for biodiesel production [2]. Vegetable oils and animal fats which are extracted or pressed to obtain crude oil or fat usually contain free fatty acids, water, sterols, phospholipids, odorants and other impurities. The free fatty acid and water contents have significant negative effects on the alcoholysis of glycerides using alkaline or acid catalysts. They also interfere with the separation of fatty acid esters (biodiesel) and glycerin. To overcome these challenges, in the past 10 years many experimental studies have been carried out in order to enhance the biodiesel production yield and reduce the reaction time [1].

Alkaline conditions are not suitable for biodiesel production from residual animal fats and waste vegetable oils, which are viewed as interesting alternative raw materials considering environmental and economic issues. This is important since a promising alternative to vegetable oils for biodiesel production is the use of lower cost feedstocks, such as waste cooking oils, acidic Brazil nut oils and animal fats, which could contribute to reducing the amount of agricultural land dedicated to fuel production instead of food. Acid catalysts must be employed if a high content of free fatty acids (FFAs) is present, as in some low-cost raw materials or in waste frying oils [4,5], since the catalytic activity is not strongly affected by the presence of FFAs in the feedstock. H_2SO_4 and HCl are the acid catalysts most commonly employed in the transesterification process [5]. Although the homogeneous acid-catalyzed reaction provides an increase in the biodiesel yield it is much slower than the alkali-catalyzed reaction and requires higher temperatures and pressures [5].

In this regard, the high potential of microwave irradiation in organic synthesis [6] has been applied to overcome the characteristic reaction drawbacks associated with conventional heating in the homogeneous or heterogeneous base or acid-catalyzed transesterification of triacylglycerides, such as long reaction time and higher temperatures [2,3]. The microwave-assisted transesterification reaction is efficiently accelerated resulting in a short reaction time and a considerable reduction in the quantity of by-products [7–9]. Several examples of microwave-irradiated transesterification methods have been reported in the literature using batch laboratory ovens and domestic ovens adapted for their use as flow systems [10–12]. Heterogeneous or homogeneous catalytic ethanolysis of triglycerides induced by microwaves may be a viable alternative technology for ethylic biodiesel production, especially in Brazil, one of the world's largest producers of ethanol; however, very few reports in this regard can be found in the literature [12–15].

Microwave dielectric heating is a macroscopic effect of the interaction of electromagnetic fields in the microwave region with continuous media characterized by their intrinsic dielectric properties [16]. Microwave heating can be enhanced by controlling variables such as the power level, frequency of applied field and initial temperature of the sample, but unlike these variables, which can be selected for a specific application, dielectric properties require empirical measurement for both simple and complex materials, especially for mixtures such as reaction solutions. Dielectric properties are frequency and temperature-dependent and in general applications of microwave heating an understanding of the dielectric properties of the materials is important from the theoretical point of view in fundamental studies on microwave processing applications as well as in terms of addressing environmental and economic issues [16]. In the specific case of microwave-assisted transesterification reactions understanding the behavior of the dielectric properties of the components and the reaction mixture required to produce biodiesel certainly will aid process design calculations, the execution and control of the microwave heating and the identification of the catalysts which can most efficiently enhance the reaction under microwave irradiation. Dielectric properties of materials are defined by their relative complex permittivity $\hat{\varepsilon} = \varepsilon' - j(\varepsilon'' + \frac{\sigma}{\omega\varepsilon_0}) = \varepsilon' - j\varepsilon''_{ef}$ where the real part ε' is the relative dielectric constant and $\varepsilon''_{ef} = (\varepsilon'' + \frac{\sigma}{\omega\varepsilon_0})$ is the dielectric loss factor of the material with σ being the conductivity and ε'' the imaginary part of the relative permittivity that accounts for the dielectric relaxation process [16]. The dielectric loss factor is related to the electromagnetic energy dissipation in the material which occurs through major mechanisms: ionic conduction and dipolar rotation. The interaction of ions and dipoles with the oscillating electrical field creates inter- and intra-molecular friction which generates heat throughout the volume of the material. The electromagnetic energy (average power) absorbed by the volume V of a dielectric material which is converted into heat is obtained from Maxwell's equations and is given by [16] $\langle P \rangle = \omega\varepsilon_0\varepsilon''_{ef}E^2_{rms}V$, where P is the power (W) absorbed by the material, ε_0 is the vacuum permittivity (=8.85 $\times$ 10^{-12} F/m), ε''_{ef} is the loss factor and E_{rms} is the root mean square of the applied oscillating electrical field (V/m) with frequency f ($\omega = 2\pi f$) over the volume V (m^3) of the sample. The loss tangent is defined by $\tan\delta = \varepsilon''_{ef}/\varepsilon'$ and is an important parameter in describing the dielectric response of materials in terms of, for example, the penetration depth (D_p), the distance at which the amplitude of the electrical field is damped to $1/e = 0.369$ of its initial value at the surface of the material [17].

The dielectric properties of most pure solvents are widely available in the literature [18–23]. However, data on the dielectric properties of vegetables oils, animal fats, or even their mixtures with methylic or ethylic alcohols, are scarce [24–27]. A recent study addressed the measurement of the dielectric properties of the reaction mixture in the alkaline-catalyzed transesterification of soybean oil [28]. However, to the best of our knowledge there are no reports in the literature which describe the measurement of the dielectric properties of the acid-catalyzed transesterification reaction. In an effort to better understand the microwave-assisted transesterification reaction this study was focused on the measurement of the dielectric properties of biodiesel precursors: soybean and Brazil nut oils, ethanol and acid catalyst (H_2SO_4) and the reaction mixture of the acid-catalyzed ethanolysis of Brazil nut oil using ethanol as the solvent and sulfuric acid as the catalyst. The dependence of the results on the field frequency was studied in the range of 0.3–13 GHz at different temperatures.

2. Materials and methods

In this study ethanol (99%, Tedia) and methanol (99.8%, FM) were used as the solvents and H_2SO_4 (95–99%, SPECTRUM) as the acid catalyst. Brazil nut and soybean oils were obtained from a store with water and free fatty acids (FFAs) contents of around 0.11 wt.% and 0.03 wt.%, respectively. The measurements were performed with an open-ended coaxial probe (HP 85070B, Agilent, Palo Alto, CA, USA) connected to a network analyzer (HP 8753C, Agilent, Palo Alto, CA, USA), in a 101-point frequency sweep from 300 MHz to 13 GHz. The network analyzer was controlled by the Hewlett–Packard 85070B dielectric probe kit software (Agilent, Palo Alto, CA, USA) and calibrated using the 3-point method